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FOREIGN TECHNOLOGY DIVISION

ELEMENTARY PROCESSES OF HIGH-ENERGY CHEMISTRY (COLLECTION OF ARTICLES)

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EDITED MACHINE TRANSLATION

ELEMENTARY PROCESSES OF HIGH-ENERGY CHEMISTRY
(COLLECTION OF ARTICLES)

English Pages: 395

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PREPARED BY:

TRANSLATION DIVISION
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Akademiya Nauk SSSR
Institut khimicheskoy fiziki

ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY

Trudy Simpoziuma
Po Elementarnym Protsessam Khimii
Vysokikh Energiy

(Moskva, 18-22 marta 1963 g.)

Izdatel'stvo "Nauka"

Moskva - 1965

Page 1-318

CIRC ABSTRACT WORK SHEET

0897 0315

(01) Acc Nr. TT6500291	(65) SIS Acc Nr. AT5023426	(40) Country of Info UR	(41) Translation Nr. MT6600004
(42) Author GUR'YEV, M. V.; SUMIN, L. V.			Priority II Distribution STD

(43) Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39) Topic Tags ion energy, mass spectrum, particle collision, electron energy, excited state, mass spectrometry

(66) Foreign Title I. ELEMENTARNYYE PROTSESSY S UCHASTIYEM ELEKTRONOV I IONOV. DISSOTSIATSIYA MOLEKUL PRI ELEKTRONNOM UDARE I RADIATSIONNAYA KHIMIYA

(09) English Title 1. ELEMENTARY PROCESSES WITH PARTICIPATION OF ELECTRONS AND IONS. DISSOCIATION OF MOLECULES DURING ELECTRON IMPACT AND RADIATION CHEMISTRY

	(97) Header Clas	(63) Clas	(64) Rel	(60) Release Expansion
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ABSTRACT: Primary products of dissociation of molecules, excited by electron impact, were investigated by the mass spectrometry method. In the case of n-hexane the mass spectra of ion fragments containing two or three carbon atoms were taken using a MV23-02 instrument with a resolution (based on line half-height) of about 9000. Most of the ions of a general formula C_nH_m ($m < 2n + 1$) are formed during 10^{-7}-10^{-8} sec and for a given "n" the smaller the "m" the greater is the lifetime of these ions. A similar reaction also applies to the ion fragment kinetic energy indicating that the ions are formed during secondary disintegrations. The CH_2^+ ion is formed from CH_4^+ within $5-10^{-3}$ sec. The $C_3H_7^+$ and $C_2H_5^+$ ions are formed in less than $5-10^{-8}$ sec. Statistical energy distribution occurred in ion fragments. Molecule excitation energies were determined using electrons with an energy 3-4 times greater than the ionization energy. In collision with such energetic electrons, molecules assume a kinetic energy of the order of 10^{-5} ev. The accurancy determination excitation energies for H_2^+ and He^+ using this method was as high as 30%. In the case of slow disintegration processes, the method can be applied successfully to all secondary ions. Orig. art. has: 1 formula.

8

CIRC ABSTRACT WORK SHEET 0897 0316

(01)Acc Nr. TT6500292	**(65)SIS Acc Nr.** AT5023427	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KARACHEVTSEV, G. V.; TAL'ROZE, V. L.

Priority II
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(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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(39)Topic Tags excited state, mass spectrum, ion, ion energy

(66)Foreign Title O METODE OPREDELENIYA VREMENI RASPADA VOZBUZHDENNYKH IONOV

(09)English Title CONCERNING A METHOD OF DETERMINATION OF DISINTEGRATION TIME OF EXCITED IONS

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
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ABSTRACT: A new method for determining disintegration time of molecular ions is described. Knowledge of the disintegration time is essential in determining correlation between mass spectra obtained at low pressures and the product composition obtained from radiolysis in the range of atmospheric pressures. Determination of the disintegration rate of primary ions obtained from a collision with electrons in the gas phase is based on energetic analysis of ions during their ionization in a strong electrical field. Secondary ions generated in the strong field have a relatively small kinetic energy. This kinetic energy of secondary ions serves as a measure of the life of the primary ions. The schematic drawing of the ion source and electrode potentials when using an electron discellaration technique is shown in figure 1. The filament diameter is $5 \cdot 10^{-2}$ mm, the cylinder length is 10 mm and the potential difference between the filament and the cylinder can be varied from 0 to +100 volts. Using a filament potential of +100 volts and an ion discellaration to +10 volts, the disintegration time of $C_6H_4^+$ ion in

0853 0317

argon according to

$$C_6H_{14}^{+} + C_3H_7^{+} + (C_3H_7^{-})$$

is less than 10^{-8} sec. Orig. art. has: 2 figures.

Fig. 1. 1,2,3,4-- electrodes which shape the ion beam.

CIRC ABSTRACT WORK SHEET 0897 0318

(01)Acc Nr. TT6500293	(68)SIS Acc Nr. AT5023428	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author SUMIN, L. V.; GUR'YEV, M. V.; TUNITSKIY, N. N.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags mass spectrum, ion, kinetic energy, ion energy, electron energy

(66)Foreign Title
OB ISTINNYKH MASS-SPEKTRAKH I KINETICHESKIKH ENERGIYAKH IONOV

(09)English Title CONCERNING TRUE MASS-SPECTRA AND KINETIC ENERGIES OF IONS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: The problem of deviation of the actual mass spectra of ions from the corresponding true mass spectra is discussed. The larger the initial kinetic energy of an ion the greater its discrimination in the mass spectrometer. The relation between the ion energy distribution, determined from analysis of the line structure $\Psi(E)$ and the initial ion energy distribution $\Phi(E)$ is

$$\Phi(E) = \frac{\text{const}}{V_1 V_2} F\,\text{[illegible]}$$

where V_1 and V_2 are the two dimensions characterizing the orifice of the mass spectrometer. The collection coefficient P is equal to

$$P = \text{const}\,\frac{f_0 k_1}{f_1 k_0}$$

where f_0 and k_0 are experimentally determined peak areas for ion and molecule, respectively and f_1 and k_1 are initial points of the respective mass peaks. It was found that there is a significant discrepancy between the literature data on mass spectra of ions of

organic compounds (e. g. n-hexane) ionized with 70 ev electrons and their true values. A partial mass spectrum of n-hexane considering the initial energy of ions is shown in fig. 1. Orig. art. has: 1 figure, 2 formulas.

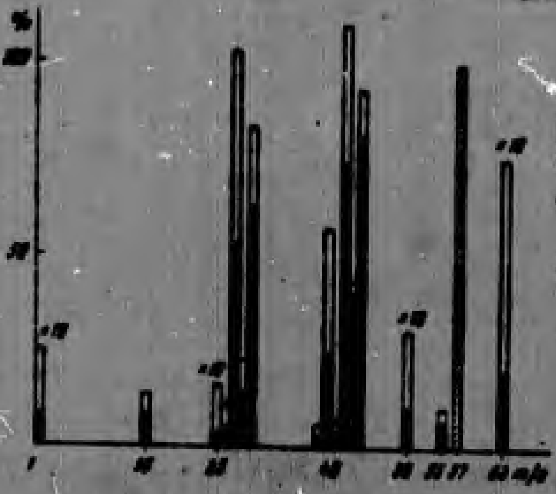

Fig. 1. ▯ -mass spectra according to handbook

■ -intensity of m/e = 57 line, assuming units of 100

⊏ -peak differential due to discrimination.

CIRC ABSTRACT WORK SHEET

0897 0320

(01)Acc Nr. TT6500294	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author MARKIN, M. I.; TAL'ROZE, V. L.

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(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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(39)Topic Tags ionization cross section, oxygen, hydrogen, molecule, charge exchange, heavy particle, collision cross section

(66)Foreign Title O VLIYANII KINETICHESKOY ENERGII OTNOSITEL'NOGO DVIZHENIYA IONA I MOLEKULY NA SECHENIYE I MEKHANIZM IONNO-MOLEKULYARNOY REAKTSII

(09)English Title ON THE INFLUENCE OF KINETIC ENERGY OF RELATIVE MOTION OF IONS AND MOLECULE ON CROSS SECTION AND MECHANISM OF AN ION-MOLECULE REACTION

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: This article investigates the statement that, from the dependence of charge exchange and transition cross section of a heavy particle upon kinetic energy, as kinetic energy increases the charge exchange cross section should generally outstrip the transition cross section if both transitions are energetically permitted during collision. A mixture of oxygen and hydrogen (O_2: H_2 = 1:100) was ionized; the formed packet of ions was extracted from the chamber, accelerated to a definite energy and entered the collision chamber. The secondary ions formed in the collision chamber have a velocity close to thermal and thus can be found in the collision chamber for a relatively long time. The dependence of the ratio of the cross sections of the processes

$$H_2^+ + O_2 \quad O_2H^+ + H \quad \text{and} \quad H_2^+ + O_2 \quad O_2^+ + H_2$$

upon the energy of the H_2^+ ions is given and the sharp change of the path of the curve at approximately 10 ev is considered connected with the expected sharp decrease of the first reaction cross section. English Translation: 5 formulas, 2 figures and 5 pages.

CIRC ABSTRACT WORK SHEET

0897 0321

(01)Acc No. TT6500205	(65)SIS Acc No. AT5023429	(40) Country of Info UR	(41)Translation No. MT6600004
(42)Author KUPRIYANOV, S. YE.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18-22 MARTA 1963)

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Language RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags excited state, particle collision, ion energy, mass spectrum, neon

(66)Foreign Title VOZBUZHDENIYE I DISSOTSIATSIYA IONOV V REZUL'TATE SOUDARENIY S ATOMAMI I MOLEKULAMI I SVYAZ' S MASS-SPEKTRAMI

(09)English Title EXCITATION AND DISSOCIATION OF IONS AS A RESULT OF COLLISIONS WITH ATOMS AND MOLECULES AND THEIR RELATION WITH MASS-SPECTRA

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: Mass spectre of excited molecules and ions and mass spectra of their dissociation due to collision with atoms and molecules were studied to determine the structure, nature, and energetic state of molecular ions. Good correlation was found between the mass spectra of C_3H_3N and n-C_4H_{10} obtained during electron impact with the mass spectra of dissociation of the corresponding ions due to single collision with neon atoms. An excellent agreement was found among mass spectra of dissociation of $C_2H_4^+$ ions which originated from C_2H_2, C_2H_4, C_3H_3N, C_3H_8, and n-C_4H_{10}. This agreement for the mass spectra of dissociation of ions stems from the fact that the energy of all C-C in ions is equal. Orig. art. has: 2 tables.

CIRC ABSTRACT WORK SHEET

C897 0322

(01)Acc Nr.	(65)SIS Acc Nr.	(40) Country of Info	(41)Translation Nr.
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(42)Author LATYPOV, Z. Z.; KUPRIYANOV, S. YE.

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(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18-22 MARTA 1963)

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(39)Topic Tags mass spectrum, particle collision, excited electron state

(44)Foreign Title O MASS-SPEKTRAKH VOZBUZHDENNYKH MOLEKULYARNYKH IONOV

(09)English Title CONCERNING MASS-SPECTRA OF EXCITED MOLECULAR IONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: Mass spectra (reported in the literature) obtained during collisions of molecules with electrons photons and slow ions and those obtained during collisions of ions with atoms and molecules were cross-compared with the aim of finding their common features. A coincidence of mass spectra was found in various collision processes having a similar average ion excitation energy and a similar ion energy distribution function. Mass spectra of the ion-electron collision coincide with mass spectra of the ion-photon collisions when $E_e - I < I$, where E_e is electron energy, and I is ionization energy of a molecule. When $E_e - I > I$, mass spectra of the fragment ions resulting from ionization of molecules due to collision with electrons coincide with mass spectra of dissociation of fast ions due to collision with neutral particles. Both the established dependence of mass spectra upon excitation energy and the found correlation between the mass spectra of molecule-electron, ion-atom, and ion-molecule collisions, make it possible to predict the mass spectra of molecular ions resulting from molecular ion-electron collisions. Thus the mass spectra taken during the collision of NH_3^+ and CH_4^+ ions with electrons have common features. Orig. art. has: 2 formulas.

CIRC ABSTRACT WORK SHEET

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(01)Acc No. TT6500297	(65)SIS Acc No.	(40) Country of Info UR	(41)Translation No. MT6600004

(42)Author PEROV, A. A.

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(39)Topic Tags ethylene, butane, benzene, methane, hydrogen ion, excitation cross section, ionization cross section

(66)Foreign Title VLIYANIYE ENERGII VOZBUZHDENIYA NA IONNO-MOLEKULYARNYYE REAKTSII V SHIROKOM DIAPAZONE ENERGII

(09)English Title INFLUENCE OF EXCITATION ENERGY ON ION-MOLECULE REACTION IN A WIDE RANGE OF ENERGY

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: H_2^+ ions from ethylene, n-butane and benzene are investigated and the obtained dissociation cross sections of H_2^+ are found to be below that of these ions from methane. This is explained by the lower vibrational excitation caused by the process of pyrolysis on the hot walls of the ionization chamber, with the formation of unexcited hydrogen molecules, and delayed disintegration of molecules. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET 0897 0324

(01)Acc Nr. TT6500298	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author TUKHOMIROV, M. V.	**Priority** II **Distribution** STD

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Language RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags ionization cross section, positive ion, nitrogen, particle collision, mass spectrum

(66)Foreign Title EKSPERIMENTAL'NOYE ISSLEDOVANIYE IONNO-MOLEKULYARNYKH REAKTSIY I SOUDARENIY IONOV I MOLEKUL V AZOTE

(09)English Title EXPERIMENTAL INVESTIGATION OF ION-MOLECULE REACTIONS AND COLLISIONS OF IONS AND MOLECULES IN NITROGEN

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
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ABSTRACT: This work proposes these ion-molecule reactions

$$N_2^{++} + N_2 \rightarrow N_3^+ + N; \qquad (1)$$

$$N_2^+ + N_2 \rightarrow N_4^{+*} \text{(vibrationally excited [6]).} \qquad (2)$$

from the appearance of N_4^+ and N_3^+ ion potentials of 15.8 and 22.1 v and the square dependence of the intensity of ion currents upon the nitrogen pressure in the ion source. Mass-spectra of nitrogen at elevated pressures were investigated, the dependences of ion line strength, the relative intensity of the fractional peak and the cross section of the process

$$N_2^{2+} + N_2 \rightarrow N_2^+ + N_2^+. \qquad (3)$$

upon electron energy are given and it is concluded that N_4^+ ions were not observed in the region of pressures up to 10μ. English Translation: 3 formulas, 3 figures and 4 pages.

CIRC ABSTRACT WORK SHEET

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(01)Acc No. TT6500299	(65)SIS Acc No.	(40) Country of Info UR	(41)Translation No. MT6600004

(42)Author DZANTIYEV, B. G.; SHVEDCHIKOV, A. P.	Priority II Distribution STD

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(39)Topic Tags ethylene, helium, ammonia, tritium, gas irradiation

(66)Foreign Title II. REAKTSII GORYACHIKH ATOMOV. REAKTSII GORYACHIKH ATOMOV VODORODA S ETILENOM

(09)English Title 2. REACTIONS OF HOT ATOMS. REACTIONS OF HOT ATOMS OF HYDROGEN WITH ETHYLENE

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: This work studies the interaction of hot radioactive atoms of hydrogen (tritium) with ethylene and mixtures of ethylene-ammonia and ethylene-helium in the gaseous phase at elevated pressures (up to 10 atm). Tagged products of the interaction of hot tritium atoms with ethylene were investigated and the radiolysis products of ethylene were identified. The effects of ammonia additions on the tritium distribution in the tagged products and of helium additions on the formation of tagged ethylene are illustrated. Relative radiation yields of products for the ethylene-ammonia mixture are tabulated. English Translation: 2 figures, 1 table and 8 pages.

CIRC ABSTRACT WORK SHEET

0892 0326

(01)Acc No. TT6500300	(65)SIS Acc No.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author BRODSKIY, A. M.; TEMKIN, A. YA.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18-22 MARTA 1963)

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Language RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags
ionization cross section, scattering cross section, scattering amplitude, particle collision, wave function

(44)Foreign Title
O MEKHANIZME REAKTSIY GORYACHIKH ATOMOV S MOLEKULAMI

(09)English Title CONCERNING THE MECHANISM OF REACTION OF HOT ATOMS WITH MOLECULES

	(97) Header Clas 0	(63) Clas 00	(64)Rel 0	(60) Release Expansion

ABSTRACT: This article presents arguments in favor of the hypothesis about the resonance character of the reactions of hot atoms with molecules. It is assumed that the scattering amplitude and cross section of these reactions are mainly determined by the resonance terms and are described by the Breit-Wigner formula. This assumption also pertains to certain other bimolecular processes. An important result of using the Breit-Wigner formula is constancy of the ratio of the rates of any two reactions proceeding in the same resonance: in any case, this ratio is equal to the ratio of the partial widths. Experimental determination of this ratio allows a judgement about the relative contribution of different valence schemes in the wave function of a compound molecule. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

0897 0327

(01)Acc No. TT6500301	**(65)SIS Acc No.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KONDRAT'YEV, V. N.

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(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18-22 MARTA 1963)

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(39)Topic Tags vibration relaxation, spin resonance, collision, ozone, molecule

(66)Foreign Title III. OBSHCHIYE VOPROSY TEORII ELEMENTARNYKH GAZOVYKH REAKTSIY. K VOPROSU O MEKHANIZME KOLEBATEL'NOY RELAKSATSII

(09)English Title 3. GENERAL QUESTIONS OF THEORY OF ELEMENTARY GAS REACTIONS. CONCERNING QUESTION ABOUT MECHANISM OF VIBRATIONAL RELAXATION

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: This paper presents a general discussion of the processes of quantum transformations occurring in an isolated molecule: vibrational energy into translational energy; vibrational energy into spin-orbital energy; electron energy into vibrational energy; the roles of these transformations in chemical and physical reactions are also discussed. English Translation: 6 pages.

CIRC ABSTRACT WORK SHEET

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(01)Acc Nr. TT6500302	(68)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author IVANOV, G. K.; SAYASOV, YU. S.

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(39)Topic Tags particle collision, molecule, scattering amplitude, approximation method, differential cross section, wave function

(66)Foreign Title IMPUL'SNOYE PRIBLIZHENIYE V TEORII ATOMNYKH I ATOMNO-MOLEKULYARNYKH STOLKNOVENIY

(09)English Title PULSE APPROXIMATION IN THEORY OF ATOMIC AND ATOMIC-MOLECULAR COLLISIONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
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ABSTRACT: The pulse approximation is based on the assumptions that the wavelength of the incident particle and its effective radius of interaction with particles of the scattering system are less than the average distance between them and that the time of paired interaction is much less than the time of an essential change of state of the scattering system. This method is applied for ionization during atomic collisions and scattering of fast atoms on molecules. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

C897 0329

(01)Acc No. TT6500303	**(65)SIS Acc No.**	**(40) Country of Info** UR	**(41)Translation No.** MT6600004

(42)Author KOZHUSHNER, M. A.; SAYASOV, YU. S.'

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0053	0055	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags scattering cross section, particle collision, inelastic scattering, inelastic interaction, nuclear physics

(66)Foreign Title O SVYAZI SECHENIY UPRUGIKH I NEUPRUGIKH PROTSESSOV PRI NEADIABATICHESKIKH ATOMNYKH STOLKNOVENIYAKH

(09)English Title CONCERNING THE RELATION BETWEEN CROSS SECTIONS OF ELASTIC AND INELASTIC PROCESSES DURING NONADIABATIC ATOMIC COLLISIONS

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
0	00	0	

ABSTRACT: This paper discusses the relation between cross sections of elastic and inelastic processes during nonadiabatic atomic collisions with participation of two atoms under these assumptions: 1) all interactions are centrally symmetric; 2) there are only two interacting states; 3) the energy terms of the initial and final states intersect; 4) the point of intersection of the terms lies below the energy threshold of reaction. English Translation: 2 formulas and 4 pages.

CIRC ABSTRACT WORK SHEET

0897 0330

(01)Acc No.	(65)SIS Acc No.	(40) Country of Info	(41)Translation Nr.
TT6500304		UR	MT6600004

(42)Author PODLUBNYY, L. I.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

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UR	0000	65	000	000	0056	0058	NONE	20

Language			
RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags gas ionization, argon, particle collision, inelastic interaction, approximation method

(66)Foreign Title K TEORII NEUPRUGIKH ATOMNYKH STOLKNOVENIY V ADIABATICHESKOY OBLASTI

(09)English Title ON THE THEORY OF INELASTIC ATOMIC COLLISIONS IN THE ADIABATIC REGION

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The theory of inelastic atomic collision in the adiabatic region is discussed as it applies to argon ionization and an approximating formula for this reaction is obtained. English Translation: 10 formulas and 8 pages.

CIRC ABSTRACT WORK SHEET

OS97 0331

(01)Acc Nr. TT6500305	(65)SIS Acc Nr. AT5023431	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author DANILOV, A. D.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMNTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0062	0064	NONE	04

Language RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags ionosphere, ionization, atmospheric recombination

(66)Foreign Title IV. REAKTSII V IONOSFERE. ROL' PROTSESSOV TIPA $X^+ + YZ \to XY^+ + Z$

(09)English Title ROLE OF PROCESSES OF TYPES $X^+ + YZ \to XY^+ + Z$ IN TERRESTRIAL IONOSPHERE

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The rate constants of such dissociative recombinations, reported in the literature, as

$$N_2 + O^+ \to NO^+ + N, \qquad O^+ + O_2 \to O_2^+ + O, \qquad N^+ + N_2 \to N_2^+ + N$$

and the disappearance of Ar^+ in the earth's ionosphere are discussed. These rates are verified by comparison with corresponding laboratory determined rate constants, α^*, which conform to the equation

$$\alpha^* \approx 3 \cdot 10^{-7}\sqrt{\frac{300}{T}}\ \text{cm}^3 \cdot \text{sec}^{-1}$$

where T is the gas temperature in °K. A comparison of the rate constants of dissociative recombinations based on actual information obtained from the earth's ionosphere with the corresponding rate constants determined in the laboratory allows determination of the altitude at which a given process may occur. Orig. art. has: 4 formulas. English Translation: 4 pages and numerous equations.

CIRC ABSTRACT WORK SHEET

0897 0332

(01)Acc Nr. TT6500306	(65)SIS Acc Nr. AT5023432	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author IVANOV-KHOLODNYY, G. S.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0066	0066	NONE	04

Language			
RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags ionization, ionosphere, reaction rate

(66)Foreign Title ISSLEDOVANIYE DISSOTSIATIVNOY REKOMBINATSII ATMOSFERNYKH IONOV N_2^+, O_2^+ I NO^+

(09)English Title INVESTIGATION OF DISSOCIATIVE RECOMBINATION OF ATMOSPHERIC IONS N_2^+, O_2^+ AND NO^+

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: A critical evaluation of laboratory determined rate constants of dissociative recombinations of N_2^+, O_2^+, and NO^+ is given in light of the information from the earth's ionosphere (100 km altitude) transmitted to earth by rockets and satellites. A satisfactory agreement of the geophysical data on dissociative recombination reactions with the results of laboratory tests is essential for studies involving simulated ionospheric conditions. The accuracy of the recent laboratory determinations of the rate constants of molecular dissociative recombination is within 150-200%. This accuracy is due to a proper treatment of the effect of ambipolar ion diffusion in the laboratory test chambers. Recent experimental improvements will be useful in investigating details of elementary processes occurring in the ionsphere, the energy balance, etc. English Translation: 2 pages.

CIRC ABSTRACT WORK SHEET

0897 0333

(01)Acc Nr. TD500307	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004
(42)Author YATSENKO, S. P.			**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0068	0070	NONE	04, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO NAUKA

(39)Topic Tags ionosphere, ion concentration, particle distribution, upper atmosphere

(66)Foreign Title OB ISSLEDOVANII KHIMICHESKIKH PROTSESSOV V IONOSFERE

(09)English Title ON THE INVESTIGATION OF CHEMICAL PROCESSES IN THE IONOSPHERE

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
0	00	0	

ABSTRACT: This article proposes the investigation of elementary chemical processes in the ionosphere through rocket technology. English Translation: 10 pages.

CIRC ABSTRACT WORK SHEET

0807 0334

(01)Acc Nr.	(65)SIS Acc Nr.	(40) Country of Info	(41)Translation Nr.
TT6500308		UR	MT6600004

(42)Author TAL'ROZE, V. L.; LARIN, I. K.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHMII VYSOKIKH ENERGIY. (MOSKVA 18-22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0077	0079	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags gas ionization, hydrogen ion, argon, ion concentration, positive ion

(66)Foreign Title V: MEKHANIZM NEKOTORYKH SOLZHNYKH PROTSESSOV PRI VYSOKIKH TEMPERATURAKH I V PLAZME. ROL' UTYAZHELENNYKH IONOV V TERMICHESKOY RAVNOVESNOY IONIZATSII GAZOV

(09)English Title THE ROLE OF HEAVY IONS IN THERMAL EQUILIBRIUM IONIZATION OF GASES

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: The authors calculated equilibrium concentrations of ions formed during thermal ionization of water vapor, hydrogen and argon, taking into account processes of formation of H_3O^+, H_3^+ and Ar_2^+ ions. Calculations showed that for H_2O and H_2 up to 4000°K, and for Ar, up to 6000°K, ionization is caused by formation of H_3O^+, H_3^+ and Ar_2^+ ions respectively, where concentration of heavy ions exceeds concentration of positive ions calculated without taking into account the former, in the region of 2000°K for water by three orders of magnitude, for hydrogen by two orders and for argon by four orders. This result is consequence of the large value of affinity of protons for water (169 kcal/mole) and hydrogen (70 kcal/mole) and of the Ar+ ion to Ar(≥99.3 kcal/mole). At the same time, from the entropy point of view, processes of formation of heavy ions

$$2M \rightleftarrows M_2^+ + e \qquad (I)$$

are less suitable than processes of direct ionization:

$$M \rightleftarrows M^+ + e. \qquad (II)$$

Therefore, with increase of temperature, when influence of heats of corresponding processes on degree of ionization decreases, and role of

0807 0335

TT6500308 MT6600004

entropy factor increases, equilibria of type (II) become decisive, the degree of ionization of which is calculated by the Saha formula. At present the authors have considered question about influence of pressure on role of heavy ions in equilibrium ionization should decrease in importance. As an example, for argon and hydrogen there were calculated pressures at which $P_{Ar_2^+}$ and $P_{H_3^+} = P_{H_2^+} + P_{H^+}$. English Translation: 11 formulas and 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0336

(01)Acc Nr. TT6500309	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author FILIPPOV, YU. V.; YEMEL'YANOV, YU. M.; SAMOYLOVICH, V. G.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI: "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0079	0081	NONE	20, 07

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags ozone, oxygen, kinetic theory, arc discharge

(66)Foreign Title OTSENKA SOOTNOSHENIYA KINETICHESKIKH KONSTANT ELEMENTARNYKH PROTSESSOV PO NAPRYAZHENIYAM GORENIYA ELEKTRICHESKOGO RAZRYADA

(09)English Title ESTIMATION OF RELATIONSHIP BETWEEN KINETIC CONSTANTS OF ELEMENTARY PROCESSES ACCORDING TO THE ARCING VOLTAGE OF AN ELECTRIC DISCHARGE

(97) Header Clas 0	(63) Clas 00	(64)Rel 0	(60) Release Expansion

ABSTRACT: This article proposed the method of total determination of inelastic losses from the arcing voltages of a discharge as a means of estimation the ratio of the kinetic constants of elementary processes. The magnitude of a reduced field E/p determined from the arcing voltage of discharge in a special discharger was used to estimate the ratio of the kinetic constants of the reactions: $O_3 + e$ and $O_2 + e$. English Translation: 2 formulas and 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0337

(01)Acc Nr. TT6500310	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author STUPOCHENKO, YE. V.; OSIPOV, A. I.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0081	0084	NONE	20, 07

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags gas state, fast particle, particle bombardment, activation energy, kinetic energy, maxwell distribution

(66)Foreign Title K VOPROSU O STATSIONARNYKH SOSTOYANIYAKH GAZOVOY SISTEMY, USTANAVLIVAYUSHCHIKHSYA POD VOZDEYSTVIYEM ISTOCHNIKOV BYSTRYKH CHASTITS.

(09)English Title CONCERNING THE QUESTION OF STATIONARY STATES OF A GAS SYSTEM ESTABLISHED UNDER THE ACTION OF SOURCES OF FAST PARTICLES

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
0	00	0	

ABSTRACT: This paper considers a gas system under the influence of a source of fast particles. These particles have a certain initial kinetic energy E_0 considerably exceeding the average thermal energies. During the direct influence of particles, in the system processes can occur with activation energy less than or near to E_0. However, this is not the only possibility. The action of particles causes disturbance in Maxwellian distribution of the gas particles which propagates (for comparable masses) far into the region of energies greater than E_0. The energy distribution of bombarding particles also changes as a result of their elastic scattering in the gas. In this way the mechanism by means of which a source of particles with energy E_0 can lead to processes with activation energy considerably exceeding E_0 is realized. This paper considers two simplified models of sucah a mechanism. English Translation: 11 equations and 4 pages.

CIRC ABSTRACT WORK SHEET

C897 C338

(01)Acc No. TT6500311	(65)SIS Acc No.	(40) Country of Info UR	(41)Translation No. MT6600004

(42)Author KALINENKO, R. A.; BRODSKIY, A. M.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0084	0087	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags hydrocarbon, photolysis, ethylene, excied state

(66)Foreign Title O PRYAMOM MOLEKULYARNOM RASPADE UGLEVODORODOV

(09)English Title CONCERNING DIRECT MOLECULAR DISINTEGRATION OF HYDROCARBONS

(97) Header Clas 0	(63) Clas 00	(64)Rel 0	(60) Release Expansion

ABSTRACT: This paper notes that there are essential differences between the mechanisms of molecular processes above and below 7 ev. During photosensitized photolysis of ethylene in the excited state, internal exchange of hydrogen atoms is realized (the ratio H_2:HD:D_2 is approximately identical during photolysis of CH_2CD_2 and cis-CHD-CHD). During photolysis by light with the wavelengths in the region of vacuum ultraviolet, such exchange in the excited state is absent (the ratio H_2:HD:D_2 is equal to 2:8:1 during photolysis of trans-CHDCHD and 2:2:1 during photolysis of CH_2CD_2). During photosensitized decomposition of hydrocarbons, there occurs the isotope effect. During photolysis by light with wavelengths in the region of vacuum ultraviolet of mixtures $C_2H_4 + C_2D_4$, $C_2H_6 + C_2H_6$, $C_3H_8 + C_3D_8$, the isotope effect is absent, and during decomposition under these conditions of CHDCHD, CH_2CD_2, CH_3CD_3, the isotope effect occurs. English Translation: 1 formula and 5 pages.

CIRC ABSTRACT WORK SHEET

0897 0339

(01)Acc Nr. TT6500312	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KAPLAN, I. G.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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UR	0000	65	000	000	0091	0094	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags excitation energy, excited electron state, nuclear physics, radiation physics

(66)Foreign Title I. PEREDACHA ENERGII ELEKTRONNOGO VOZBUZHDENIYA. SRAVNITEL'NAYA POL' VOZMOZHNYKH MEKHANIZMOV PERENOSA ENERGII PRI RADIOLIZE ZHIDKIKH RAZBAVLENNYKH RASTVOROV

(09)English Title COMPARATIVE ROLE OF POSSIBLE MECHANISM OF ENERGY TRANSFER DURING RADIOLYSIS OF LIQUID DILUTE SOLUTIONS

(97) Header Clas 0	**(63) Clas** 00	**(64)Rel** 0	**(60) Release Expansion**

ABATRACT: This paper discusses the causes of deviation from the additive law during radiolysis of mixtures: energy transfer between separate components; resonance transfer of electron excitation energy from the low singlet excited level to the singlet excited level; diffusion of excitation between molecules; resonance transfer of energy through upper singlet levels; transfer of charge; selectivity in absorption of energy by components of the solution. These deviations from additivity during radiolysis were divied into two groups: sensitized radiolysis and radiation shielding. English Translation 5 pages.

CIRC ABSTRACT WORK SHEET

0897 0340

(01)Acc Nr. TT6500315	**(65)SIS Acc Nr.** AT5023433	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004
(42)Author PROTOPOPOV, KH. V.			**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0095	0098	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags exciton, excited state, molecular interaction, particle interaction

(66)Foreign Title ESKITONY V ZHIDKOY FAZE I STRUKTURA ZHIDKOSTEY

(09)English Title EXCITIONS IN THE LIQUID PHASE AND STRUCTURE OF LIQUIDS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The problem of weak, medium, and strong interactions between excited and nonexcited molecules in liquid phase is discussed in detail. The structure of aromatic liquids and solutions is discussed in terms of molecular interaction. In the case of strong interaction, there occur free excitons the life of which is $\tau_c < \tau_2/n$, where $\tau \times 10^{-11}$ sec is the life of orientative relaxation and n - the number of molecules in a domain. As a result of the interactionwith the defects of a domain the free exciton becomes localized and forms an excited aggregate (eximer) with several neighboring molecules of the liquid through resonance interaction. The eximer along with other molecules in a close ordering is called an orienton. The concepts of eximers and orientons explain many important features of such an excited liquid organic system as anthracene in benzene. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0341

(01)Acc Nr. TT5500314	(65)SIS Acc Nr. AT5023434	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author YERMOLAYEV, V. L.

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Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0100	0102	NONE	20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags particle interaction, excited state, phosphorescence, particle collision, molecular interaction

(66)Foreign Title RAZLICHNYYE TIPY BEZYZLUCHATEL'NOGO PERENOSA ENERGII OT TRIPLETNYKH MOLEKUL AROMATICHESKIKH SOYEDINENIY

(09)English Title DIFFERENT TYPES OF NONRADIATIVE ENERGY TRANSFER FROM TRIPLET MOLECULES OF AROMATIC COMPOUNDS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: Various types of nonradiative energy transfer in solid solutions involving aromatic molecules in the triplet state are discussed. The first type occurs during the sensibilized phosphorescence of organic compounds in glassy solution at low temperatures. The process of deactivation occurs here according to the triplet-triplet scheme

$$^3\Gamma_D + {}^1\Gamma_A \rightarrow {}^1\Gamma_D + {}^3\Gamma_A$$

where A is acceptor and D is donor. The probability of the triplet-triplet energy transfer is independent of the singlet-triplet transformation of the acceptor molecule. The triplet-triplet type energy transfer (nonradioactive) conforms to the Wigner rule of preservation of total spins of the donor and the acceptor during the energy transfer act and the nonradioactive transfer of electronic excitation energy from organic molecules in the triplet state follows the inductive-resonance mechanism. In the case of this triplet-singlet transfer the acceptor molecule transforms into the excited singlet state according to

$$^3\Gamma_D + {}^1\Gamma_A \rightarrow {}^1\Gamma_D + {}^1\Gamma_A$$

The triplet-singlet type energy transfer need not conform to Wigner's

0677 0342

rule. This indicates that in the absence of photochemical reaction the internal decay of the electronic excitation energy of aromatic molecules occurs via triplet state. Orig. art. has: 2 figures. English Translation: 2 pages.

CIRC ABSTRACT WORK SHEET

FR47 0343

(01)Acc Nr. TT5500315	**(65)SIS Acc Nr.** AT5023435	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author TUNITSKIY, N. N.; BAGDASAR'YAN, KH. S '

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0105	0108	NONE	20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags fluorescence, excited electron state, excited state, radiation effect

(66)Foreign Title PROTSESSY PEREDACHI ENERGII V KONDENSIROVANNYKH SISTEMAKH

(09)English Title PROCESSES OF ENER[illegible]RANSFER IN CONDENSED SYSTEMS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: A methematical treatment of the resonance mechanism of electronic excitation energy transfer is given. This mechanism operates during extinguishing of fluorencence of excited molecules B* by the acceptor molecules A, during sensibilized fluorescence of A molecules, during inhibition of chemical decomposition of B* by A, and during sensibilized photolysis or radiolysis of A molecules. For strong resonance type excitation energy transfer, the radius of the molecular interaction R depends only upon α and D where α is the energy transfer constant depending upon molecule orientation and D is diffusion constant. R is independent of molecular dimension. In general the magnitude of α is within 10^{-33}-10^{-31} cm^6/sec range and the magnitude of D is about 10^{-5} cm^2/sec; consequently, the magnitude of R is the order of 10^{-7} sec. The values of the effective molecular interaction radius R can be applied to the steady state process. If excitation energy transfer from B* to A results in chemical transformation of A and concentration of A is sufficiently small, then the steady-state concentration of A molecules is expressed by $\frac{dv}{dt} = - Nv$. Orig. art. has: 10 formulas. English Translation: 5 pages and numerous equations.

FTD FORM SEP 64 0-493d

CIRC ABSTRACT WORK SHEET

6809 0344

(01)Acc Nr. TT6500316	**(65)SIS Acc Nr.** AT5023436	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KRONGAUZ, V. A.; VASIL'YEV, I. N.; KIRSANOV, B. P.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYEE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0110	0112	NONE	20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags excited state, particle interaction, molecular interaction, particle collision, luminescence

(66)Foreign Title ISSLEDOVANIYE MEKHANIZMA MEZHMOLEKULYARNOGO PERENOSA ENERGII V ORGANICHESKIKH RASTVORAKH VLIYANIYE DIFFUZII

(09)English Title INVESTIGATION OF MECHANISM OF INTERMOLECULAR ENERGY TRANSFER IN ORGANIC SOLUTION. THE INFLUENCE OF DIFFUSION

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
C	00	0	

ABSTRACT: The transfer of excitation energy between benzene and toluene, 2,5-diphenyloxazole, and 2,5-diphenyloxazole and isopropyldiphenyl and cyclohexane was studied. The dependence of the relative intensity (I) of luminescence of a diphenyloxazole solution (0.005 moles/l) in isopropyldiphenylcyclohexane mixture upon the reciprocal viscosity of the solvent os shown in figure 1. For all three systems, the experimentally determined rate constants of energy transfer k_{AB} are lower than those calculated from the formula

$$k_{AB} = 4\pi D r_0 N \left(1 + \frac{r_0}{\sqrt{D\tau_0}}\right)$$

where D is diffusion coefficient, r is critical radius for instantaneous intermolecular energy transfer by exchange mechanism, τ_0 is life of excited molecules. This discrepancy is probably due to deviation from the probability of resonance interaction W(r) between molecules A and B as calculated from the formula

$$W(r) = \frac{1}{\tau_0}\left(\frac{r_0}{r}\right)^6,$$

where r is intermolecular distance. Orig. art. has: 1 figure, 1 table, 7 formulas. English Translation: 4 pages, 1 figure, 1 table, numerous

FTD FORM SEP 64 0-493d

equations.

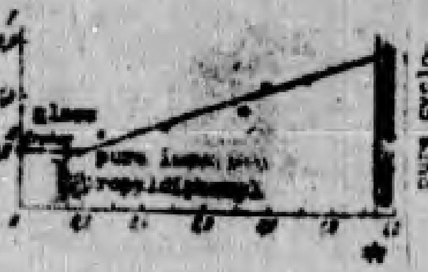

Fig. 1. Diphenyloxazole in a glossy isopropyldiphenyl solvent at -78°C.

CIRC ABSTRACT WORK SHEET

0897 0346

(01)Acc Nr. TT6500317	**(65)SIS Acc Nr.** AT5023437	**(40) Country of Info** UR	**(41) Translation Nr.** MT6600004

(42)Author BRODSKIY, A. M.; KOLBANOVSKIY, YU. A.; POLAK, L. S.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ERERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0113	0115	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags radiation effect, excited state, electron energy, excited electron state

(66)Foreign Title O PEREDACHE ENERGII PRI RADIOLIZE UGLEVODORODOV

(09)English Title ENERGY TRANSFER DURING RADIOLYSIS OF HYDROCARBONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The effect of inhabition (by aromatic molecules, molecules of iodine, etc.) on electron excitation energy transfer during radiolysis of hydrocarbons at low and medium temperatures was studied. For highly excited states with a relaxation time of the order of 10^{-13}-10^{-14}, the probability (in vacuum) of energy transfer from the excited molecules to the molecules of the inhabitor by the dipole-dipole mechanism is

where w_I and w_{II} are probabilities of dipole generation by excited molecules and molecules of the inhabitor, respectively, $\rho(\omega)$ is density distribution in the ultimate state of the inhibitor molecules, α is a dimensionless parameter. In many cases, the excitation level of a chemically active molecular system, particularly ions, is below the first excitation level of most molecules in the reacting system. In the case of strong absorption by the molecules of the inhibitor, the dependence of the probability of inhibition ω upon concentration is

where B_1 and B_2 are constants depending upon the intensity of molecular

interaction; their values are close to unity. The equation describes the characteristic features of inhibition of electronic energy transfer. Orig. art. has: 2 formulas. English Translation: 5 pages and numerous equations.

CIRC ABSTRACT WORK SHEET 0897 0348

(01)Acc Nr. TT6500318	**(65)SIS Acc Nr.** AT5023438	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author VASIL'YEV, R. F.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0118	0121	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags excited state, chemiluminescence, oxidation, ethylbenzene, anthracene, particle collision

(66)Foreign Title ISSLEDOVANIYE PEREDACHI ENERGII METODOM KHEMILYUMINESTSENTSII

(09)English Title INVESTIGATION OF ENERGY TRANSFER BY METHOD OF CHEMILUMINESCENCE

(97) Header Clas 0	**(63) Clas** 00	**(64)Rel** 0	**(60) Release Expansion**

ABSTRACT: The mechanism of energy transfer was studied using a molecule excitation technique based on chemiluminescence. The dosage was as low as 2-4 ev. The mechanistic aspects were treated in terms of triplet-triplet and triplet-singlet transformation. The energy level schans for the oxidation of ethylbenzene and energy transfer to acetylene derivatives as reflected in chemiluminescence is shown in fig. 1. The effect of substituents on the probability of triplet-singlet type inter- and intermolecular energy transfers in oxidation of cyclohexane in benzene at 50° C is shown in fig. 2. The effect of halogens on intra- and intermolecular energy transfer conforms to the same mechanism. Orig. art. has: 2 figures. English Translation: 5 pages and numerous equations.

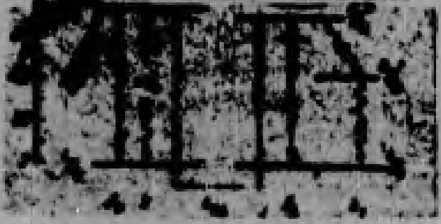

Fig. 1. Solid line--rate constants of energy transfer without chemiluminescence, wavy line--energy transfer without chemiluminescence, dotted line--course of transfer.

FTD FORM SEP 64 0-493d

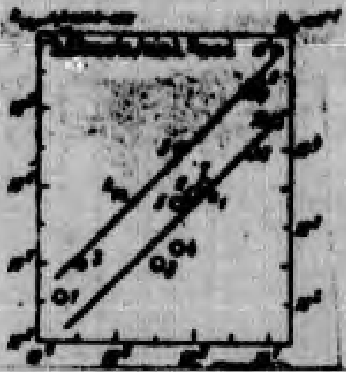

Fig. 2. K_1--based on the data of D. S. McClure, J. Chem. Phys., 17, (1949); K_{pA}--according to R. F. Vasil'yev, A. A. Vichutinskiy, A. S. Cherkasov, Dokl. Akad. Nauk SSSR, 149, 124 (1963) assuming f_p for cyclohexane equal to 10^3 sec $^{-1}$: 1--anthracene; 2-10--anthracene derivatives; 2--9,10-diphenyl; 3--1-chloro; 4--1,5-dichloro; 5--9,10-dichloro; 6--2,9,10-tichloro; 7--1,5,9,10-tetrachloro; 8--9-bromo; 9--9-bromo; 10--phenyl and 9,10--dibromo.

CIRC ABSTRACT WORK SHEET 0897 0350

(01)Acc Nr. TT6500319	**(65)SIS Acc Nr.** AT5023439	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KILIN, S. F.; ROZMAN, I. M. — **Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)City	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0122	0126	NONE	20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags luminescence quenching, excited electron state, electron energy, luminescence, electron bombardment, photoluminescence, fluorescence

(66)Foreign Title SPETSIFICHESKOYE TUSHENIYE LYUMINESTSENTSII ORGANICHESKIKH SOYEDINENIY PRI VOZBUZHDENII BYSTRYMI ELEKTRONAMI

(09)English Title SPECIFIC QUENCHING OF LUMINESCENCE OF ORGANIC COMPOUNDS DURING EXCITATION BY FAST ELECTRONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The yield and duration of luminescence in several organic compounds was studied during their excitation by fast electrons to assess the dynamic quenching effect. Luminescence duration was measured on a phase fluorometer with a modulation frequency $\omega = 1.25 \cdot 10^8$ sec. Dependence of luminescence duration of plastic scintillators upon concentration of luminescence additive is shown in fig. 1. Dependence of luminescence yield of liquid and plastic scintillators upon additive concentration is shown in fig. 2. For dependence of luminescence duration of anthranilic acid in alcohol upon concentration see fig. 3. For antharenilic acid CCl_4 system, the rate constant of luminescence quenching is $4.7 \cdot 10^9$ 1/mol·sec and the rate constant of photoluminescence quenching is $2.4 \cdot 10^9$ 1/mol·sec. Orig. art. has: 3 figures, 1 table, 3 formulas. English Translation: 5 pages, numerous figures and equations.

Fig. 1. 1 and 2--1,3,5-triphenyl-A^2-pirazole in polyvinyltoluene; 3 and 4--1,1,4,4-tetraphenyl-1-3-butadien in polystyrene; curves 1 and 3--excitation by x-rays and curves 2 and 4--excitation by UV light (λ = 3200-3000 Å).

9597 0351

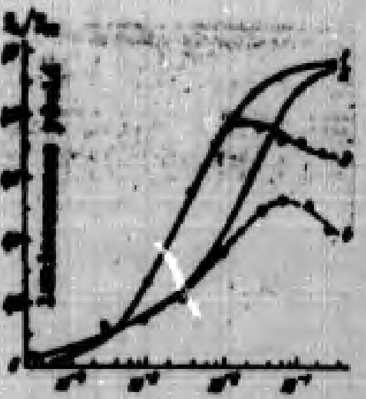

Fig. 2. 1 and 2--ratios of quantum yields of additive fluorescence during excitation of solvent (λ = 2652 Å) and indirect excitation of additive (λ = 3650 Å), 3 and 4 --ratios of luminescence intensity during excitation of C^{14}-compound by β-particles and photons (λ = 3650 Å), curves 1 and 3--liquid phase; curves 2 and 3--2 and 3--plastic state.

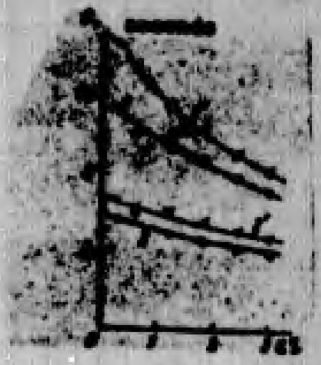

Fig. 3. 1 and 1'--optical excitation; 2 and 2' --excitation with x-rays, 1 and 2--oxygen saturated solutions; 1' and 2'--O_2-free solutions.

CIRC ABSTRACT WORK SHEET

0847 0352

(01)Acc No. TT6500320	**(65)SIS Acc No.**	**(40) Country of Info** UR	**(41)Translation No.** MT6600004

(42)Author KOLBANOVSKIY, YU. A.; PEPELYAYEV, YU. V.; POLAK, L. S.; KHAIT, YU. L.; SHLIKHTER, E. B.

Priority Distribution

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY." TRUDY S'MPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY, (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0126	0128	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags heptane, aluminum oxide, catalyst, catalytic decomposition, radiation heat transfer

(66)Foreign Title O PEREDACHE POGLOSHCHENNOY TVERDYM TELOM ENERGII MOLEKULAM, NAKHODYASHCHIMSYA NA YEGO POVERKHNOSTI

(09)English Title TRANSMISSION OF ENERGY ABSORBED BY A SOLID BODY TO MOLECULES ON ITS SURFACE

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: There was studied gamma-radiolysis of n-heptane adsorbed on the following catalysts: γ-oxide of aluminum (I), aluminum-chromium, activated K_2O (II), aluminum-molybdenum (III), cobalt-aluminum-molybdenum (IV). Linear dependence of radiolysis rate (ΔP/gm $C_7H_{16}\cdot$hr) on ratio of electronic fractions, catalyst II/heptane, in interval of values corresponding to the limiting cases of a monomolecular layer and a homogeneous system indicates that radiation energy transfer from catalyst to heptane occurs only in the monolayer. On the basis of formal-kinetic scheme there is conducted estimation of probability of transfer z, which strongly depends on preliminary conditioning of catalyst. With identical conditioning, spearate values of $\Delta P = \varphi(z)$ for different catalysts lie on one straight line. The most active is the catalyst, irradiation of which together with the absorbed substance does not change the electron paramagnetic resonance [EPR] (ЭПР) spectrum as compared to the spectrum of the initial irradiated catalyst. The greater the change in spectrum (I < IV < II < III), the less active the catalyst is (I > IV > II > III). It has been established that the greater the electrical conductivity of the catalyst, the less the change of intensity of the EPR signal. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0357

(01)Acc Nr. TT6500321	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author AGRANOVICH, V. M.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0129	0131	NONE	20, 07

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags exciton, molecular crystal, excitation energy

(66)Foreign Title K VYPROSU O DIFFUZII EKSITONOV V MOLEKULYARNYKH KRISTALLAKH

(09)English Title CONCERNING THE QUESTION OF DIFFUSION OF EXCITONS IN MOLECULAR CRYSTALS

	(97) Header Clas 0	(63) Clas 00	(64)Rel 0	(60) Release Expansion

ABSTRACT: This article discusses the diffusion of excitons in molecular crystals, differentiating between localized and free excitons. English Translation: 3 formulas and 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0354

(01)Acc Nr. TT6500322	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author ZHEVANDROV, N. D.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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UR	0000	65	000	000	0132	0133	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags molecular crystal, solid solution, nonaqueous solution luminescence, crystal luminescence, polarized luminescence

(66)Foreign Title POLYARIZATSIONNO-LYUMINESTSENTNYY METOD ISSLEDOVANIYA MIGRATSII ENERGII V MOLEKULYARNYKH KRISTALLAKH

(09)English Title POLARIZATION-LUMINESCENCE METHOD OF INVESTIGATION OF MIGRATION OF ENERGY IN MOLECULAR CRYSTALS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: Luminescence methods of investigation of migration of energy in solid and liquid solutions are based on concentration effects or on differences between optical properties of solvent and impurity. It is obvious that these methods can be applied to the study of migration in single-component crystals and in mixed crystals - to the study of migration between molecules if impurity. For study of migration of energy in these cases, we have used the polarization-luminescence method based on the independence of polarization of luminescence of molecular crystals from polarization of the exciting light. Essence of it is the following: From principle of dense packing it follows that in a crystal there are not one, but several types of orientation of molecules. Their oscillators of radiation with linearly polarized excitation will be excited with various probabilities. This difference depends on position of electrical vector of exciting light. It follows from this that the degree of polarization of luminescence should depend on polarization of exciting light. This dependence in turn should be determined by orientation of crystal. Without going into detail here, we will note the investigations have always been conducted with an orientation which should correspond to the sharpest dependence. Calculations conducted for certain crystals show that dependence should be very strong; in individual cases, change of degree of polarization composes from -50 to +100%. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

C897 0355

(01)Acc Nr. TT6500323	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author DAVYDOV, A. S.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0151	0153	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags excitation energy, electron energy, polymerization, solid state, liquid state, excited state

(66)Foreign Title K VOPROSU O MIGRATSII ENERGII

(09)English Title ON THE QUESTION OF ENERGY MIGRATION

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: The particular question of energy migration in the general problem of transfer of electron excitation energy is discussed, as it pertains to polymerization in the liquid or solid state. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0587 0356

(01)Acc Nr. TT6500324	(65)SIS Acc Nr. AT5023440	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author PROTOPOPOV, KH, V.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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UR	0000	65	000	000	0153	0156	NONE	20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags luminescence, excition, excited state, excited electron state, electron energy

(66)Foreign Title K VOPROSU O MIGRATSII ENERGII V ZHIDKOY FAZE

(09)English Title CONCERNING THE QUESTION OF MIGRATION OF ENERGY IN THE LIQUID PHASE

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The mechanism of electronic excitation energy transfer in liquid solutions of aromatic compounds is discussed in terms of excimers and orientons. The excimer represents an electronically excited aggragate involving a localized exciton and several neighboring molecules. The orienton is a domain involving an excimer and several molecules surrounding it in short range order through resonance interaction. An orienton in characterized by reduced potential energy and entropy, and a structure resembling that of a crystalline material. Any transformation occurring in an excimer is reflected in a corresponding transformation in the orienton. The orienton concept is supported by the following experimental evidence: quantum yields, scintillation, and long wave electron work function during luminescence are increased when the concentration of benzene, xylene, naphthalene or anisola in various solvents is increased. English Translation: 4 pages.

FTD FORM SEP 64 -4934

CIRC ABSTRACT WORK SHEET

C807 0357

(01)Acc Nr. TT6500325	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KAPLAN, I. G.; GALANIN, M. D.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0156	0157	NONE	20, 07

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags excitation energy, electron energy, electromagnetic effect, nonaqueous solution, excited state, solid solution

(66)Foreign Title OB ELEKTROMAGNITNOM MEKHANIZME PERENOSA ENERGII ELEKTRONNOGO VOZBUZHDENIYA PRI RADIOLIZE RAZBAVLENNYKH RASTVOROV

(09)English Title CONCERNING THE ELECTROMAGNETIC MECHANISM OF ELECTRON EXCITATION ENERGY TRANSFER DURING RADIOLYSIS OF DILUTE SOLUTIONS

	(97) Header Clas 0	**(63) Clas** 00	**(64)Rel** 0	**(60) Release Expansion**

ABSTRACT: This paper discusses the electromagnetic mechanism of electron excitation energy transfer during radiolysis of dilute solutions. English Translation: 2 pages.

CIRC ABSTRACT WORK SHEET

0557 0358

(01)Acc Nr. TT6500326	**(65)SIS Acc Nr.** AT5023441	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004
(42)Author YERMOLAYEV, V. L.			**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMNTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0158	0159	NONE	20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags particle interaction, excited state, excited electron state, particle collision

(66)Foreign Title O MAGRATSII (PERENOSE) ENERGII S UCHASTIYEM TRIPLETNYKH SOSTOYANIY ORGANICHESKIKH SOYEDINENIY

(09)English Title ON MIGRATION (TRANSFER) OF ENERGY WITH PARTICIPATION OF TRIPLET STATES OF ORGANIC COMPOUNDS

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
0	00	0	

ABSTRACT: The mechanism of energy transfer between organic molecules in solid solutions, liquid solutions and crystals is discussed in terms of resonance theory. In solid solutions, if the Wigner rule of preservation of total spin is satisfied, the energy is transferred from an organic molecule in a triplet state to another in a singlet state and is in accord with the exchange-resonance mechanism

$$ {}^{3}\Gamma_D + {}^{1}\Gamma_A + {}^{1}\Gamma_D + {}^{3}\Gamma_A $$

where D is a donor and A is an acceptor. This "triplet-triplet" mechanism is operative at a donor concentration in solid solution of $5 \cdot 10^{-2}$-$5 \cdot 10^{-1}$ moles/l and for the intermolecular distance of 10-15 Å. An inductive-resonance mechanism is operative and the Wigner rule is not followed when the intermolecular distance (donor-acceptor) in the solid solution is 25-50 Å. In this case, the acceptor molecule converts into an excited singlet state according to:

$$ {}^{3}\Gamma_D + {}^{1}\Gamma_A + {}^{1}\Gamma_D + {}^{a}\Gamma_A $$

C897 C259

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In the oxygen-free liquid solution, the energy transfer is of a triplet-triplet type and follows the exchange resonance mechanism. In liquid solutions the life of organic molecules in triplet state is 10^{-6}-10^{-3} sec. In case of benzene, triplet-triplet type energry transfer proceeds at an appreciable rate at an acceptor concentration of 10^{-5}-10^{-5} moles/1 (293°K, $[O_z] = 0$, libe of the donor triplet state = 10^{-3} sec). The problems of triplet-singlet type energry transfer in the liquid solutions and of the triplet-triplet type energy transfer in crystals remain unsolved. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0597 0360

(01)Acc Nr. TT6500327	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author BAGDASAR'YAN, KH. S.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0160	0161	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags gamma radiation, ion radical, primary aromatic amine, radical concentration

(66)Foreign Title OBRAZOVANIYE ION-RADIKALOV PRI RADIOLIZE ZAMOROZHENNYKH ORGANICHESKIKH ZHIDKOSTEY I POLIMEROV; SODERZHASHCHIKH RASTVORENNYYE DOBAVKI

(09)English Title FORMATION OF ION-RADICALS DURING RADOILYSIS OF FROZEN ORGANIC LIQUIDS AND POLYMERS CONTAINING DISSOLVED ADDITIONS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: This article presents a survey of three recent investigations of the author during gamma-irradiation of dilute solutions of aromatic amines frozen in organic liquids and polymers. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

08 97 0361

(01)Acc Nr. TT6500328	**(65)SIS Acc Nr.** AT5023442	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author NIKOL'SKIY, V. G.; TOCHIN, V. A.; BUBEN, N. YA.

Priority Distribution II STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0163	0165	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags alkene, mass spectrum, photoluminescence, free radical, electron trapping, electron bombardment, spectrophotometer

(66)Foreign Title ISSLEDOVANIYE OPTICHESKIMI METODAMI ELEKTRONOV, STABILIZIROVANNYKH V NEKOTORYKH PREDEL'NYKH UGLEVODORODAKH

(09)English Title INVESTIGATED BY OPTICAL METHODS OF ELECTRONS STABILIZED IN CERTAIN SATURATED HYDROCARBONS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: Photoluminescence and color of hexane, nonane, 2,4-dimethyldecane, tetradecane, cyclohexane, dicylohexyl-4-decane, 1,2-dicylohexyldodecane, and high density polyethylene were studied during irradiation with fast electrons at 77°K. The irradiation dose varied from $5 \cdot 10^4$ to $2 \cdot 10^8$ rads. The spectra were taken with CF-2M spectrophotometer. The objective was to learn more about the nature of the electron traps which fix electrons during radiolysis of saturated hydrocarbons at low temperatures. After radiolysis saturated hydrocarbons exhibit photoluminescence (4000-6000 Å). The photoluinescence and color are due to stabilized ions present in the saturated hydrocarbons. The number and depth of electron traps increase with the irradiation dosage. By nature, the electron traps occurring in saturated hydrocarbons during irradiation are stabilized radicals. These radicals are capable of recombination under heating. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

0897 0362

(01)Acc Nr. TT6500329	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author FRANKEVICH, YE. L.; YAKOVLEV, B. S.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0167	0170	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags electric polarization, hydrocarbon, electric conductivity

(66)Foreign Title O MIGRATSII ZARYADA VDOL' UGLEVODORODNOY TSEPI

(09)English Title ON MIGRATION OF CHARGE ALONG A HYDROCARBON CHAIN

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: This paper reports on investigation of high-voltage polarization appearing in saturated hydrocarbons irradiated at 77K. Semilogarithmic anamorphoses of the dependence of reverse current on time and the dependence of the electrical conductivity of irradiated polyethylene on temperature are given. English Translation: 7 pages.

CIRC ABSTRACT WORK SHEET

0557 0363

(01)Acc No. TT6500330	**(65)SIS Acc No.**	**(40) Country of Info** UR	**(41)Translation No.** MT6600004

(42)Author VASIL'YEV, G. K.; TAL'ROZE, V. L.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)City	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0178	0180	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags radical concentration, thermodynamic equilibrium, equilibrium constant, free radical

(66)Foreign Title K TEORII NAKOPLENIYA ZAMOROZHENNYKH RADIKALOV V TVERDYKH TELAKH

(09)English Title ON THE THEORY OF ACCUMULATION OF FROZEN RADICALS IN SOLID BODIES

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: As is known [1, 2], during accumulation of radicals in solid bodies there are observed gradual deceleration of growth of their concentration and transition to limiting, or almost limiting, i.e., to very slowly increasing concentrations. In this work there are considered certain hypothetical mechanisms of processes leading to the phenomenon of "limiting concentration." Part of these mechanisms have been to various degrees considered by other authors; certain are considered in this work for the first time. First of all, we should note that inasmuch as in all cases concentrations of radicals are many orders higher than thermodynamically equilibrium concentrations, then the nature of the phenomenon is undoubtedly connected with kinetic processes occurring in the system, either during radiation influence or in a thermodynamically nonequilibrium system in the absence of a field of radiation. Conducted comparison with experimental data shows that it is possible to satisfactorily explain the observed concentrations of free radicals (in particular nitrogen atoms) at the temperature of liquid helium with the help of the thermal-chain model. Actually observed concentrations of radicals at higher temperatures (in particular in organic compounds) are 1-2 orders lower than predicted by the obtained formulas. The conclusion is drawn that in certain real systems it is probably not possible to expect obtaining of concentrations of frozen radicals exceeding 0.01 (if we express them as a fraction of all bonds in the system). English Translation: 6 pages.

CIRC ABSTRACT WORK SHEET

0597 0364

(01)Acc Nr.	(65)SIS Acc Nr.	(40) Country of Info	(41)Translation Nr.
TT6500331		UR	MT6600004

(42)Author LEBEDEV, YA. S.; MIKHAYLOV, A. I.; BUBEN, N. YA.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0183	0186	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags free radical, recombination radiation, radical concentration, polynuclear organic compound

(66)Foreign Title K VOPROSU O MEKHANIZME "STUPENCHATOY" REKOMBINATSII SVOBODNYKH RADIKALOV V OBLUCHENNYKH TVERDYKH VESHCHESTVAKH

(09)English Title CONCERNING THE QUESTION OF THE MECHANISM OF "STEP" RECOMBINATION OF FREE RADICALS IN IRRADIATED SOLID SUBSTANCES

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The step character of recombination of free radicals in irradiated inorganic systems for the first time was observed in works [1-3]. Lately there has been observed the same recombination in cyclohexane and n-octyl alcohol [4]. Recently it was shown that recombination of macroradicals in irradiated polyethylene [5] and polypropylene [6] at low temperatures also occurs in "steps", in distinction from recombination at temperatures higher than room temperature [7]. We studied processes of recombination of free radicals in various frozen organic substances - phenol, naptnalene glycine, malonic and palmitic acids, and others. In majority of studied cases, destruction has a step character, i.e., at a given temperature there disappears only a definite part of the accumulated radicals (Fig. 1). Analysis of results obtained here and in the literature permits us to make the following conclusions with respect to phenomenology of "step" recombination: 1) "steps" are observed in a very wide range of temperatures (phenol ~70°, malonic acid ~100°, glycine ~250°); 2) magnitude of concentration of free radicals remaining on a "step" (n_{CT}), is for a given sample a function only temperature, this is confired by experiments on "splitting of steps" (Fig. 1). 3) dependence of n_{CT} on T in a number of cases satisfied the empirical relationship $\frac{n_{CT}}{n_0} = a - bT$ (Fig. 2). English Translation: 2 formulas, 2 figures and 4 pages.

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CIRC ABSTRACT WORK SHEET

0597 0365

(01)Acc Nr. TT6500332	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author BUBEN, N. YA.; TOLKACHEV, V. A.; CHKHEIDZE, I. I.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0187	0188	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags aromatic hydrocarbon, optic radiation stability, epr spectrum, epr spectrometry

(66)Foreign Title OBRAZOVANIYE RADIKALOV PRI NIZKOTEMPERATURNOM RADIOLIZE AROMATICHESKIKH SOYEDINENIY

(09)English Title ROMATION OF RADICALS DURING LOW-TEMPERATURE RADIOLYSIS OF AROMATIC COMPOUNDS

	(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
	07	00	0	

ABSTRACT: Investigation of radiolysis of aromatic compounds and their derivatives is of great interest due to their high radiation stability. In our work, by [EPR] (ЭПР) method, there was studied formation of radicals during low-temperature radiolysis of certain derivatives of benzene. In analysis of EPR spectra of the investigated irradiated substances, there were used spectra of simple radicals - phenyl [1] benzyl [2] cyclohexadienyl [3], phenoxyl [4], obtained in our laboratory and by other authors. Analysis of spectra of benzene and its mono- and dialkyl-substituted derivatives and also such derivatives of benzene as benzoic acid, analine and thiophenol (group I) showed that a characteristic peculiarity of radiolysis of these compounds is formation of secondary cyclohexadienyl radical as a result of attachment of a hydrogen atom to a phenyl ring. Spectrum of radicals of such type has been thoroughly studied in works [3, 5, 6]. It is the characteristic triplet with splitting of components ΔH = 45-50 oe. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

C597 0366

(01)Acc Nr. TT6500333	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author BUBEN, N. YA.; PRISTUPA, A. P.; SHAMSHEV, V. N.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0190	0192	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags free radical, cyclohexane, organic crystal, epr, epr spectrum, epr spectrometry

(66)Foreign Title REKOMBINATSIYA RADIKALOV V TSIKLOGEKSANE; OBLUCHENNOM V GAZOKRISTALLICHESKOM SOSTOYANII

(09)English Title RECOMBINATION OF RADICALS IN CYSLOHEXANE IRRADIATED IN GAS CRYSTALINE STATE

	(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
	0	00	0	

ABSTRACT: Recombination of free radicals constitutes on of the simplest reactions in the solid phase. However, mechanism of recombination has till now been insufficiently studied. It is obvious that meeting of two radicals can occur either as a result of their diffusion, or during transfer of free valence throught the substance without displacement of molecules. It is possible to expect that mechanisms of second type are especially essential in case of high-molecular compounds. Nonetheless, it seems to us that even for polymers it is impossible to exclude completely recombination of radicals caused by thawing of motion of separate sections of the macromolecule. Estimation of magnitude of diffusion coefficient of the entire polymer molecule as a whole, as this is done in the work of S. Ye. Bresler and colleagues [1], certainly does not solve the problem. English Translation: 5 pages.

CIRC ABSTRACT WORK SHEET

0847 0367

(01)Acc Nr. TT6500334	**(65)SIS Acc Nr.** AT5023443	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author MILINCHUK, V. K.; PSHEZHETSKIY, S. YA.

Priority Distribution

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELENETARNYM PRCTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0194	0200	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags radiation polymerization, isoprene, polyisobutylene, polybutadiene, EPR spectrum, gamma irradiation, free radical

(66)Foreign Title NEKOTORYYE DANNYYE O REKOMBINATSII I PREVRASHCHENII SVOBODNYKH RADIKALOV V GAMMA-OBLUCHENNYKH POLIMERAKH

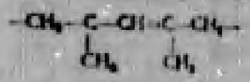
(09)English Title CERTAIN DATA ON RECOMBINATION AND TRANSFORMATION OF FREE RADICALS IN γ-IRRADIATED PCLUMERS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: Recombination and transformation of free radicals in γ-irradiated (15-1500 megarads, 77-323°K, γ-irradiation duration 0-40 min) polyisobutylene, polyisoprene, polypropylene, and polybutadiene were investigated using the EPR technique. The object of the study was to elucidate the mechanistic details of the free radical reactions in polymers. The EPR spectra show, that during γ-irradiation of polypropylene (77°K and 25 megarads), recombination of

$-CH_2-\underset{CH_3}{\underset{|}{C}}-CH_2$

alkyl radicals, and the transformation of these radicals into



$-CH_2-\underset{CH_3}{\underset{|}{C}}-CH-\underset{CH_3}{\underset{|}{C}}-CH_2-$

alkyl radicals and

$-CH_2-\underset{CH_3}{\underset{|}{C}}-CH-\underset{CH_3}{\underset{|}{C_2}}-CH_2-$

polyene radicals, take place. The B_1 parameter as a function of γ-irradiation duration at various temperatures is shown in fig. 1. Similar graphic data on the B_2 parameter are given. In polypropylene and polyisobutylene, the radical recombination proceeds via the migration of hydrogen atoms from one carbon atom of the polymer chain to another. This mechanism does not apply to radical recombination in polyisoprene and polyisobutylene.

Fig. 1. B_1--ratio of concentrations of alkyl radicals to alkyl radicals; 1--273°K; 2--290°K; 3--308°K; 4--323°K.
Orig. art. has: 4 figures, 3 formulas. English Translation: 11 pages.

CIRC ABSTRACT WORK SHEET

2597 - 0269

(01)Acc No. TT6500335	**(65)SIS Acc No.**	**(40) Country of Info** UR	**(41)Translation No.** MT6600004

(42)Author NIKOL'SKIY, V. G.; CHKHEIDZE, I. I. BUBEN, N. YA.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0206	0209	NONE	07

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags alkyl radical, hydrocarbon oxidation, oxidation, amorphous polymer, gamma transition, epr spectrometry, epr, epr spectrum

(66)Foreign Title OKISLENIYE ALKIL'NYKH RADIKALOV PRI GAMMA-PEREKHODE V AMORFNYKH VESHCHESTVAKH

(09)English Title OXIDATION OF ALKYL RADICALS DURING γ-TRANSITION IN AMORPHOUS SUBSTANCES

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: To clarify the cause of the two light flashes observed during heating of irradiated amorphous substances, the authors investigated the epr spectra of high-pressure polyethylene, commerical paraffin, natural rubber, dicyclohexyl-4-decone and 1,2-dicyclohexyldodecone, which were irradiated with fast electrons at 77K. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

0P57 C370

(01) Acc Nr. TT6500336	(65) SIS Acc Nr.	(40) Country of Info UR	(41) Translation Nr. MT6600004
(42) Author USATYY, A. F.; LAZURKIN, YU. G.			Priority II Distribution STD

(43) Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02) Ctry	(03) Ref	(04) Yr	(05) Vol	(06) Iss	(07) B. Pg	(45) E. Pg	(73) Date	(47) Subject Code
UR	0000	65	000	000	0209	0213	NONE	07,06

Language			
RUSS	N/ A	MOSK[illegible]	IZD-VO "NAUKA"

(39) Topic Tags radiation chemistry, polymerization degree, free radical, electron radiation, amino acid, peptide, polypeptide, protein

(66) Foreign Title PROTSESSY OBRAZOVANIYA I UNICHTOZHENIYA RADIKALOV V BELKAKH I POLIPEPTIDAKH V KRISTALLICHESKOM SOSTOYANII

(09) English Title PROCESSES OF FORMATION AND DESTRUCTION OF RADICALS IN PROTEINS AND POLYPEPTIDES IN CRYSTAL STATE

	(97) Header Clas	(63) Clas	(64) Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: The formation and destruction of radicals in about 30 different amino acids, peptides and proteins of various molecular weights (degree of polymerization) during electron irradiation at room temperature were investigated. The dependence of radiation yield of radicals and number of radicals per molecule at full saturation on degree of polymerization is given. English Translation: 10 formulas, 1 table, 1 graph and 7 pages.

CIRC ABSTRACT WORK SHEET

C897 C371

(01)Acc Nr. TT6500337	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author TUPIKOV, V. I.; PSHEZHETSKIY, V. S.; PSHEZHETSKIY, S. YA.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0215	0219	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags free radical, ammonia, radical polymerization, UV radiation, gamma radiation, acetaldehyde

(66)Foreign Title ISSLEDOVANIYE PREVRASHCHENIY I REAKTSIY RADIKALOV S MOLEKULAMI V NEKOTORYKH TVERDYKH MOLEKULYARNYKH MATRITSAKH PRI NIZKIKH TEMPERATURAKH METODOM EPR

(09)English Title INVESTIGATION OF TRANSOFRMATIONS AND REACTION OF RADICALS WITH MOLECULES IN CERTAIN SOLID MOLECULAR MATRICES AT LOW TEMPERATURES BY THE EPR METHOD

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: Transformations and reactions of radicals with molecules in solid ammonia during γ-and UV-irradiation at low temperatures were investigated by the EPR method. It was found that UV-irradiation of solid acetaldehyde in which radicals had been preliminarily formed by gamma-irradiation decelerated polymerization of acetaldehyde. English Translation: 4 formulas, 3 figures, 1 table and 6 pages.

CIRC ABSTRACT WORK SHEET

C847 0372

(01)Acc No.	(65)SIS Acc No.	(40) Country of Info	(41)Translation No.
TT6500338	AT5023444	UR	MT6600004

(42)Author	Priority	Distribution
KOZLOV, V. T.	II	STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0220	0229	NONE	07, 11

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags radiation polymerization, radical polymerization, polychloroprene, polybutadiene, EPR, natural rubber, irradiation effect, gamma irradiation, free radical

(66)Foreign Title O RADIATSIONNOM SSHIVANII KAUCHUKOVYKH POLIMEROV

(09)English Title RADIATION CROSS-LINKING OF RUBBER POLYMERS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: The effect of irradiation on cross linking of NK natural rubber, SKI-3 polyisoprene rubber, KhK chloroprene rubber, SKD polybutadiene rubber, SKS-30 and ARM butadiene-styrene rubbers, SKMS-30 and ARKM butadiene-methylstyrene rubbers, and SKEP ethylene-propylene rubber is studied. The yields of free radicals under γ-irradiation of solid rubbers (-196°C) were measured by EPR technique at -196°C and the yields of cross linking were measured in terms of maximum swelling in xylene at room temperature. Radiative cross linking of natural rubber and the sol fraction of natural rubber with various contents of diphenylpicrylhydrazine (DPPH) as a function of irradiation dose is shown in fig. 1.

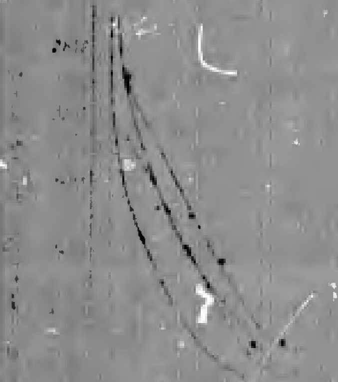


Fig. 1. 1--NK natural rubber sol; 2--NK natural rubber sol + 1.25 wt % DPPH; 3--NK natural rubber; 4--NK natural rubber + 10 wt % DPPH (Δ); 5--NK natural rubber + 16 wt % methylstyrene (o).

FTD FORM SEP 64 0-493d

[illegible]

TT6500338

MT6600004

The radiative cross linking of rubbers proceeds mainly via the ionic-molecular mechanism. It was found that irradiation of rubbers results in an initial loss of free radicals due to recombination and that for each type of rubber there is an optium irradiation dose for maximum free radical buildup and cross linking. Orig. art. has: 3 figures, 1 table. English Translation: 10 pages.

CIRC ABSTRACT WORK SHEET

C897 0403

(01)Acc Nr. TT6500339	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KOTOV, A. G.; PSHEZHETSKIY, S. Ya.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0230	0233	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags epr spectrometry, gamma radiation, free radical, ammonium salt, aqueous solution

(66)Foreign Title ISSLEDOVANIYE METODOM EPR OBRAZOVANIYA I PREVRASHCHENIYA SVOBODNYKH RADIKALOV POD DEYSTVIYEM GAMMA-IZLUCHENIYA V SOLYAKH NH_4Cl, N_2H_4 HCl, N_2H_4 H_2SO_4 I IKH ZAMOROZHENNYKH VODNYKH RASTVORAKH

(09)English Title INVESTIGATION BY EPR METHOD OF FORMATION AND TRANSFORMATION OF FREE RADICALS UNDER ACTION OF γ-RADIATION IN SALTS NH_4Cl, N_2H_4 . HCl, N_2H_4 . H_2SO_4 AND THEIR FROZEN WATER SOLUTIONS

(97) Header Clas 0	**(63) Clas** 00	**(64)Rel** 0	**(60) Release Expansion**

ABSTRACT: This paper presents the results of a study of the EPR spectra of gamma-irradiated ammonium salts and their frozen aqueous solutions directly after irradiation by different doses and after heating to different temperatures. English Translation: 2 figures and 5 pages.

CIRC ABSTRACT WORK SHEET 0897 0374

(01)Acc Nr. TT6500340	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author BOYARCHUK, Yu. M.; BUBEN, N. Ya.; DUBOVITSKIY, A. V.; MANELIS, G. B.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0234	0236	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags
epr spectrometry, ammonium salt, ionizing radiation, crystal lattice

(66)Foreign Title ISSLEDOVANIYE OBLUCHENNOGO PERKHLORATA AMMONIYA METODOM ELEKTRONNOGO PARAMAGNITNOGO REZONANSA

(09)English Title INVESTIGATION OF IRRADIATED AMMONIUM PERCHLORATE BY METHOD OF ELECTRON PARAMAGNETIC RESONANCE

	(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
	0	00	0	

ABSTRACT: This paper discusses the nature, accumulation and recombination of paramagnetic centers appearing under the action of ionizing radiation in pure ammonium perchlorate and with addition of thermal decomposition catalysts. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0375

(01)Acc Nr. TT6500341	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author GURMAN, V. S.; SERGEYEV, G. B.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0240	0242	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags photolysis, aqueous solution, hydrogen peroxide, alcohol

(66)Foreign Title K VOPROSU O MEKHANIZME FOTOLIZA VODNYKH ZAMOROZHENNYKH RASTVOROV

(09)English Title CONCERNING THE QUESTION ABOUT MECHANISM OF PHOTOLYSIS OF AQUEOUS SOLUTIONS

(97) Header Clas 0	(63) Clas 00	(64)Rel 0	(60) Release Expansion

ABSTRACT: Free valence transfer to a distance of 15-17 molecular diameters of water was checked by photolysis of fast frozen solutions of hydrogen peroxide and n-propyl alcohol in water. English Translation: 2 graphs and 2 pages.

CIRC ABSTRACT WORK SHEET

0897 0376

(01)Acc Nr. TT6500342	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KUZ'MIN, M. G.; BEREZIN, I. V.;, UZHINOV, B. M.; MIKHEYEV, Yu. A.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0242	0243	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags exchange reaction, excitation energy, photochemistry, nuclear energy level, electron energy level, uv radiation, hydrocarbon

(66)Foreign Title FOTOSENSIBILIZIROVANNYYE BIMOLEKULYARNYYE REAKTSII

(09)English Title
PHOTOSENSITIZED BIMOLECULAR REACTIONS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: Photosensitized bimolecular reactions of isotope exchange were detected in liquid and solid phases during UV irradiation of a mixture of saturated hydrocarbons in the presence of sensitizers. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

C897 0377

(01)Acc Nr. TT6500343	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author SHELIMOV, B. N.; FOK, N. V.; VOYEVODSKIY, V. V.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0245	0248	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags photolysis, photochemistry, methyl alcohol, uv radiation, epr spectrometry, radical concentration

(66)Foreign Title KINETIKA FOTOKHIMICHESKOGO RAZLOZHENIYA METILOVOGO SPIRTA PRI NIZKIKH TEMPERATURAKH

(09)English Title KINETICS OF PHOTOCHEMICAL DECOMPOSITION OF METHYL ALCOHOL AT LOW TEMPERATURES

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: To clarify the mechanism of photochemical transformations occurring with participation of alcohol radicals, the authors studied the kinetics of the accumulation of radicals and gaseous products during UV irradiation of dilute solutions of hydrogen peroxide and C_6H_6 in methyl alcohol by the EPR mass spectrometric method. English Translation: 2 graphs and 5 pages.

CIRC ABSTRACT WORK SHEET

0897 0378

(01)Acc Nr. TT6500344	(65)SIS Acc Nr. AT5023445	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author SHELIMOV, B. N.; FOK, N. V.; VOYEVODSKIY, V. V.

Priority II

Distribution STD

(43)Source A' SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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UR	0000	65	000	000	0249	0252	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO"NAUKA"

(39)Topic Tags alkane, UV radiation, EPR

(66)Foreign Title O FOTOSENSIBILIZIROVANNOM BENZOLOM I YEGO PROIZVODNYMI RASPADE UGLEVODORODOV PRI NIZKIKH TEMPERATURAKH

(09)English Title KINETICS OF PHOTOCHEMICAL DECOMPOSITION OF METHYL ALCOHOL AT LOW TEMPERATURES

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: Initial rate of formation of hexatriene, alkyl radical, and hydrogen were studied at 77°K as a function of C_6H_6 and C_6D_6 concentrations in 3-methylpentane. The dependence of formation rates of hexatriene and hydrogen upon temperature was studied in various solvents using a $2 \cdot 10^{-2}$ moles/l benzene concentration. All samples were UV irradiated at 77°K. Free radicals were monitored by the EPR technique. The object was to elucidate the mechanism of the simultaneous formation of alkyl radicals and hydrogen during UV irradiation of benzene solutions at 77°K. The hexatriene formation and the photosensitization were not found to the interrelated. The UV irradiation of $C_6H_5CD_3$ in 3-methylpentane at 77°K results in formation of 94% H_2 and 6% HD; hydrogen is the sole product when o-D- and p-D-toluene in 3-methylpentane are subjected to UV irradiation; H_2, HD, and D_2 resulted from UV irradiation of $C_6H_5CH_3$ in 3-methylpentane. A photosensitized decomposition of hydrocarbons according to the following scheme

$$C_6H_5CH_3 + RH \xrightarrow{h\nu} \text{substituted hexatriene}$$

$$C_6H_5CH_3^{*} + RH\,(RD) \to C_6H_5CH_3 + R + H\,(D)$$

$$H(D) + RH\,(RD) \to H_2\,(HD, D_2) + R$$

$$H(D) + C_6H_5CH_3 \to H_2\,(HD) + C_6H_5CH_2$$

occurs in the case of toluene. Results obtained with

$C_6H_5CD_3 + RH + h\nu$,

system revealed that the rate of formation of $C_6H_5CH_2$ radical is 10-12 times smaller than the rate of formation of alkyl radicals. It was condlued that photosensitized decomposition of hydrocarbons at 77°K also occurs in ethylbenzene, cumene, o-, m-, and p-xylenes, diphenyl- and triphenylmethane and other compounds. Orig. art. has: 1 formula. English Translation: 5 pages.

CIRC ABSTRACT WORK SHEET

0897 0380

(01)Acc Nr. TT6500345	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KAPLAN, I. G.

Priority II

Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0253	0255	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags ionizing radiation, excited state, benzene, luminescence, gamma radiation

(66)Foreign Title K VOPROSU OB OTNOSITEL'NOY KONTSENTRATSII PERVICHNYKH VOZBUZHDENNYKH SOSTOYANIY PRI DEYSTVII IONIZIRUYUSHCHEGO IZLUCHENIYA NA RASTVORY

(09)English Title CONCERNING THE QUESTION OF RELATIVE CONCENTRATION OF PRIMARY EXCITED STATES DURING THE ACTION OF IONIZING RADICATION ON SOLUTIONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: This report presents certain considerations on the stationary distribution of concentrations of primary excited states during the action of ionizing radiation on solutions. English Translation: 4 pages.

CIRC ABSTRACT WORK SHEET

0897 0381

(01)Acc Nr. TT6500346	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author BYAKOV, V. M.; ERSHLER, B. V.; FIRSOV, V. G.; NEZHEVENKO, M. A.	**Priority** II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0256	0257	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags
gamma radiation, electron radiation, aqueous solution, hydrogen, hydrogen peroxide

(66)Foreign Title EKSPERIMENTAL'NYYE KRITERII OPREDELENIYA PRIRODY PERVICHNYKH PROTSESSOV PRI RADIOLIZE

(09)English Title EXPERIMENTAL CRITERIA OF DETERMINING THE NATURE OF THE PRIMARY PROCESSES DURING RADIOLYSIS

(97) Header Clas 0	**(63) Clas** 00	**(64)Rel** 0	**(60) Release Expansion**

ABSTRACT: The authors propose using two experimental criteria, the I-regularities (I-dose rate) and the dependence of H_2 and H_2O_2 yield upon the concentration of the acceptor of active particles, to determine the nature of the primary processes during radiolysis. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0597 0382

(01) Acc Nr.	(65) SIS Acc Nr.	(40) Country of Info	(41) Translation Nr.
TT6500347		UR	MT6500004

(42) Author	Priority / Distribution
BRODSKIY, A. M.; TITOV, V. B.; LAVROVSKIY, K. P.	II STD

(43) Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTESSAM KHIMII VYSOKIKH ENERGIY, (MOSKVA 18---22 MARTA 1963)

(02) Ctry	(03) Ref	(04) Yr	(05) Vol	(06) Iss	(07) B. Pg	(45) E. Pg	(73) Date	(47) Subject Code
UR	0000	65	000	000	0258	0260	NONE	07, 06

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39) Topic Tags
hydrocarbon, activation energy, recombination, free radical, radiation cellular effect

(66) Foreign Title O KLETOCHNOM EFFEKTE PRI RADIOLIZE UGLEVODORODOV

(09) English Title THE CELLULAR EFFECT DURING RADIOLYSIS OF HYDROCARBONS

(97) Header Clas	(63) Clas	(64) Rel	(60) Release Expansion
0	00	0	

ABSTRACT: This report discusses the cellular effect during radiolysis of liquid hydrocarbons based on a study of the temperature dependence of the radiolysis rate. The mechanism of radical formation in a liquid cell is represented through, first, disintegration of the molecule with the formation of a hot hydrogen ion (or another light radical), which then enters into a substitution reaction in direct proximity to the point of its formation, including with the initial molecule. English Translation: 13 formulas and 6 pages.

CIRC ABSTRACT WORK SHEET

C897 0383

(01)Acc Nr. TT6500348	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author REVINA, A. A.; PODSOBLYAYEV, A. P.; BAKH, N. A.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0264	0266	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags epr spectrum, epr spectrometry, radiation effect, fatty acid, ester, organic salt, oxygen, alkyl radical, hydrogen peroxide

(66)Foreign Title ISSLEDOVANIYE VLIYANIYA KISLORODA NA PERVICHNYYE PROTSESSY RADIOLIZA ORGANICHESKIKH SOYEDINENIY

(09)English Title INVESTIGATION OF THE EFFECT OF OXYGEN ON THE PRIMARY PROCESSES OF RADIOLYSIS OF ORGANIC COMPOUNDS

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: Through the EPR method the authors investigated radiolysis and radiation-oxidation of a fatty acid, its salt and ester, which differed only by substitution in the carboxyl group, in the presence and absence of oxygen. Irradiation at -196C produced identical radicals and radiation yields for the fatty acid, led to a decrease in G for the ester and the salt and to a change in the character of the spectrum for the salt. English Translation: 2 figures, 1 table and 4 pages.

CIRC ABSTRACT WORK SHEET

0897 0384

(01)Acc Nr. TT[illegible]0340	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004

(42)Author BARKALOV, I. M.; GOL'DANSKIY, V. I.; YENIKOLOPOV, N. S.; TROFIMOVA, G. M.	Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0268	0271	NONE	07, 20

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags radiation polymerization, polymerization rate, acrylonitrile, polyvinyl acetate, electron radiation, epr spectrum

(66)Foreign Title O SPETSIFIKE RADIATSIONNOY TVERDOFAZNOY POLIMERIZATSII V KHODE OBLUCHENIYA

(09)English Title THE SPECIFIC CHARACTER OF RADIATION SOLID-PHASE POLYMERIZATION DURING IRRADIATION

	(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
	0	00	0	

ABSTRACT: The authors investigated solid-phase radiation polymerization of acrylonitrile and vinyl acetate under the action of 1.6 Mev electrons with calorimetry of the heat liberated or absorbed during thawing and irradiation and with observation of the EPR signals under the beam and after irradiation. Brief irradiation of acrylonitrile by large doses (8 Mrad) with thawing of the monomer above -130C (the phase transition point), the sample not necessarily fusing, and reverse freezing after each irradiation led to an increase in polymer yield proportional to the number of irradiations. Radiation polymerization of vinyl acetate was lacking at all temperatures in the glasslike and crystal states. English Translation: 1 figure and 9 pages.

CIRC ABSTRACT WORK SHEET 0897 0385

(01)Acc Nr. TT6500350	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author KOVALEV, G. N.; SERGEYEV, G. B.

Priority II **Distribution** STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18---22 MARTA 1963)

(02)Ctry	(03)Ref	(04)Yr	(05)Vol	(06)Iss	(07)B. Pg	(45)E. Pg	(73)Date	(47)Subject Code
UR	0000	65	000	000	0276	0277	NONE	07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags UV radiation, ethylene, bromination, brominated organic compound, hydrogen compound, bromide, light radiation effect

(66)Foreign Title OSOBENNOSTI PROTEKANIYA FOTOKHIMICHESKOGO GIDROBROMIROVANIYA ETILENA V TVERODY FAZE

(09)English Title PECULIARITIES OF THE FLOW PHOTOCHEMICAL HYDROBROMINATION OF ETHYLENE IN THE SOLID PHASE

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: A mixture of hydrogen bromide and ethylene was frozen at 77K and irradiated with UV light for a definite time. After thawing, ethyle bromide and dibromomethanie (500:1) were found in the reaction products and the depth of transformation attained 70%. English Translation: 3 pages.

CIRC ABSTRACT WORK SHEET

0897 0786

(01)Acc Nr. TT6500351	**(65)SIS Acc Nr.**	**(40) Country of Info** UR	**(41)Translation Nr.** MT6600004

(42)Author STARODUBTSEV, S. V.; KIV, A. YE.

Priority II
Distribution STD

(43)Source AN SSSR INSTITUT KHIMICESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSESSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

(02)Ctry	**(03)Ref**	**(04)Yr**	**(05)Vol**	**(06)Iss**	**(07)B. Pg**	**(45)E. Pg**	**(73)Date**	**(47)Subject Code**
UR	0000	65	000	000	0278	0279	NONE	07, 20

Language RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags crystal lattice deformation, crystal lattice dislocation, crystal structure, valence band, exchange interaction, ionization cross section, excitation energy

(66)Foreign Title MOZHET LI AKTIVIROVAT'SYA SMESHCHENIYE UZLOVOGO ATOMA V MEZHDOUZLIYE V REZUL'TATE IONIZATSII KAPPA-OBOLOCHKI?

(09)English Title CAN DISPLACEMENT OF A STITIAL ATOM INTO THE INTERSTICE BE ACTIVATED AS A RESULT OF IONIZATION OF THE K-SHELL?

(97) Header Clas	**(63) Clas**	**(64)Rel**	**(60) Release Expansion**
0	00	0	

ABSTRACT: As a result of ionization of the K-shell the stitial atoms of not very heavy elements obtain a positive change thanks to Augier transitions. Their potential energy in the crystal increases and they are in the excited state, which in certain cases leads to their going into an interstice. English Translation: 6 formulas and 3 pages.

CIRC ABSTRACT WORK SHEET

0597 0352

(01)Acc Nr. TT6500352	(65)SIS Acc Nr.	(40) Country of Info UR	(41)Translation Nr. MT6600004
(42)Author TAL'ROZE, V. L.			Priority II Distribution STD

(43)Source AN SSSR INSTITUT KHIMICHESKOY FIZIKI. "ELEMENTARNYYE PROTSESSY KHIMII VYSOKIKH ENERGIY" TRUDY SIMPOZIUMA PO ELEMENTARNYM PROTSSAM KHIMII VYSOKIKH ENERGIY. (MOSKVA 18--22 MARTA 1963)

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UR	0000	65	000	000	0297	0299	NONE	20, 07

Language			
RUSS	N/A	MOSKVA	IZD-VO "NAUKA"

(39)Topic Tags chemical laser, gas laser, chemical kinetics, chain kinetics, chain reaction, laser theory

(66)Foreign Title O GENERATSII KOGERENTNOGO IZLUCHENIYA V KHIMICHESKIKH REAKTSIYAKH

(09)English Title GENERATION OF COHERENT RADIATION IN CHEMICAL REACTIONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: This report gives the results of a very general theoretical consideration of the conditions of self-excitation and the efficiency for a hypothetical generator working on a gas reaction and a transition between electron-excited levels. The derivation is made in terms of the chemical kinetics of chain reactions. English Translation: 2 formulas, 1 figure and 4 pages.

CIRC ABSTRACT WORK SHEET

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ABSTRACT: In a number of chemical reactions the compounding of separate reagents into one molecule occurs with participation of excited electron states [1]. For the appearance of states with negative temperature is necessary so that the number of excited particles, which are products of the reaction, exceed the number of analogous particles that are in the unexcited state. If in initial state products of reaction are lacking, the appearance of a state with negative temperature it is necessary and sufficient that

$$\frac{1}{g^{+}} \cdot k^{+} > \frac{1}{g^{-}} k^{-}. \qquad (1)$$

where k^{+}(k^{-}) is the specific rate of the reaction leading to the appearance of excited (unexcited) electron states in the products of reaction; $g^{\pm}$ is the statistical weight of the states. English Translation: 8 formulas and 5 pages.

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(39)Topic Tags laser theory, chemical laser, photochemistry, excited state, equilibrium constant

(66)Foreign Title POLUCHENIYE "OTRITSATEL'NYKH" TEMPERATUR PRI OBRATIMYKH FOTOKHIMICHESKIKH REAKTSIYAKH

(09)English Title OBTAINING "NEGATIVE" TEMPERATURES DURING REVERSIBLE PHOTOCHEMICAL REACTIONS

(97) Header Clas	(63) Clas	(64)Rel	(60) Release Expansion
0	00	0	

ABSTRACT: A system with negative temperature (population inversion) can be produced through optical excitation if the difference in the chemical properties of the ground and excited states is used. The fast reactions of dissociation into ions, recombination of ions, isomeration, dimerization, polymerization, compound-detachment and oxidation-reduction are considered as means of producing negative temperature. English Translation: 4 pages.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

PREFACE

This collection offered to the reader contains a reduced account of reports made at the Symposium on Elementary Processes of High-Energy Chemistry and discussion of these reports. The Symposium, taking place 18-22 March 1963 in Moscow, with respect to the group of questions covered by it, was apparently the first of its kind. Goals and methods of organization of symposium are presented in the introduction from the organizing committee.

One of the important peculiarities in the carrying out of the symposium and preparation of the present collection was the tendency to carry the discussion to the future reader. All questions and statements in the discussion were recorded on magnetic tape. During preparation of discussion for the press, scientists, secretaries of sessions and editors introduced certain purely literary corrections. Statements in the discussion and also questions are given with indication of the surname of the speaker. In rare cases, nevertheless, surname of the person asking the question was not established.

Especially animated was discussion of mechanisms of elementary energy transfer processes in the condensed phase. In view of the fact that this discussion did not lend to sufficient clarity (special arguments were caused by questions concerning the character of dependences between magnitude of radiation yield and concentration of additions of radiolysis inhibitors, see p. 179), the symposium designated a group of scientists under the chairmanship of academician V. V. Voyevodskiy, which had to develop a certain unified point of view on the controversial questions. Since apparently these questions can be solved only in further experimental and theoretical works, the designated group succeeded only in obtaining from certain scientists additional materials and judgements. Inasmuch as these materials are of general interest, and are intimately connected with the whole discussion at the symposium, the editors included them in the present collection (see pp. 197-209).

On the whole, the symposium in its theme and form turned out to be very useful for presentation of results of experimental and theoretical works in the region of high-energy chemistry, and, which is especially important, for bringing to light unsolved questions and formulation of problems for the future.

Preparation of transactions for press was conducted by the editorial board consisting of Doctor of Chemical Sciences Kh. S. Baydasar'yan, Candidate of Physico-Mathematical Sciences Ye. L. Frankevich, Candidate of Chemical Sciences V. Ye. Skurata and the author of the preface.

V. L. Tal'roze

INTRODUCTION

Chairman of Organizational Committee of the Symposium
and Doctor of Chemical Sciences V. L. Tal'roze

Esteemed comrades!

The present symposium is in many respects experimental, and first of all certainly the thematic respect. For the first time there is made an attempt for a collective of scientists of studying regions frequently little interacting with each other (radiation chemistry, photochemistry, plasma chemistry, ionospheric chemistry and high-temperature chemistry) to consider theoretical problems connected with elementary processes which have common importance for all or part of the enumerated areas.

If we speak strictly, then the general theory of the elementary process, the foundation of chemical kinetics is unified. For instance, questions of energy transfer and transformation of one form of energy (for instance translational) into another (for instance of vibrational excitation energy) and back are common for chemical kinetics on the whole.

However, undoubtedly with the appearance of radiation and high-temperature effects, with increase of role of plasma state in different regions of technology, with simulation of the ionosphere in the laboratory of man, the attention of kinetics is attracted to elementary processes which in, so to speak, "usual" chemistry are not decisive.

First of all, here are included processes proceeding through strong excitation and ionization of electron shells, transmission of excitation through electron levels, reactions of fast particles.

Therefore, in developing a program, the Organizing Committee tried to "saturate" it with works dedicated to namely such processes. As I have already said, chemical kinetics is unified, and probably namely therefore into our program there have "leaked" a certain number of works on elementary processes with participation, for instance, of free radicals in thermal equilibrium with the lattice of a solid body, and certain other works which to an equal, or possibly, to a greater degree interest the orthodox chemist.

Program of symposium is composed of three sections:

I. Elementary processes in gases.

II. Elementary processes in the condensed phase.

III. Elementary processes in quantum generators.

The last section, included in the program by the proposal of the Physics Institute of Academy of Sciences of USSR, certainly does not cover all questions of this new rapidly developing region; its task is only the formulation of certain problems, and especially the attracting of attention of a new group of scientists to this new area of physics and chemical physics.

There has been made an attempt to experiment with the method of preparation of the program and carrying out of the discussion. Approximately one hundred scientists were sent invitations to formulate concrete questions and to report on which of these questions they would want to answer in their reports, and on what they await answers from their colleagues.

Questions obtained in the first round were again reported to the comrades with whom we were corresponding. Finally, the whole list of questions was included in the appendex to the program with indication which questions would be discussed and in what reports.

Preparation of symposium was promoted by the help of three scientific councils: Scientific Council on Use of Atomic Energy in Chemistry (Chairman, Academician A. P. Vinogradov), Scientific Council on the Theory of Chemical Structure, Kinetics and Reactivity and Catalysis of the Department of Chemical Sciences of the Academy of Sciences of the USSR (Chairman, Academician V. N. Kondrat'yev) and the Scientific Council on complex problem of "High-Temperature Thermophysics" (Chairman, Academician V. A. Kirillin). The organizing committee thanks the leaders of these councils for their help.

Organizing committee is grateful to all lecturers and all scientists participating in formulation of questions of the program.

INTRODUCTION

Academician N. N. Semenova

Dear comrades!

In recent years there has occurred considerable expansion of sphere of interests in field of application of chemical kinetics. This expansion is especially strongly connected with development of chemistry of processes occurring at extreme parameters. Here are included processes at very high and very low temperatures, at very high and very low pressures, processes in fields of different high-power radiations, etc.

In connection with this, the importance of understanding what elementary processes are characteristic for such conditions and what the quantitative of these processes are, was increased.

The present symposium is dedicated to elementary processes of radiation chemistry, photochemistry, plasma chemistry, high-temperature chemistry and ionosphere chemistry. Totality of chemical transformations characteristic for these types of effects and media has been called by organizers of this symposium high-energy chemistry. I think that in these areas of chemistry there are indeed a large number of related elementary processes, and from this point of view the first experiment in joint consideration of these enumerated areas in world science, which is being started at this symposium, seems to me to be very useful.

At the same time, it is necessary, certainly, not to forget that kinetics of a complicated process in real systems is determined by a complicated set of elementary events and by the general conditions under which this system is found — let us say the degree of proximity to equilibrium, distribution of energy, etc. It is necessary to consider this in order not to fall into "overgeneralization" on the basis of only one consideration of elementary processes.

Questions outlines to the symposium for consideration have very great theoretical value for many regions of contemporary science and technology. There is no sense in enumerating these regions — they are known to every participant of the symposium.

It is necessary to note that Soviet scientists have made a serious contribution to the study of the elementary chemical process. It is pleasant for me, for instance, to note that the chairman of this session, Academician V. N. Kondrat'yev and Academician A. N. Terenin are two of the pioneers in the region of experimental study of elementary processes. The laboratory of V. N. Kondrat'yev, since its founding has been called the laboratory of elementary processes. Now in the field of study of elementary processes, which lies within the group of interests of the present symposium, there are working a very large number of scientists of many scientific establishments of our country.

I began my statement appearance with the fact that the range of questions considered by the symposium seems to me to pertain to an extensive region of extreme effects, by part which consists of high-energy chemistry itself. I would like to note what great interest a combination of different types of extreme effects on matter can present. For instance, in recent years, new prospects have been opened by a combination of methods of high-energy chemistry with low temperatures. This combination, in the conditions of a solid body, creates a situation in which the processes determining chemical transformations are processes of energy transfer and processes of charge exchange. Of processes studied up to the present time, very interesting have turned out to be, for instance, processes of radiation polymerization in solid bodies at low temperature. On the other hand, processes of solid-phase polymerization, possibly, even in the absence of radiation are connected with transmission of excitation, and application of radiation methods serves here for interpretation of the role of energy transfer in general.

What has been said is only an example from that extensive region to which our symposium awaits to introduce a contribution.

Allow me to wish to you successful work.

I. ELEMENTARY PROCESSES IN GASES

1. ELEMENTARY PROCESSES WITH PARTICIPATION OF ELECTRONS AND IONS

*

DISSOCIATION OF MOLECULES DURING ELECTRON IMPACT AND RADIATION CHEMISTRY

M. V. Gur'yev and L. V. Sumin

High-energy chemistry, in particular radiation chemistry, awaits from investigations of elementary processes (mass-spectrometry) first of all data about yields of initial products of every process, their states and kinetics of molecular transformations. In radiation chemistry, as the distribution of initial products there are frequently directly used experimental mass-spectra of electron impact. Thus it is implied that disintegration of molecular ions occurs "instantly," i.e., during a time not exceeding in order of magnitude the time between collisions of one molecule (10^{-10} sec in a gas under standard conditions).

Information about state of initial products is very limited. Knowledge of time of formation of experimental mass-spectrum gives the answer, first of all, to the question concerning initial products, and only indirectly information about their states. Certain data on disintegration rate of molecular ions is given by radiation chemistry itself. Numerous cases of correlation between mass-spectra and yields of radiolysis products in gas and sometimes even in liquid phase can be explained by presence of "instantaneous" disintegrations.

However, usually it is impossible to obtain reliable information in such a way.

In mass-spectrometry there are known fast as well as slow disintegrations. The first are strictly proven and observed for diatomic molecules during electron impact and for organic molecules during autoionization. Slow disintegrations appear in particular as metastable ions. For explanation of mass-spectra, there are used two hypotheses. According to statistical hypothesis, all remaining disintegrations are also basically slow (time to disintegration greater than 10^{-10} sec); according to the "local" hypothesis, breaking of C – C bonds occurs during the time ~10^{-13} sec, and subsequent detachment of H atoms can be slow. These hypotheses give qualitatively different predictions for initial radiolysis products. Thus, there appears the problem of finding the distribution of dissociation products according to disintegration rates.

We investigated slow disintegrations by the method of line shapes. Measurements for ions containing two or three C atoms formed from n-hexane were conducted on the instrument [MV23-02] (MB23-02) with resolution (on semiheight of line) ~9000. It turned out that among ions $C_nH_m^+$ ($m < 2n + 1$) there is always a considerable part formed during a time of 10^{-7}-10^{-8} sec, the time to disintegration is bigger, the smaller m is (for given n). It is interesting to note that kinetic energy of fragmates, as a rule, increases in the same direction. These results will agree with the assumption of formation of these ions due to consecutive disintegrations. CH_2^+ ion will be formed from CH_4^+ during a time of about $5 \cdot 10^{-8}$ sec. All enumerated ions cannot be primary radiolysis products, and the initial ions for them (probably the "instantly" formed ions $C_nH_{2n+1}^+$) must be strongly excited. For ions $C_3H_7^+$ and $C_2H_5^+$ the time of formation in any case is less than $5 \cdot 10^{-8}$ sec. Calculations conducted with use of the quantity of kinetic energy of fragments as excitation energy per degree of freedom (according to the statistical hypothesis) for these ions lead to the conclusion of inapplicability of the hypothesis of statistical distribution of energy to them.

For estimation of small disintegration times, we assume to use the method of angular distributions of fragmentation ions, which gives us the possibility only to determine excitation energy, which till now (with rare exceptions) has only been the subject of speculative conclusions.

The proposed method of determination of excitation energy consists in that at sufficiently high electron energies, (3-4 times higher than ionization energy or greater) momentum transmitted by electron to molecular ion as a whole is simply connected with excitation energy transmitted to ion.

Transmitted momentum is measured experimentally according to the distribution function of ions with respect to projections of velocity onto the direction of the electron beam. Thus a motionless molecule acquired kinetic energy of the order of 10^{-5} ev. Measurements (with calculation in the approximation of very high electron energies) gave for excitation energies of H_2^+ and He^+ results with an accuracy of 30%. It is very important that this method can also be applied for fragmentation ions (in the case of slow disintegrations).

Discussion

V. N. Kondrat'yev. You said that C — H bonds are broken "more slowly" than others. Is there a theory with the help of which it is possible to estimate the rate of this process?

M. V. Gur'yev. We assume that the C — C bond is broken during a time of $\sim 10^{-13}$ sec, and later there occurs detachment of H atoms. These are qualitative ideas. A theory does not exist.

V. N. Kondrat'yev. Were these observed cases when an ion during disintegration gives a saturated molecules? Now in very many schemes of chemical reactions it is assumed that during disintegration of a radical there is obtained H_2.

M. V. Gur'yev. This question was considered only in one work.[1] As an example can serve the ion of propane, which during disintegration gives H_2. Investigation of neutral disintegration products is experimentally a difficult problem.

L. N. Ganyuk. What is the time of motion of an ion to the collector?

M. V. Gur'yev. Time of motion of ion to collector is comparatively long; in our instrument it is about 10^{-5} sec, but this magnitude does not have significance for the proposed method.

V. V. Voyevodskiy. Was the process of detachment of a separate atom from a whole molecular ion investigated?

M. V. Gur'yev. For those substances which we studied, this is a quite doubtful process, except for methane. From our data it follows that CH_2^+ ion will be formed from CH_4 in a time of about $5\text{-}10^{-8}$ sec. We did not investigate CH_3^+ ion, although our method permits doing this.

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[1] D. Beck and O. Osberghaus. Z. Phys., 160, 406 (1960).

CONCERNING A METHOD OF DETERMINATION OF DISINTEGRATION TIME OF EXCITED IONS

G. V. Karachevtsev and V. L. Tal'roze

Determination of time of disintegration of excited molecular ions formed by electron impact is a basic question in searches for correlation between mass-spectra obtained at low pressures and composition of radiolysis products at pressures of the order of one atmosphere. The authors have proposed and tested a method of measurement of disintegration rate of primary ion formed by electron impact in the gas phase, based on energy analysis of ions during ionization by electrons of a thin filament in a strong electric field. Thanks to the fact that ionization occurs in a strong electrical field, small differences in times of formation and dissociation of primary ion into fragments lead to the case in which kinetic energy which fragmentation ions obtain in this field will be noticeably less than that which they would have if dissociation occurred instantly. Magnitude of kinetic energy which ions will have can be determined, for instance, by the method of the retarding field. This energy will serve a measure of life time of the primary ion. Quantitative relation between magnitude of energy and lifetime of primary ion can be established only on the assumption of a definite mechanism of disintegration.

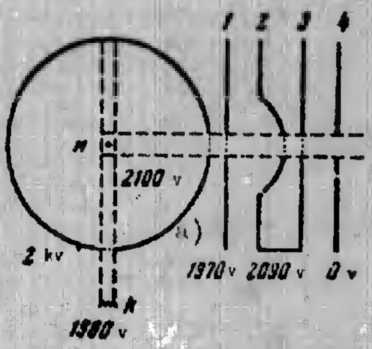

Fig. 1. Diagram of ion source: k – cathode; n – filament; a – cylinder, 1, 2, 3, 4) electrodes forming ion beam. There are shown electrode potentials during operation with deceleration of ions.

We have considered the comparatively simple case of disintegration into two fragments (ionized and neutral).[1] It is assumed that disintegration of one part of all ions occurs according to the usual single-molecule law; the other part is considered to be not at all able to disintegrate. Under this assumption, for disintegration of ions in the cylindrical field of a filament, there is obtained a formula (see footnote) with the help of which there can be performed estimation of rate constants according to the ratio of fragmentation ion current to nondisintegrated ion current under a given decelerating potential.

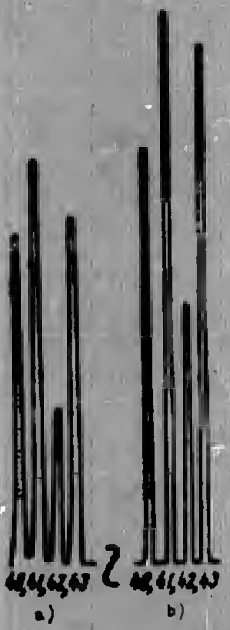

Fig. 2. Sections of mass-spectra of a mixture of n-hexane and argon (contribution of Ar^+ ions to 40 amu line is shaded): a) with deceleration of ions; b) without deceleration of ions.

In preliminary experiments the ion source (Fig. 1) with filament (n) in its cylindrical ionization chamber was assembled and installed on a usual magnetic mass-spectrometer. Diameter of filament was $5 \cdot 10^{-2}$ mm, diameter of cylinder was 10 mm and potential applied to filament relative to cylinder could be varied from 0 to +100 v. As a source of electrons served tungsten cathode (k). Rough energy analysis of ions could be produced by means of creation of a retarding electrical field between plates 1 and 2 of the ion source and controlled according to change of width of mass-spectrometric peak.

As first example of investigation was selected dissociative ionization of n-hexane. Into source was admitted mixture of argon and n-hexane, and there was taken mass-spectrum of mixture at zero potential of filament with respect to cylinder (as in the usual ion source of a mass-spectrometer) and at potential of filament equal to +100 v, with subsequent deceleration of ions to +10 ev. In Fig. 2 are given sections of mass-spectra of mixture of n-hexane and argon (contribution of Ar^+ ions in 40 amu line is shaded). Ratios $I_{C_3H_7^-}/I_{Ar+}$, $I_{C_3H_6^+}I_{Ar+}$ and I_{C3H5^+}/I_{Ar+} remain, with 20% accuracy, constant when decelerating potential is turned on. This signifies that decay time of $C_6H_{14}^+ \rightarrow C_3H_7^+ + (C_3H_7)$ is less than 10^{-8} sec.

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[1] G. V. Karachevtsev and V. L. Tal'roze. Kinetika i kataliz, 4, 923 (1963).

Time resolution obtained in these first experiments is still one-two orders less than is required for prediction of behavior of ions at atmospheric pressure, but it is nevertheless one-two orders greater than ever attained by the direct method. Calculations (see footnote) show that by increasing potential of filament to 2 ev relative to potential of cylinder and applying or decelerating system, which ensures decrease of energy of ions to 10 ev, it is possible to measure decay times of 10^{-10} sec for the same fragments of n-hexane. At present experiments in this direction are being prepared.

Discussion

V. V. Voyevodskiy. Did results of your work coincide with those presented in the report of M. V. Gur'yev?

V. L. Tal'roze. Our results do not contradict results reported in the paper of M. V. Gur'yev, since according to their estimate decay time of ions with only breaking of C — C bonds, which we investigated, is less than $5 \cdot 10^{-8}$ sec. Regarding the delay of detachment of hydrogen, within the framework of our method it is still impossible to say anything about this.

M. V. Gur'yev. Did you consider the kinetic energy of fragments during partial disintegration of an already accelerated ion?

V. L. Tal'roze. No, this was not taken into account.

S. Z. Roginskiy. Do your conducted experiments mean than for reactions in plasma at pressures when characteristic time of collision exceeds 10^{-8} sec, it is possible not to consider secondary processes, but directly to use results obtained in the mass-spectrometer?

V. L. Tal'roze. If we could guarantee that particles formed during disintegration do not enter into any other reactions, then this would signify that mass-spectral data represent the final result, which it is possible to use at pressures when characteristic time > 10^{-8} sec (~1 mm Hg). However, this is not so, inasmuch as ions formed after disintegration can enter into secondary reactions, which we have to consider. The problem here is to answer the question, just what secondary processes it is necessary for us to consider. If, for instance, in the case of CH_4, all disintegrations occur in a very short time, then there will be formed a definite quantity of CH_4^+, CH_3^+ ions, etc., which is known to us from mass-spectrum of CH_4. Then these ions start in a definite way to react with molecules of methane and other particles. If, however, we say that disintegration occupies a much larger time than time between collisions, then we are not right in transferring results of investigation of processes taking place during electron bombardment in a vacuum to conditions of considerable pressures, and are obliged to think about how excited but undecomposed ion CH_4^+ will react with other molecules.

L. N. Ganyuk. Does magnitude of field in which lifetime of excited ion is studied have any influence on disintegration of ions?

V. L. Tal'roze. No, those fields which we have applied still do not render such an influence. Influence of electric field on disintegration of ions is well-known, and was studied in experiments with nonuniform electrical fields obtained near very sharp points. In order for such an influence to occur, energy obtained by charged particle at distance of the order of atomic dimensions should be of the same order as dissociation energy. The fields at which such influence starts to be "felt" have to be two or three orders higher than those which we applied.

CONCERNING TRUE MASS-SPECTRA AND KINETIC ENERGIES OF IONS

L. V. Sumin, M. V. Gur'yev and N. N. Tunitskiy

Question about truth of observed mass-spectra has a direct relation to the questions of to what extent it is possible to use data of relative yields of different fragments during electron impact for study of primary processes of high-energy chemistry, and, in particular, radiation chemistry. As a rule, products of electron impact are studied on mass-spectrometers with small aperture, which introduce considerable distortions into mass-spectra due to scattering of ions with large lateral components of velocity. It is obvious that fraction of fast ions in beam passing through system of slots will be the less, the greater their energy. This phenomenon is known as discrimination of fast ions.

For correction of experimental mass-spectra, it is necessary to know, first, the initial distribution of ions with respect to energies and, secondly, to obtain an expression for collection coefficient of ions with various kinetic energies. Magnitudes of kinetic energies of fragmentation ions are also of great independent interest in investigation of processes of dissociation. In practice, during solution of the problem about obtaining the initial distribution of ions with respect to kinetic energies, it is necessary to use two methods of measurement: investigation of contour of mass-spectral line in case of large kinetic energies, and obtaining of distribution with respect to the component of velocity parallel to the axis of slots of the mass-spectrometer by method of deflection (for energies of the order of thermal energy).

During the analysis of form of mass-spectral line of a fragmentation ion, it is necessary to distinguish instrument line broadening from smearing in the direction of low accelerating voltages, which is connected with existence of initial velocity of the ion. This is attained by solution of the convolution equation, in which as the instrument function there appears the line shape of molecular ion, with natural width much smaller than the magnitude characterizing resolution of the mass-spectrometer. Theoretical distribution obtained from analysis of line shape is connected with the initial distribution of ions with respect to energies by the relationship

$$\psi(E) = \frac{\text{const}}{V_1 V_2} E \varphi(E),$$

where $\varphi(E)$ initial distribution of ions with respect to energies, and V_1 and V_2 characterize the magnitude of aperture of instrument according to two measurements.

Analogously there are found relationships for the method of deflection of ions along the slot with the difference that there is considered discrimination only with respect to one direction - perpendicularly to axis of slot. To obtain collection coefficients, complete solution of equations is replaced by determination of average energies, which considerably simplifies calculation. In the case of analysis of line shape, collection coefficient has the form

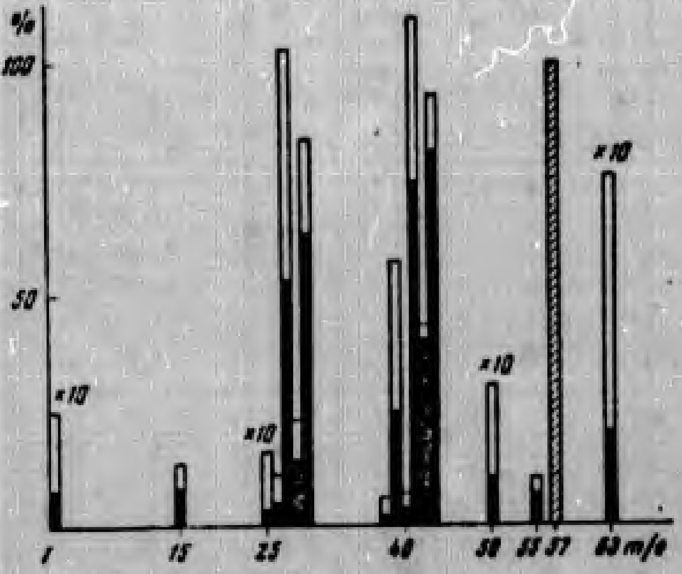
$$P = \text{const} \frac{f_0 k_0}{f_0 k_1 - f_1 k_0},$$

where f_0 and k_0 are area of experimental respectively for fragmentation and molecular peaks; f_1 and k_1 are the first moments of these lines.

Still more simply are determined magnitudes of average energies and collection coefficients during the study of component of velocity by method of deflection along slot in case of strong discrimination: average energy is directly proportional, and collection coefficient is inversely proportional to square of line width at a height e times less than height at maximum of line (e is base of natural logarithm) if experimental curve can be described by Maxwell's law. For majority of fragmentation ions of organic molecules, this approximation does not introduce essential errors. In order not to distort the initial distribution of ions with respect to energy by focusing of the ion beam, there has been created an instrument with plane electrical field in the region of ionization. Such a design permits us to apply exact calculation for determination of initial energy of ions and collection coefficients, whereas in instruments with focusing of ion beam there can be obtained only relative or approximate results, as usually has been the case.

By the method of analysis of line shape there has been investigated the fragmentation ion N^+ from N_2. Magnitude of its average kinetic energy was approximately 3 ev, which agrees with source material. Collection coefficient calculated according to the given formula turned out to be equal approximately to 1/20, and testifies to the fact that formation cross sections of N^+ and N_2^+ from N_2 are identical within the limits of experimental error.

By the method of deflection there have been investigated fragmentation ions of certain organic molecules. As an example, on the figure there are presented data for n-hexane obtained for energy of ionizing electrons equal to 70 ev. Magnitudes of average kinetic energies of fragments of organic molecules are included in range from energy of close to thermal energy to energy of about 0.3-0.5 ev. Source data for these ions are strongly exaggerated. Collection coefficients for fast ions depending upon their energy have a magnitude a few times (up to 10) smaller than for ions with thermal energies. During correction of experimentally observed relative yields of fragmentation ions with high kinetic energies, total ionization cross section in the case of n-hexane is increased by 1.5 times. It is necessary to note that besides change of total cross section, form of spectrum changes: contribution of fast ions, a considerable part of which are not recorded in experiments due to discrimination of the instrument, is greatly increased. For instance, by 2-3 times is increased the fraction of ions from n-hexane with m/e; 26-28, 38-40, 50-54 and 62-67 having average energy from 0.15 to 0.25 ev.



Part of mass-spectrum of n-hexane determined taking into account initial energy of ions: ■ – mass-spectrum according to the catalog of mass-spectra; ▨ – intensity of line m/e = 57, taken as 100 units; ⊐ – addition to magnitude of peak taking into account discrimination.

Discussion

R. A. Khmel'nitskiy. How was instrument function chosen?

L. V. Sumin. Instrument function was determined experimentally according to line of molecular ion.

R. A. Khmel'nitskiy. How do you explain the fact that mass-spectra obtained on essentially different instruments little differ from each other?

L. V. Sumin. All mass-spectrometers, as a rule, possess strong discrimination and therefore mass-spectra are similar.

R. A. Khmel'nitskiy. What you can say about discrimination in a time-of-flight mass-spectrometer?

L. V. Sumin. Time-of-flight instrument in this sense was not considered by us.

V. L. Tal'roze. In connection with question about influence of kinetic energy of fragments on mass-spectra, it is necessary to say the following: It is difficult nevertheless to understand why discrimination in all mass-spectrometers of the world does not lead to very different mass-spectra. If we leave aside problems of high-energy chemistry, then simply for analytic mass-spectrometry it is very important that this question be clearly answered.

M. V. Gur'yev. In reality, mass-spectra obtained on various instruments differ from each other. At the same time, from strict consideration of different discrimination, it follows that mass-spectra can be similar, even while being strongly discriminated. Thus, every separate type of instrument requires, naturally, special considerations and exact numerical calculations. Regarding the time-of-flight instrument, discrimination in it is not so small, as it may seem at first glance due to the small magnitude of accelerating voltage and application of pulse ejection.

ON THE INFLUENCE OF KINETIC ENERGY OF RELATIVE MOTION OF ION AND MOLECULE ON CROSS SECTION AND MECHANISM OF AN ION-MOLECULE REACTION

M. I. Markin and V. L. Tal'roze

In preceding investigations of authors [1] dedicated to ion-molecule reactions there were obtained direct experimental indications that charge exchange at low velocities of particles has a resonance character. At the same time, it is known that the cross section of resonance or close to resonance charge exchange at high speeds only slowly decreases with increase of energy of relative motion of particles.

On the other hand, the authors several years ago was assumed that ion-molecule reactions with transition of heavy particles should be sharply decelerated with increase of speed to the speed when energy, which is transformed in accordance with law of conservation of momentum inside the complex, starts to noticeably exceed a magnitude of the order of binding energy [2]. This assumption found confirmation in works [3, 4].

From comparison of given characteristics of dependence of charge exchange and transition cross sections of a heavy particle on kinetic energy, it ensued that with growth of this energy, charge exchange cross section should as a rule "outstrip" the transition cross section of the heavy particle if during collision both transitions are energetically permitted.

The present work was dedicated to checking this statement, for which there was required development of a special method, inasmuch as joint investigations of transition of electron and heavy particle at low speeds is methodologically very difficult.

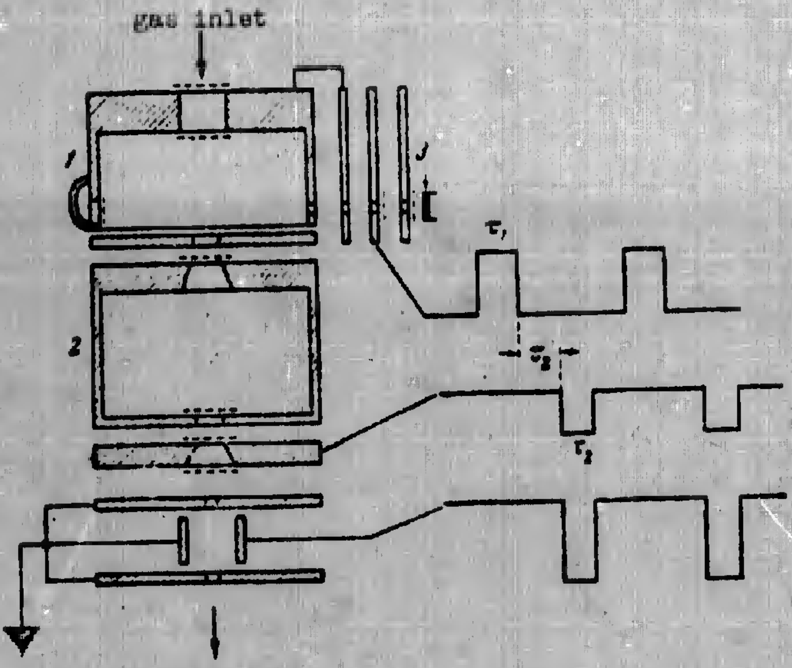


Fig. 1. Diagram of ion source: 1) ionization chamber; 2) collision chamber; 3) cathode.

As the object of investigation served the competition of the reactions:

$$H_2^+ + O_2 \rightarrow O_2H^+ + H, \quad (\sigma_1); \tag{1}$$

$$H_2^+ + O_2 \rightarrow O_2^+ + H_2. \quad (\sigma_2) \tag{2}$$

(in parentheses there are given symbols of corresponding cross sections).

In the ionization chamber of the special source of the mass-spectrometer (Fig. 1), under the action of a pulse of electrons there occurred ionization of mixture of oxygen and hydrogen ($O_2:H_2 = 1:100$). The formed "packet" of ions was extracted from this chamber, accelerated to a definite energy, entered collision chamber and, after emerging from it, was deflected by deflector plates, and thus did not enter the mass-analyzer. Secondary ions formed in collision chamber have velocity close to thermal, and can therefore be found in collision chamber for a relatively large interval of time. After time τ_2 (usually 10-15 microseconds), after cessation of action of ionizing pulse on extracting electrode, there was given a voltage pulse, under the action of which secondary ions were extracted from the collision chamber. For the time of action of the extracting pulse, voltage was removed from the deflector plate, and secondary ions could pass into the mass-analyzer.

The measured value of ion currents O_2H^+ and O_2^+ are proportional to cross sections of processes σ_1 and σ_2, inasmuch as special experiments have shown that

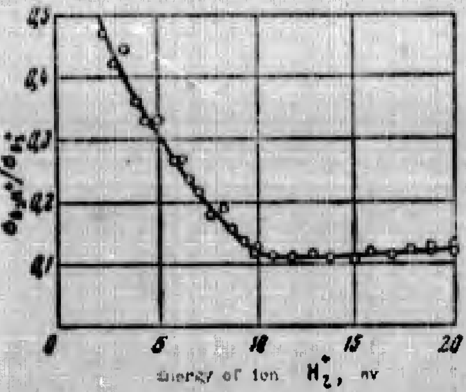


Fig. 2. Dependence of ratio of cross sections of processes $H_2^+ + O_2 \rightarrow O_2H^+ + H$ and $H_2^+ + O_2 \rightarrow O_2^+ + H_2$ on energy of H_2^+ ions.

overwhelming fraction of O_2^+ ions will be formed as a result of reaction (2), and not as a result of charge exchange reaction

$$O_2^+ + O_2 \rightarrow O_2 + O_2^+. \qquad (3)$$

As can be seen (Fig. 2), with increase of energy of H_2^+ ions there occurs relative decrease of reaction cross section (1) up to energy ~10 ev, at which there occurs quite a sharp break of the curve, and measured ratio of cross sections remains practically constant at energies higher than ~10 ev, and does not drop to zero as was assumed. It turned out, however, that at energies higher than 10 ev, and does not drop to zero as was assumed. It turned out, however, that at energies higher than 10 ev, formation of considerable number of O_2H^+ ions occurs as a result of the following set of processeses:

$$H_2^+ \text{ (fast)} + H_2 \rightarrow H_2^+ \text{ (slow)} + H_2 \text{ (fast)} ; \qquad (4)$$

$$H_2^+ \text{ (slow)} + O_2 \rightarrow O_2H^+ + H. \qquad (5)$$

Thus, it is possible to consider that sharp change of path of curve at energy ~10 ev is indeed connected with expected sharp decrease of reaction cross section (1). At this magnitude of kinetic energy of H_2^+ ions, excitation energy of complex is

$$E_{\text{возб.}} = E_{H_2^+} \frac{m_{O_2}}{m_{O_2} + m_{H_2}} \approx 10 \cdot \frac{32}{34} \approx 9{,}4 \text{ ev.}$$

The authors are grateful to technician S. V. Nikitin for his help in this work.

Literature

1. G. V. Karachevtsev, M. I. Markin and V. L. Tal'roze. Kinetics and catalysis, 5, 377 (1964).

2. G. K. Lavrovskaya, M. I. Markin and V. L. Tal'roze. Kinetics and catalysis, 2, 21 (1961).

3. R. F. Pottie, A. J. Lorquet and W. H. Hamill. J. Am. Chem. Soc., 84, 529 (1962).

4. C. F. Giese and W. B. Maier II. J. Chem. Phys., 39, 739 (1963).

Discussion

N. N. Tunitskiy. Was electron energy varied?

M. I. Markin. In our experiments energy of electrons was constant and equal to 60 ev.

V. N. Kondrat'yev. During charge exchange which occurs with large cross section, there practically does not occur exchange of kinetic energy. Formation of complexes, however, occurs with exchange of kinetic energy. Was kinetic energy of products measured in the case of formation of complexes?

M. I. Markin. Measurement of kinetic energy was not conducted. In our case kinetic energy of the actual complex should be about 6% of kinetic energy of hydrogen ion.

M. V. Gur'yev. If O_2H^+ ions are formed as a result of a tertiary process, then there should be a specific dependence of current intensity of these ions on pressure of hydrogen.

M. I. Markin. Such a dependence was observed, and according to it there was determined the contribution of the tertiary process.

A. Ya. Temkin. Does there exist an energy region in which first and second processes are resonance processes?

M. I. Markin. The first process, which passing through a stage of formation of an intermediate complex, is not a resonance process. The second process we considered to be resonance in the entire measured region. Endotherm of this process is ~0.1 ev, where this energy can be "taken" for the H_2^+ ion.

V. I. Gol'danskiy. Is it not expedient to interpret the mechanism of processes studied by you in terms of an intermediate state and partial width and, let us assume, to formulate the following question: how does partial width affect electron transport?

V. L. Tal'roze. Here it is necessary to distinguish two questions. The first of them is the question about intermediate states having a lifetime of the order of, let us say, the electron transition time (for instance, it is possible to consider resonance charge exchange to be such). Naturally, such states are always formed. But there appears the second question - will there be formed after this "something" with long lifetime, greater than 10^{-4}-10^{-13} sec, which then disintegrates, giving products of elementary reaction. This "something with long lifetime" is an ionic-molecular complex, lifetime of which frequently is not only 10^{-13}-10^{-12} sec, but larger, sometimes exceeding a microsecond. It is natural that if lifetime is so great, then there has time to occur quasi-resonance distribution of energy with respect to degrees of freedom of such a complex. The question which we studied could have been formulated in the following way: how does relationship between charge exchange cross section and transport cross section of heavy particle affect the fact of formation of such an ionic-molecular complex?

In accordance with the point of view expressed by us both in this report and earlier, processes requiring a lone lifetime of the complex with kinetic energy of about 10 ev are practically eliminated, and there remain only those processes which correspond to short-lived intermediate states, apparently exactly those which V. I. Gol'danskiy has in mind. As follows from our results, with increase of kinetic energy, charge exchange processes start to predominate over transport processes of the heavy particle, i.e., processes which are favored by formation of a complex.

N. N. Tunitskiy. In the report of V. L. Tal'roze and M. M. Markin it was indicated that excitation of ion H_2^+ affected the character of its ion-molecule reactions. In connection with this, it would be possible to suggest an experiment in which H_2^+ is obtained near its appearance potential. As follows from our data, in this case there is obtained an H_2^+ ion practically without vibrational excitation.

EXCITATION AND DISSOCIATION OF IONS AS A RESULT OF COLLISIONS WITH ATOMS AND MOLECULES AND THEIR RELATION WITH MASS-SPECTRA

S. Ye. Kupriyanov

Data on mass-spectra and appearance potentials permit us to estimate average excitation energy of molecular ions. This magnitude turns out to be [1, 2] of the order of several electron-volts for ions of hydrocarbons. In case of dissociation of ions as a result of collision with atoms and molecules, their excitation energy can be estimated likewise. It is natural that in the case of identical excitation of ions obtained in different inelastic processes, mass-spectra formed as a result of dissociation of these ions should be similar. As can be seen [3], this occurs in processes of ionization of molecules by electrons, α-particles, in processes of dissociation of ions as a result of collisions with atoms and molecules and during charge exchange.

From the conducted analysis [4], it follows that approximately identical spectra are also obtained during ionization of molecules by photons. We will note that similarity of mass-spectra obtained in different processes is observed for various energy regions: energy of ions ~1-5 Kev, energy of α-particles ~5 Mev, energy of electrons >40 ev. Mass-spectra obtained by ionization of molecules by electrons of low energies (close to ionization potentials). For example, in Table 1 are given mass-spectra of C_3H_3N and n-C_4H_{10} and dissociation spectra of these ions as a result of single collisions with neon atoms. Dissociation spectra of ions are obtained on the double mass-spectrometer, description of which is given in work [5]. Mass-spectra of ions are approximately identical. Analogous results are obtained for molecules and ions of water, ammonia, methane and propane [6].

Molecular and fragmentation ions in approximately 10^{-6}-10^{-5} sec after their appearance have excitation energy of the order of dissociation energy. The presence of such energy in the case of separate polyatomic ions can be judged according to known spontaneous decays of metastable ions. From results of investigations [7, 9] one may see that such energy is possessed by many complicated and simple molecular and fragmentation ions. It is known that dissociation cross section of H_2^+ ions were kinetic energy attains several [8, 10] and even hundreds of Kev [11], depend on energy state of these ions.

Table 1. Comparison of Mass-Spectra of Electron Impact and Mass-Spectra of Disintegration of Corresponding Ions During Collisions with Neon (energy of Ions is 3.5 Kev). (In the Table there are Contained the Most Intense Lines; m/e is Ratio of Mass to Charge)

C_5H_5N ($C_5H_5N^+$)			n-C_4H_{10} ($C_4H_{10}^+$)		
m/e	mass-spectrum of electronic impact	mass-spectrum of disintegration	m/e	mass-spectrum of electronic impact	mass-spectrum of disintegration
52	29,5	36,0	57—48	2,9	2,1
51	12,8	12,2	43	35,8	44,0
50	3,2	1,3	42	4,2	13,8
38	2,6	3,4	41	9,8	6,9
37	1,7	1,4	39	4,6	4,0
27	7,1	6,3	29	15,8	12,1
26	30,4	36,2	28	11,6	6,1
25	8,9	3,2	27	13,3	9,1
			26	1,8	1,9
Σ	100,0	100,0	Σ	100,0	100,0

In the case of dissociation of simple ions of different origin, there are obtained strongly differing dissociation cross sections. Thus, for instance, it has been shown [12] that dissociation cross section of ions H_2^+ obtained during electron bombardment of methane is approximately 2.7 times greater than dissociation of cross section H_2^+ ions from hydrogen. However, during dissociation of larger hydrocarbon ions, dissociation cross sections of identical ions of different origin differ from each other to a lesser degree, as can be seen from data in Table 2. Dissociation cross sections of the same ions of different origin with breaking of the C — C bond do not strongly differ. By considering the influence of excitation energy on dissociation cross sections of ions [10], it is apparently possible to assume that C – C binding energy for these ions is approximately identical,[1] although, it is known, C – C binding energy for corresponding molecules is different. Consequently, distribution of ions requiring for their formation breaking of C – C bond with respect to excitation energy in the given case does not change so strongly as it changes in the case of H_2^+ ions [11] when they are obtained from various molecules. Detailed consideration of these data will be conducted in another work; we will note only that structures of $C_2H_4^+$ ions of different origin are not the same. If we assume that for $C_2H_4^+$ ions from ethylene, near every C atom there are two H atoms, although ions with different number of H atoms can be regrouped, then among $C_2H_4^+$ ions from propane and n-butane there are definitely those for which one C atoms has three H atoms and the other has one.

Table 2. Dissociation Cross Sections of $C_2H_4^+$ and $C_2H_2^+$ of Different Origin, 10^{-16} cm^2 (Ion Energy 3.5 Kev, Collisions with Neon).

Process of disintegration	Initial molecule				
	C_2H_2	C_2H_4	C_3H_3N	C_3H_8	$n\text{-}C_4H_{10}$
$C_2H_4^+ \to C_2H_3^+$		2,60		2,90	2,42
$C_2H_2^+$		2,80		2,90	2,27
C_2H^+		0,37		0,48	0,33
C_2^+		0,06		0,08	0,06
CH_2^+		0,16		0,20	0,20
CH^+		0,07		0,10	0,09
C^+		0,04		0,06	0,08
$C_2H_2^+ \to C_2H^+$	2,07	2,00	1,80	2,10	1,97
C_2^+	0,26	0,29	0,23	0,34	0,27
CH^+	0,12	0,13	0,15	0,15	0,12
C^+	0,06	0,07	0,08	0,08	0,07

From mass-spectrum of C_3H_3N it is impossible[2] to establish that ions form the peak m/e = 26. Dissociation spectrum shows that contribution of CN^+ ion to intensity of this peak is small. Consequently, this peak is formed mainly by $C_2H_2^+$ ions. Thus, study of dissociation spectra of ions formed during collision with atoms and molecules permits us in certain cases to judge concerning the structure, nature and energy state of the ions.

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[1] Energy is averaged over all ions of the beam, since in the beam there are ions with different degree of excitation.

[2] If we do not apply mass-spectrometers of high resolution.

Literature

1. Yu. G. Sazhinov and S. Ye. Kupriyanov. Journal of Physical Chemistry, 36, 1969 (1962).

2. D. P. Stevenson. Radiation Res., 10, 610 (1959).

3. S. Ye. Kupriyanov. Journal of Physical Chemistry, 36, 218 (1962).

4. Z. Z. Latypov and S. Ye. Kupriyanov. Journal of Physical Chemistry (in press).

5. S. Ye. Kupriyanov and A. A. Perov. ZhTF (Journal of Theoretical Physics), 33, 823 (1963).

6. S. Ye. Kupriyanov and A. A. Perov. News of the Academy of Sciences of the USSR, physics series, 27, 1102 (1963).

7. S. Ye. Kupriyanov, M. V. Tikhomirov and V. K. Potapov. ZhETF (Journal of Experimental and Theoretical Physics), 30, 569 (1956).

8. N. N. Tunitskiy, R. M. Smirnova and M. V. Tikhomirov. Reports of the Academy of Sciences of the USSR, 101, 1083 (1955).

9. N. N. Tunitskiy, S. Ye. Kupriyanov and A. A. Perov. News of Academy of Sciences of USSR, Department of Chemical Science, 1962, 1945.

10. S. Ye. Kupriyanov, N. N. Tunitskiy and A. A. Perov. ZhTF 33, 1259 (1963).

11. A. C. Riviere and D. P. Sweetman. Proc. Roy. Soc., A278, 1215 (1961).

12. S. Ye. Kupriyanov and A. A. Perov. Journal of Physical Chemistry, 38, 2263 (1964).

Discussion

<u>V. N. Kondrat'yev</u>. Electronic levels for a number of diatomic and triatomic particles are known. Has anyone tried to compare data obtained by your method with optical data?

<u>S. Ye. Kupriyanov</u>. Such attempts have still not been made by anyone. Besides, we should stress that from the moment of formation of the ion in the source of the mass-spectrometer to the time when this ion collides with a molecule or atom and reacts (or dissociates), there passes a time of the order of 10^{-5}-10^{-6} sec. Therefore, ions formed in the source for the most part have time to deexcite, and will react only in the vibrationally excited state and also in the metastable state.

CONCERNING MASS-SPECTRA OF EXCITED MOLECULAR IONS

Z. Z. Latypov and S. Ye. Kupriyanov

In this work there are compared mass-spectra described in the literature, which are obtained in processes of collision of molecules with electrons [MS] (МС) mass-spectrum, with photons [FMS] (ФМС) photon mass-spectrum, with slow ions (charge-exchange) [PMS] (ПМС) charge-exchange mass spectrum, collision of ions with atoms and molecules [DMS] (ДМС) dissociation mass spectrum. There were conducted approximate calculations of excitation of ions in different processes.

In all these processes, distribution functions of molecular ions with respect to excitation energies can be different. Therefore, we should expect similarity of mass-spectra obtained in different processes under the condition of proximity of average excitation energies of ions and distribution functions of ions with respect to excitation energies in these processes. Comparison of mass-spectra of different molecules and ions confirms such an approach.

There have been made conclusions: Dissociation of molecular ions depends basically on the value of excitation energy, but not on the method of excitation. Similarity of mass-spectra of electron impact to mass-spectra of photon impact, and especially with charge-exchange spectra is observed at energies E_e of electrons satisfying the condition $E_e - I < I$ (I is ionization energy of molecule), i.e., for the case when distribution functions of molecular ions with respect to excitation energies are comparatively narrow. Similarity of mass-spectra of fragmentation ions during ionization of molecules by electron impact and mass-spectra of dissociation of fast ions colliding with neutral particles is discovered at E_e satisfying the condition $E_e - I > I$, i.e., in cases when distribution functions become complicated. This indicates the similarity of mechanisms of excitation in these processes. Since in the DMS process there occurs considerably greater excitation of molecular ions than in the MS process, and their subsequent large fragmentation, on the basis of what was said above, dissociation mass-spectrum DMS can be considered as a continuation of mass-spectrum of fragmentation ions MS into the region of high excitation energies. Dependence of mass-spectra on excitation energy and the relation between MS and DMS mass-spectra permit us to predicting mass-spectra of molecular ions which can be obtained in collisions of the molecular ion + electron type. Thus, there are predicted basic feature of mass-spectra of NH_3^+ and CH_4^+ during collision with electrons.

INFLUENCE OF EXCITATION ENERGY ON ION-MOLECULE REACTIONS IN A WIDE RANGE OF ENERGY

A. A. Perov

There are investigated H_2^+ ions of different origin: from ethylene, n-butane and benzene. Obtained dissociation cross sections of H_2^+ during collision with Ne atoms have magnitude near $1.4 \cdot 10^{-16}$ cm^2 (below dissociation cross section of H_2^+ from methane). Dissociation cross section of H_2^+ from methane $\sim 2.7 \cdot 10^{-16}$ cm^2 at energy of H_2^+ ~3.0 Kev. This effect is explained by lower vibrational excitation of H_2^+ formed from these molecules as compared with H_2^+ obtained from CH_4, and can be explained by two causes: 1) the process of pyrolysis of substance on hot walls of ionization chamber of source, with formation of unexcited H_2 molecules, and 2) delayed disintegration of molecules. As a result H_2^+ will not have noticeable vibrational excitation. During disintegration of molecular ions CH_4^+, ions H_2^+ with high vibrational excitation are formed as a result of a fast process with conservation of internuclear distance up to disintegration, as a consequence of which the ion is obtained to be excited.

Discussion

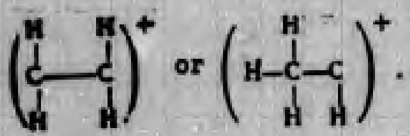
V. K. Bykhovskiy. Is it possible to estimate excitation energy and cross section of the process according to interatomic distances of methane?

A. A. Perov. Experiments were carried out under conditions of collision of H_2^+ with atoms, and dissociation cross section is very difficult to estimate.

S. Ye. Kupriyanov. From investigations of dissociation spectra of ions as a result of collisions with atoms and molecules, one may see that during disintegration of excited ions, for instance $C_2H_4^+$ with formation of $C_2H_2^+$, there occurs detachment of H_2 molecules and two H atoms in approximately equal amounts. The same followed and from reports about reactions of hot atoms with molecules and about direct molecular disintegration of hydrocarbons at high temperature, and also from certain photochemical works. From our data it ensues that detachment of two atoms of hydrogen is carried out basically by means of consecutive detachment, and not simultaneously. Detachment of first H atom occurs sufficiently fast, at least not more slowly than breaking of the C – C bond. Detachment of a large number of H atoms occur during a longer time, since this is a stepwise process. Ions formed by breaking of C – C bond also disintegrate by means of fast and slow process. Investigation of dissociation spectra of ions gives one experimental methods for determination of time of disintegration of excited ions. There is reason to expect that by this means it is possible to obtain time resolution of $\sim 10^{-10}$ sec.

__V. N. Kondrat'yev.__ You said that during dissociation of various molecules there can be formed ions of identical composition but with different excitation and different structures. Explain, please, how you propose to distinguish between these structures?

__Ye. S. Kupriyanov.__ Investigation of dissociation spectra permits us, with required accuracy of determination of cross sections, to conclude if the ion has the structure:



In an ion beam of identical composition, there can be ions which are different in structure. Investigation of dissociation spectra shows what the predominant structure of ions in the beam is. On the basis of magnitudes of cross sections, there can be made a conclusion about excitation energy of the given type of ions of different origins. It turns out that all ions $C_2H_2^+$, $C_2H_2^+$ from various molecules have on the average, with respect to all ions of the beam, approximately identical C – C binding energies, although in neutral molecules these bonds are essentially different – single, double and triple.

__V. L. Tal'roze.__ Concerning the question about influence of energy of ions on ion-molecule reactions in a wide range of energies. Apparently, one should consider two ranges of energies: of the order of several ev, where kinetic energy still plays a small role, and high velocities of relative motion.

V. N. Kondrat'yev. It is known that in the low-voltage range of energies, cross section σ of ion-molecule reaction with transition of the heavy particle is proportional to $E^{1/2}$ (E is kinetic energy).

V. L. Tal'roze. There is no full clarity in this. Calculations according to the classical model of interaction between ion and induced dipole, with formation of an intermediate complex [1], give $\sigma \sim E^{1/2}$. Such a dependence was observed for a number of cases by Stevenson [2]; however, there are known deviations from this law [3]. In any case it is clear that starting from certain energies, when excitation of intermediate complex becomes strong, there should be observed large deviations from this law. Several years ago we predicted [4] that at a certain energy, reactions proceeding through such a complex are totally ceased. This found confirmation in experiments of Hamill [5]. Final qualitative clarity into this question was introduced, as it seems to me, by results presented in our report with M. I. Markin at this symposium.

Literature

1. P. Langevin. Ann. chim. phys., 5, 245 (1905).
2. G. Gioumousis and D. P. Stevenson. J. Chem. Phys., 29, 294 (1958).
3. F. H. Field, G. J. Franklin and F. W. Lampe. J. Am. Chem. Soc., 61, 1456 (1957).
4. V. L. Tal'roze. In: "Chemical Effects of Nuclear Transformations," Vol. 1. Vienna, Internat. Atomic Energy Agency, 1961, p. 103.
5. R. P. Pottie and W. H. Hamill. J. Phys. Chem., 63, 877 (1963).

EXPERIMENTAL INVESTIGATION OF ION-MOLECULE REACTIONS AND COLLISIONS OF IONS AND MOLECULES IN NITROGEN

M. V. Tikhomirov

The majority of investigated ion-molecule reactions do not have activation energy. There are also known, however, endothermic ion-molecule reactions [4], i.e., reactions in which excited ions participate. The most thoroughly studied endothermic reaction is formation of the ion N_3^+ from N_2^{+*} and N_2.

N_3^+ and N_4^+ ions in a glow discharge in nitrogen were revealed with help of mass-spectrometer in 1933 [2]. However, in later works [3, 4] there was observed only formation of N_3^+ ion; N_4^+ was not detected. Mechanism of formation of N_3^+ and N_4^+ ions was investigated in detail in work [5]. In this work, according to appearance potentials of ions N_3^+ and N_4^+, which are respectively equal to 22.1 and 15.8 v, and the square dependence of intensity of ion currents on pressure of nitrogen in the ion source, there were suggested the following ion-molecule reactions leading to formation of heavy nitrogen ions:

$$N_2^{+*} + N_2 \rightarrow N_3^+ + N; \qquad (1)$$

$$N_2^+ + N_2 \rightarrow N_4^{+*} \text{ (vibrationally excited [6]).} \qquad (2)$$

In process (1) there participates molecular nitrogen ion N_2^{+*}, which, as was considered in work [1] by Cermak and Herman, correspond to the state of nitrogen ion $B^2\Sigma_u^+$; in the later work [7], they assumed the existence of the metastable state $N_2^{+4}\Sigma$.

In view of contradictory nature of results obtained in works [2-5], we conducted investigation of mass-spectra of nitrogen elevated pressures. Work was carried out on mass-spectrometer [MI-1303 [8]] (МИ-1303). Pressure in ion source was measured by thermocouple manometer and was varied from 10^{-4} to 10^{-2} mm Hg. Pressure in analyzer thus did not exceed $5 \cdot 10^{-5}$ mm Hg (residual pressure $<10^{-7}$ mm Hg). Nitrogen used in experiments contained 0.5% Ar and less than 10^{-3}% O_2.

In Fig. 1 are given ionization functions for formation of Ar^+ and ions m/e = 42 and 56. There were also investigated initial segments of these curves, and it was shown that appearance potentials of ions m/e = 42 and 56 are respectively equal to 20.4 ± 1.3 and 46.5 ± 1.0 v. Magnitude of peak m/e = 42 depends on pressure of N_2; therefore, this peak we consider as the peak of ion N_3^+. Formation cross section of this ion is approximately equal to $5 \cdot 10^{-18}$ cm^2, i.e., is close to the value obtained in work [1]. Let us note the presence of a distinct maximum on ionization curve of N_3^+, which is characteristic for ion-molecule reactions with participation of excited atoms and molecules [9, 10].

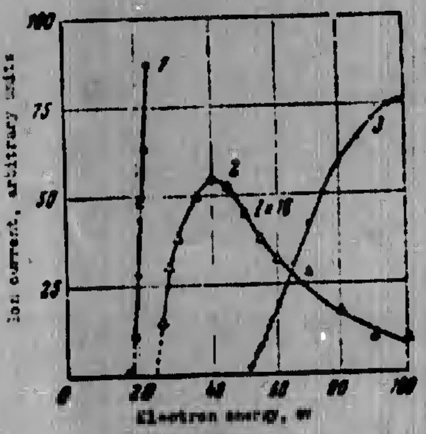


Fig. 1. Dependence of line strength of ions on energy of electrons: 1 – m/e = 40 (A_r^+); 2 – m/e = 42 (N_3^+); 3 – m/e = 56.

In order to obtain additional information about excitation of initial ions, there was conducted investigation of dependence of relative intensity of peak m/e = 7, which appears due to disintegration of ion N_2^+ ($N_2^+ \xrightarrow{N_2} N^+ + N$) as a result of collision with molecules of nitrogen in the region between electric and magnetic fields of the mass-spectrometer from the energy of the electrons [11, 12] (Fig. 2). From the figure one may see that, just as in the case of hydrogen [12], relative intensity of "fractional" peak in region of low energies of electrons increases with increase of electron energy. This result is interpreted by us as growth of vibration excitation of N_2^+ ion. It is necessary to emphasize, however, that with increase of electron energy higher than 35 ev, relative intensity of "fractional" peak drops. It is possible that vibrational excitation of N_2^+ ion is important in reaction (1). In favor of such ideas witnesses the data of Giese and Maier [13], who, investigating collisions of N_2^+ ions with kinetic energy ~4-5 ev with N_2 obtained N_3^+ ions with appearance potential equal to appearance potential of N_2^+.

Magnitude of peak m/e = 56 also depends on pressure squared. However, appearance potential of this peak practically coincided with appearance potential of doubly charged $^{14}N^{15}N^{2+}$ ion (m/e = 14.5). Thus in the spectrum there was absent isotope peak m/e = 57. Therefore it could not have been caused by N_4^+ ions, but was caused by charge exchange of N_2^{2+} ions in the analyzer of the mass-spectrometer [11, 14]:

$$N_2^{2+} + N_2 \to N_2^+ + N_2^+. \tag{3}$$

Cross section of this process in order of magnitude is equal to 10^{-15} cm^2, and does not depend on electron energy from 50 to 100 ev (Fig. 3). To an analogous conclusion about formation of peak m/e = 56 arrived the authors of work [13].

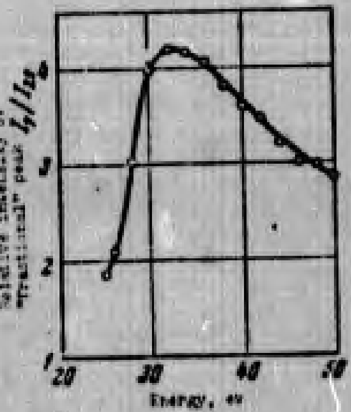


Fig. 2. Dependence of relative intensity of "fractional" peak on electron energy.

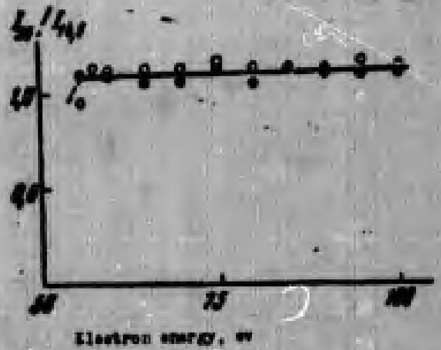


Fig. 3. Dependence of cross section of process $N_2^{2+} + N_2 \to N_2^+ + N_2^+$ on energies of electrons.

Thus, the conducted investigation permits us to make the conclusion that in region of pressures to 10 microns of mercury, N_4^+ ions were not observed. In work [5] investigations were conducted at electron energy of 50 ev, i.e., at energy higher than appearance potential of N_2^{2+}. Therefore the process (3) occurred.

Literature

1. V. Cermak and Z. Herman. J. chim. phys., 57, 717 (1960).

2. O. Luhr. Phys. Rev., 44, 459 (1933).

3. H. Dreeskamp. Z. Naturforsch., 12a, 876 (1955).

4. W. Kaul and R. Fuchs. Z. Naturforsch., 15a, 326 (1960).

5. M. Saporoschenko. Phys. Rev., 96, 1550 (1958).

6. R. N. Varney. Phys. Rev., 89, 708 (1953).

7. V. Cermak and Z. Herman. Collection Czechosl. Chem. Communs., 27, 1493 (1962).

8. V. A. Pavlenko, A. E. Rafal'son, and A. M. Shereshevskiy. PTE (Instruments and Experimental Technique, No. 3, 3 (1958).

9. I. A. Hornbeck and I. P. Molnar. Phys. Rev., 84, 621 (1951).

10. M. S. B. Munson, F. H. Field and J. L. Franklin. J. Chem. Phys., 34, 1790 (1962).

11. I. Mattauch and H. Lichtblan. Phys. Z., 40, 16 (1939).

12. N. N. Tunitskiy, R. M. Smironova and M. V. Tikhomirov. Reports of Academy of Sciences of USSR, 103, 1083 (1955).

13. C. F. Giese and W. B. Maier. J. Chem. Phys., 33, 1913 (1961).

14. F. J. Norton. Natl. Bur. Standards Circ., No. 522, 201 (1953).

2. REACTIONS OF HOT ATOMS

REACTIONS OF HOT ATOMS OF HYDROGEN WITH ETHYLENE

B. G. Dzantiyev and A. P. Shvedchikov

Ideas concerning the special chemical behavior of hot (possessing nonequilibrium energy) atoms and radicals have recently been more and more frequently utilized for explanation of phenomena observed in the area of radiation chemistry and photochemistry. In majority of such cases, we speak of hot hydrogen atoms [1-4]. Introduction of ideas concerning the specific character of chemical behavior of hot hydrogen atoms frequently has a speculative character. However, it is possible to directly observe peculiarities of reactions of hot atoms of hydrogen by generating them with the help of the nuclear reactions $Li^6(n, \alpha)T$ or $He^3(n, p)T$. In this case there appear atoms of hydrogen H^3 possessing high energy and being simultaneously tagged, which greatly facilitates tracing of their chemical fate.

In this work there was studied interaction of hot radioactive atoms of hydrogen (tritium) with ethylene and mixtures of ethylene with other substances (ammonia, helium) in the gas phase at elevated pressures (to 10 atm). Along with investigation of tagged interaction products of hot atoms of tritium with ethylene, there were simultaneously identified radiolysis products of ethylene.

Hot atoms of tritium were obtained by means of the nuclear reaction $Li^6(n, \alpha)T$. As a detector of tritons was used Li_2CO_3 salt. Irradiation was conducted in vertical channel of reactor [IRT-1000] (ИРТ-1000) at a flux of thermal neutrons 10^{11}-10^{12} neutron/cm^2·sec. The accompanying dose rate of γ-radiation from the reactor was $1 \cdot 10^{14}$ ev/cm^3·sec. For the work there was used ethylene with 99.8% purity. Irradiation was conducted in quartz ampules. After irradiation contents of ampules was analyzed by method of gas radiochromatography. Products were separated in a column containing silica gel [SHSK-57] (ШСК-57) (length of column was 3 m, carrier gas was argon, rate was 30-40 cm^3/min). For separation of HT and CH_3T there was used a column with molecular sieve 5A. With the help of two detectors (catharometer and flow-through geiger counter) there were analyzed in parallel products of chemical interaction of hot atoms of tritium and inactive products of radiation-chemical reactions proceeding under the action of radiation from the nuclear reactor.

There have been established yields of tagged and untagged products. There was observed formation of ethylene, ethane, acetylene, hydrogen, n-butane, butene, butadiene, hexane, methane and propane. Data on distribution of T in tagged products are given in Fig. 1 and 2; along the axis of abcissas are plotted molecular % NH_3 or He in mixture with C_2H_4; along the axis of ordinates – fraction of tagged product in relation to HT (activity of HT = 100). Relative magnitudes of radiation yields G (molecules/100 ev) of inactive products in deep stages of radiolysis are presented in the table.

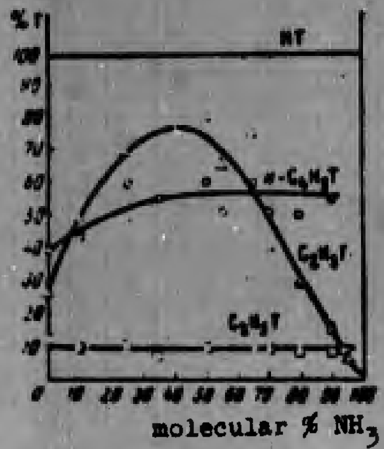


Fig. 1. Influence of NH_3 additions on distribution of tritium in tagged products.

Magnitudes G were calculated taking into account energy released in system due to gamma rays from the active zone and protons generated by the reaction $N^{14}(np)C^{14}$. Dose rate (air) $\delta = 1\cdot10^{14}$ ev/$cm^3\cdot$sec.

From the figures and table one may see that interactions of radiolytic and hot (tagged) hydrogen with ethylene essentially differ. Thus, for instance, in spectrum of tagged products, the main part of activity is due to hydrogen, ethylene and butane, but ethane (10%), and especially acetylene (2-3%), compose an insignificant part; in radiolysis products, a considerable quantity is composed of acetylene and ethane, and conversely there is little hydrogen. It is possible to assume that spectrum of final products is determined by magnitude of excitation energy imparted to ethylene or the ethyl radical.

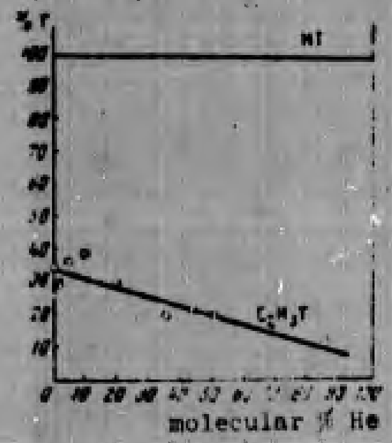


Fig. 2. Influence of helium additions on formation of tagged ethylene.

Relative Radiation Yields of Products for the Mixture C_2H_4-NH_3 (Pressure in Ampule is 5 ± 1 atm)

NH_3, molecular %	$G(-C_2H_4)$, molecules/100 ev	$G(C_2H_2)/G(H_2)$	$G(C_2H_6)/G(H_2)$	$G(C_2H_6)/G(C_4H_{10})$
0	18	2,8	4	1,5
10	—	—	—	—
25	18	4	—	2
30	17	3	5	—
40	16	3,5	6	2,3
55	20	—	—	—
70	18	—	—	—
80	19	1,3	0,7	1,1
85	17	1,0	0,4	1,0
90	15	0,8	0,2	1,0

From data on photolysis of tagged ethylene, it is known [5, 6] that excited molecule of ethylene at high pressures experiences monomolecular disintegration with formation of acetylene and molecular hydrogen:

$$C_2H_4^* \rightarrow C_2H_2 + H_2. \tag{1}$$

With increase of energy of a quantum, ratio C_2H_2/H_2 is increased, constituting for wavelengths 2537 ($Hg\,^3P_1$), 1470 and 1236A respectively 1, 2 and 2.8. This is connected with flow of the process accompanying (1)

$$C_2H_4^* \rightarrow C_2H_2 + 2H, \tag{2}$$

the role of which is increased with increase of excitation energy. During radiolysis, especially at high pressure, process (2) plays an important role; this is indicated by large magnitude of ratio $C_2H_2/H_2 \approx 4$. The appearing atomic hydrogen (which is thermal or "warm") is expended basically on hydrogenation of ethylene:

$$C_2H_4 + H \rightarrow C_2H_5. \tag{3}$$

Decrease of quantity of ethylene during radiolysis of mixtures is basically determined by process (3), with subsequent polymerization (~75%). From the table one may see that $G(-C_2H_4)$ does not depend on composition of system C_2H_4-NH_3, and is determined simply by generation of H atoms, independently of whether ethylene or NH_3 "supplies" them (dose is calculated for the whole system). The formed C_2H_5 radicals can participate in process of polymerization and also recombine and disproportionate, with formation of butane and ethane. Ratio of yields of reactions of disproportionation and recombination at the temperature of the experiments

(~40 to 50°C) should be 0.1-0.2 (in accordance with magnitudes of rate constants and activation energies of reactions). At the same time, ratio C_2H_6/C_4H_{10} exceeds 1; this may be connected with presence of excited C_2H_5 radicals formed according to [3], with participation of "warm" radiolytic H atoms.

At sufficiently high energy of atoms T, they can enter into reactions of substitution and detachment of hydrogen from molecules of the medium. Introduction of inhibitors (He, NH_3) into C_2H_4 leads to decrease of yield of tagged hydrogen, and especially ethylene (see Fig. 2), whereas yield of tagged C_2H_6 and C_4H_{10} practically does not change (see Fig. 1), and their ratio is close to 0.2. Thus reactions of substitution and detachment of hydrogen:

$$C_2H_4 + T \rightarrow C_2H_3 + HT;$$
$$C_2H_4 + T \rightarrow C_2H_3T + H$$

are hot, and reactions of attachment of T by a double bond seem to occur at energies close to thermal. However, $E_T > E_H$, and according to process (3) there would have to take place formation of excited tagged ethyl radicals. It is possible that with increase of energy of atomic hydrogen above a certain limit, cross section of process (3) decreases, and high yields of tagged butane are connected with the interaction of excited molecule $(C_2H_3T)^*$ with C_2H_4 with subsequent hydrogenation of tagged butene.

In C_2H_4-NH_3 mixtures, at high content of NH_3, with ethylene there interact only inhibited T atoms (thermal T atoms do not react with ammonia at room temperature due to the high activation energy of process $NH_3 + H \rightarrow NH_2 + H_2$ ($E_{\text{акт}}$ = 13 to 15 kcal/mole)). Taking into account corrections for thermal processes, ratio of probabilities of reactions of substitution by hot triton and detachment of H atom from ethylene is close to 0.2.

Literature

1. R. L. Carter, W. H. Hamill and R. R. Williams. J. Am. Chem. Soc., 77, 6457 (1955).

2. V. V. Voevodskii and Yu. N. Molin. Radiation Res., 17, 366 (1962).

3. T. J. Hardwick. J. Phys. Chem., 66, 1611 (1962).

4. A. N. Pravednikov, In Shen-kan, and S. S. Medvedev. Transactions of 2-nd International conference on peaceful use of atomic energy. 1958, Geneva. Reports of Soviet scientists, Vol. 4, Moscow, Atmomizdat, 1959, p. 241.

5. M. C. Sauer and L. M. Dorfman. J. Phys. Chem., 66, 322 (1962).

6. H. Okabe and I. R. McNesby. J. Chem. Phys., 36, 601 (1962).

Discussion

A. Ya. Temkin. Is it possible to limit energy range of atoms of tritium to several hundred electron volts?

B. G. Dzantiyev. This does not seem to us to be so important, since the "history" of hot atom before achievement of energy of hundreds or tens of electron volts probably doesn't essentially affect the fate of tritium or yields of products.

V. I. Gol'danskiy. What is the spectrium of tritons in the region of reactivity of tritium?

B. G. Dzantiyev. Assuming model of elastic deceleration, it is possible to expect establishment of the Fermi spectrum $\Phi \sim 1/E$.

V. N. Kondrat'yev. Have there been experiments which show that with addition of inhibitor yield of reaction products of hot atoms changes. Has this been calculated?

B. G. Dzantiyev. It was calculated by Wolfgang. He and I discussed this question. If we consider that the atom is neutral, then its thermalization is determined by the known mechanism of thermalization of neutrons according to the law of elastic collisions. For the case of methane plus rare gases, there has been shown agreement of theory of elastic collisions with results of experiments.

V. I. Gol'danskiy. How is it possible to imagine the form of the excitation function of a reaction?

B. G. Dzantiyev. With decrease of energy of tritons, excitation function of reaction passes through a maximum. It lies in the region of ten ev.

S. Z. Roginskiy. How is it possible to explain change of ratio of yields of acetylene to hydrogen? Where does the hydrogen disappear to?

B. G. Dzantiyev. With increase of excitation energy, with the process of molecular splitting, the process of detachment of atomic hydrogen starts to compete; the latter is expended on hydrogenation of ethylene. There are experimentally observed hydrogenation products — ethane and butane. It is possible to see that at that time when usually the ratio of ethane to butane corresponds to reactions constants of disproportionation and recombination, in the case of excited ethyl radicals there is observed a predominance of reactions disproportionation and direct interaction with RH, with detachment of hydrogen.

A. Ya. Temkin. Have there been observed reactions in which tritium, in knocking out hydrogen from the molecule, remains an atom itself?

B. G. Dzantiyev. These reactions in principle are not observed by the given method, since there are not obtained tagged products. Such processes obviously take place during slowing down.

V. I. Gol'danskiy. What is it possible to say about reaction of tritium in energy range, from 60 Kev to tens of ev? Is there a possibility of chemical reaction in this region?

B. G. Dzantiyev. In range of energies considerably higher than binding energy, interaction of hot atom can take place not with the whole molecule, but with separate atoms. There are known results for reactions of replacement of hydrogen by tritium in H_2 and D_2 molecules. In this case, proceeding from the interaction with separate atoms, there would be expected a considerable isotope effect which was not observed in experiment. This speaks in favor of the fact that reaction occur, in energy range, comparable with binding energy, and therefore possibility of application of pulse approximation requires special consideration.

V. N. Kondrat'yev. How, nevertheless would it be possible to formulate an answer to the question of the program: "What is the relationship between substitution reactions of atomic groups and attachment of atoms of hydrogen during interaction of hot atoms of hydrogen with organic molecules?"

B. G. Dzantiyev. Ratio of probabilities of substitution of tritium for hydrogen atom to detachment of hydrogen with formation HT is about 0.2. Regarding, however, the process of attachment, apparently, this process occurs more efficiently when energy of atoms becomes of the order of one ev or fractions of an ev. If we trace the dependence of cross section of various processes on energy, then maxima of cross section will be arranged with decrease of energy in the following order: substitution, detachment, attachment. Regarding the mechanism (pulse substitution on the one hand and formation of a short-lived complex with lifetime shorter than the time necessary for achievement of equilibrium distribution on the other), then the question of experimental distinction of these processes is vague.

V. V. Voyevodskiy. Certain considerations about relationship between reactions of substitution and detachment under action of hot atoms can be expressed in the example of radiolysis of water. It is true that our work is connected with certain assumptions about the actual scheme of radiolysis. We advanced the assumption that this scheme includes reaction of a hot hydrogen atom (we will imagine it to be tagged) H' in a water medium with a molecule of water. In principle it is possible to imagine two mechanisms of reaction: 1) detachment of H with formation of HH' and OH and 2) substitution, with ejection of H by "tagged" hydrogen and formation of $H'OH$. If we assume that radiolysis of water occurs through formation of hot atoms of hydrogen and OH radicals, then according to yields of radiolysis products it is possible to estimate ratio of rate constants of the indicated two mechanisms of reaction: substitution k_2 and detachment k_1. This ratio k_1/k_2 for H atoms was calculated by us[1] according to data on radiolysis of water and is equal approximately to 0.2. According to data of Rowland for hot atoms of tritium,[2] who, just as B. G. Dzantiyev directly measured yields of HT and HTO, there can be obtained magnitude of this ratio ~0.1, which is good enough coincidence considering the presence of isotope effect. This coincidence of two magnitudes obtained according to two different works, although it is not a direct means of measurement of relationship between reaction rates of substitution and detachment, in a given concrete case can serve as qualitative approach to determination of this relationship.

V. N. Kondrat'yev. And how is it with energies of activation? After all, this relationship should depend on temperature at various activation energies.

V. V. Voyevodskiy. Here there are such surpluses of energy that it will always suffice for overcoming the activation barrier.

V. N. Kondrat'yev. It seems to me that in the report and in our discussion, the following question which pertains here, in relation to the program, did not find reflection: "What data on excitation function of endothermic (threshold) and exothermic (but with activation energy) reactions can be obtained from analysis of already available results on reactions of hot atoms?"

V. I. Gol'danskiy. It seems to me that, concerning this question, from available results there can be obtained quite little data. It is difficult to carry macrokinetic results to some range of energy or another and existing theoretical works have the character of calculations of elementary events. This question is intimately related with another question of the program: "slow to vary conditions of experiments and what calculations to carry out in order to obtain quantitative information about excitation functions of reactions of hot atoms?" Answering both these questions, it is necessary to consider that during the analysis of material, even when there are initially obtained monochromatic hot atoms (and this occurs in the case of K-capture), is hindered by a certain ambiguity connected with the fact

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[1] V. V. Boyevodskiy. Kinetics and catalysis, 2, 14 (1961).

[2] F. Rowland. Pros. of 4th Conference on Radiation Chemistry of Water. Notre Dame, 1961.

that in the course of slowing down, all the same there appears a certain spectrum of energies. In the process of slowing down there occurs, as it were, "stratification" of hot atoms: part of them enter into reaction at the beginning part later, etc. In what interval of the spectrum of energies the center of gravity of chemical transformations falls is difficult to say. The answer of B. G. Fzantiyev on this question is a qualitative answer. Maximum of probability of chemical interaction could lie both in the range of several electron volts or hundreds of electron volts.

Direct experiments here should be made with an atomic beam of prescribed energy, obtained for instance by means of charge exchange. By changing this energy there can be obtained data on excitation functions of reactions of hot atoms. Regarding, however, theoretical calculations, it seems to me that already now it would be possible to give at least a semiquantitative slowing down theory of hot atoms in simple standard media, taking into account both elastic collisions and chemical transformations.

V. N. Kondrat'yev. It seems to me that it would be possible to answer this question if one would trace reaction products to various stages of slowing down of hot atoms. Is it possible to do this experimentally?

V. I. Gol'danskiy. In principle this is possible to do, but we should consider that results will be semiintegral. Therefore, it is subsequently necessary somehow to differentiate, and compare them with each other. The situation is similar to case when there is a pulse source of neutrons and a resonance detector, which registers neutrons of some definite energy. Observation of time distribution of appearance of such neutrons permits us to follow the kinetics of the process of thermalization of neutrons. However, concerning experimental possibilities of such kind in the case of reactions of hot atoms, it is still difficult to say anything more definite.

A. M. Brodskiy. In examining the relation between elementary processes and the "global" results to which reactions of hot atoms lead, it is necessary to consider two energy ranges separated by a value of about 10 ev. Atoms possessing energy higher than 10 ev, i.e., higher than ionizing energy as a result of multiple collisions comparatively rapidly lose energy in processes of charge exchange, and which occur with large cross section, practically do not play a role in chemical transformations. Main yield, however, is caused by reactions of atoms with energy lower than 10 ev, cross section of which in some other way, apparently in a resonant manner depends on energy.

CONCERNING THE MECHANISM OF REACTIONS OF HOT ATOMS WITH MOLECULES

A. M. Brodskiy and A. Ya. Temkin

Hot atoms and also ions, radicals and molecules cause specific bimolecular reactions which differ in certain senses from reactions of thermal atoms (at the usual, not too high temperatures), and at the same time do not lead to reactions studied by radiation chemistry in which first stage is ionization or exciting of electron terms of molecule. The indicated reactions were observed, for instance, in experiments with hot tritium atoms in saturated hydrocarbons [1]. Although initial energy of atoms of tritium in these experiments is of the order of 200 Kev, results of experiments pertain basically to range of energies lower than threshold of excitation of electron terms, since at higher energies processes of ionization and excitation of electron terms of molecules dominate, leading to fast slowing down of hot atoms. In favor of this assumption witnesses also character of dependence of yields of considered reactions on additions of inert atoms (on their mass and concentration) [2]. As is noted in works [1, 3], description of considered reactions with help of usually theory based on assumption about equilibrium complex of colliding particles is not satisfactory. At the same time it is easy to see that alternative variant – model of direct knocking out of atoms from molecule contradicts experimental data [1], since it can not explain binding of atom of tritium in one of fragments of molecule.

In the present work, there will be given arguments in favor of hypothesis about resonance character of reactions of considered type. We will assume that scattering amplitude and cross section of reactions in this case are determined mainly by resonance terms and are described by Breit-Wigner formula [4-7]. Indicated assumption also pertains to certain other inelastic bimolecular processes. Partial widths of different channels of reactions are determined only by properties of a concrete system; on them are not imposed any general relationships (in distinction from theory of equilibrium complex). Therefore, our assumption does not contradict considered experimental data. Let us consider series of arguments based on contemporary theory of scattering and nuclear reactions [6-10], witnessing in favor of the made hypothesis. We will be limited to region of energies from tenths of an ev energy of first level of electron excitation. We note that likewise it is possible in certain cases to consider processes occurring at lower and at higher energies.

Appearance of resonances is caused by strong interaction of colliding system, intensity of which should be of the order of energy of chemical bonds. Interaction can be carried out only as a result of overlapping of electron wave functions of these systems, and in the considered energy range has a local character. It is possible to consider approximately that in formation of complex (if there is no system of conjugated bonds) there participates one atom entering into composition of molecule. Influence of excitation energy transfer along molecular chain can then be taken into account if we consider this process by means of introduction of additional channels of disintegration of the local complex. Thus, in principle it is possible to pass in the limit to the case of an equilibrium complex.

Local character of strong interaction permits expanding scattering amplitude of atom on a polyatomic molecule into a number of Jacobian polynomials, just as for case of collision of two atoms. Using this expansion, it is possible to generalize the Regge concept [9, 10], considering angular momentum K of system, its projection M_K on fixed axis and projection Λ of electron momentum on axis of symmetry as complex variables and investigating pole of scattering amplitude in a space of three complex variables. Basic role is played by Λ, since resonance characteristics are determined by structure of electron shell. It is obvious that there should be satisfied the condition $\Lambda \leq K$. Reasoning by analogy with usual theory of Regge, it is possible to expect following results: 1) resonances can be only at integer $\mathrm{Re}\,\Lambda > 0$; 2) resonance lie in the electron volt range of energies, and their number is not more than two or three; 3) distance between resonances is approximately equal to distances levels of bound states of the system;[1] 4) total widths of resonances turn out to be of the order of 1 ev if resonance lies in the electron-volt range of energies (this corresponds to a lifetime of compound molecule of about $5 \cdot 10^{-15}$ sec; in that time, equilibrium is not able to be established).

Use of Breit-Wigner gives the possibility to write kinetic equation determining energy distribution of hot atoms in gas medium or to determine part of group constants during use of method of energy groups [11]. In case of presence in gas of an effective speed reducer of hot atoms, reactions rates determined with help of Breit-Wigner expression for cross sections should have maximum at certain initial energy of hot atoms. Likewise, temperature dependence of rates of bimolecular reactions at high temperatures possesses a maximum, if we apply resonance theory to them.

An important result of use of Breit-Wigner formula is constancy of ratio of rate of any two reactions proceeding in one and the same resonance: in any case, it is equal to the ratio of partial widths. Experimental determination of this ratio permits judging about relative contribution of different valence schemes in wave function of a compound-molecule.

In conclusion we express gratitude to V. G. Levich and participants in the seminar directed by him, V. G. Nosov, L. S. Polak and K. P. Lavrovskiy for their useful discussions.

Literature

1. D. Urch and R. Wolfgang. J. Am. Chem. Soc., 83, 2982 (1961).
2. P. J. Estrup and R. Wolfgang. J. Am. Chem. Soc., 82, 2661 (1960).
3. J. L. Magee and W. H. Hamill. J. Chem. Phys., 31, 1380 (1959).
4. L. Landau and Ye. Lifschitz. Quantum mechanics. Part 1. Moscow-Leningrad, State Press for Technical and Theoretical Literature, 1948.
5. N. F. Mott and G. Messi. Theory of atomic collisions. Moscow, IL, 1951.
6. G. Breit. Theory of resonance nuclear reactions. Moscow, IL, 1961.
7. A. Lane and R. Thomas. Theory of nuclear reactions at low energies. Moscow, IL, 1960.

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[1] We have in mind bound states of a system of two atoms. In case of collision of hot atom with polyatomic molecule, wave function of the corresponding valence scheme enters with a certain coefficient into the expansion of wave function of compound molecule with respect to wave functions of valence schemes. Namely this circumstance leads to redistribution of particles during collision.

8. Collection: New method in theory of strong interactions. Ed: A. M. Brodskiy. Moscow, IL, 1960.

9. T. Regge. Nuovo Cimento. 14, 951 (1936).

10. R. G. Newton. J. Math. Phys., 3, 867 (1962).

11. A. Ya. Temkin. Transactions of Tashkent conference on peaceful use of atomic energy, 28 September-3 October, 1959, Vol. 1. Tashkent, Publishing House of Academy of Sciences of UzSSR, 1961, p. 195; Reports of AS USSR, 135, 373 (1960); Radiolysis of hydrocarbons. Moscow, Publishing House of Academy of Sciences of USSR, 1962, Chapter VI, Section A.

Discussion

V. I. Gol'danskiy. Can there be made any concrete conclusion for the most simple reaction?

A. Ya. Temkin. There is considered the following: hot atoms propagating in medium of consisting of molecules of one type are slowed down. Then it is assumed that slowing down goes slowly and that slowing down cross section is nonresonance region is determined as cross section of two colliding spheres.

Considerations connected with the Regge theory are needed only in order to establish the presence of resonances in cross section, to find their position and approximate width. After position of resonances is established, with help of Breit-Wigner formula it is possible to write expression for reaction rate.

V. I. Gol'danskiy. Name some concrete reaction.

A. Ya. Temkin. For instance hot tritium plus alkanes.

V. I. Gol'danskiy. Direct interaction of two atoms it is possible to describe also in the pulse approximation. It would be nice to compare results of calculations in pulse approximation and according to Regge theory for some concrete process.

GENERAL DISCUSSION

V. L. Tal'roze. Question about influence of kinetic energy of ion on direction and cross section of ion-molecular reaction is analogous to question about mechanism of reactions of hot atoms. During collision of ion with molecule one should distinguish two processes:

1) process connected with short-range interaction, when time of interaction is small and only processes not connected with displacement of nuclei have time to occur. It is accepted to call them resonance processes during atomic collisions;

2) reaction complex can have a lifetime of the order of many vibrations, and then there occurs its disintegration through many channels.

Method of Brodskiy-Temkin, if it is true, is applied namely to processes of first type. It is possible to imagine such a scheme. As a result of some process there will be formed a short-lived complex, which has a number of channels of transformation. In the case of process of charge exchange and in chemical reactions without electron transport (for instance transmission of electron excitation), one of the channels is formation of long-lived complex, and another is transformation not connected with transfer of a heavy particle. Disintegration of long-lived complex should not depend on method of its formation.

Of interest to me is how the authors of the report feel about the scheme presented by me, and also if it is possible on the basis of their theory to answer the question: with what probability are there realized the "channel" of formation of a long-lived complex and the "channel" in which this complex not will be formed?

A. M. Brodksiy. I will briefly formulate results reported by A. Ya. Temkin. There is a system of bound states in region of negative energy levels. In region of positive kinetic energies which is equal in magnitude to interval of negative energies, there should occur resonance interactions. Bound states are determined by attractive forces on the one hand and centrifugal barrier on the other. With increase of energy there appears a decaying state, but then one or two collisions have time to occur. All this is very similar to what V. L. Tal'roze said.

What information does our method give besides a general affirmation that resonance lies in the electron-volt region of energy? If the system of bound states is known, it is possible to obtain approximately their position and width. Width is obtained to be of the order of distance between levels to the $(2l + 1)$ power. The conclusion is still: resonances are few.

With respect to applicability of method of concrete chemical systems, let us assume that bound state is close to zero, for instance recombination. In this case there can be obtained expression for reaction rate from which one may see that the on "tail" of the Maxwellian distribution reaction rate should decrease with temperature rise according to a 3/2 law, which is in accordance with experiment. Besides, with help of one resonance term it is possible to integrate the kinetic equation.

In order to compare experiment with theory in chemistry of hot atoms, it is necessary to study dependence of process on kinetic energy and angular distribution. Apparently, it is promising to use hot muonium. According to polarization of formed electrons it is possible to follow behavior of hot atom in dependence on its energy.

V. I. Gol'danskiy. There are three parameters characterizing any resonance: parameter characterizing cross section at the maximum, σ_0, full width of resonance Γ and resonance energy E_0. From these three parameters the proposed theory permits determining in essence one. I am confused by the fact that what besides resonance interaction through intermediate state, there will occur direct ("potential") interaction with characteristic time equal to, roughly speaking, time of flight. In any interaction where there can be direct interaction and interaction through an intermediate complex, we have to add not cross sections, but amplitudes of these interactions, since there many be interference. Direct interaction it is better to consider with help of the method of pulse approximation. I propose to compare results of calculation according to Brodskiy-Temkin method with calculation in the pulse approximation in the example of the concrete reaction

$$T + H_2 \rightarrow HT + H.$$

Calculation in this case can be conducted completely, and its results can then be compared with experiment.

3. GENERAL QUESTIONS OF THEORY OF ELEMENTARY GAS REACTIONS

CONCERNING QUESTION ABOUT MECHANISM OF VIBRATIONAL RELAXATION

V. N. Kondrat'yev

From experiment and theory it is known that it is comparatively easy (especially at high temperatures) to transform one vibrational quantum into translational energy. There easily occurs transformation of one vibrational quantum into another, and also into energy of spin-orbital interaction (especially in the presence of resonance).

However, concerning the process of transformation of large portions of vibrational energy into translational, vibrational or electron energy, we know very little. One of the evident ways of approach to consideration of these processes is comparison of them with well studied processes of transformation of energy inside a separately taken molecule. Such a process, for instance, is prediasociating disintegration of a molecule, which can serve as a sample of process of transformation of vibrational energy into translational, which takes place during collision of a vibrationally excited particle $AB(AB^*)$ with particle M: it is possible to treat the last process as disintegration of complex $(AB \cdot M)^*$ (similar to prediasociating molecule) into fast particles AB and M.

As another process occurring in isolated molecule it is possible to consider spontaneous transition of a molecule (taking place during monomolecular disintegration) which possesses a sufficient reserve of energy into the active state. This transition consists of a redistribution of vibrational energy inside the molecule such that energy distributed among many degrees of freedom is concentrated on the broken bonds. By analogy with this process, exchange of vibrational energy during collision of two molecules can be considered as redistribution of vibrational energy in the complex formed by them, which is similar to a complex of the type of the activated molecule.

Mutual transformation of vibrational and electron energy during collisions of molecules in the most distinct form appears in extinguishing of atomic fluorescence of di- and polyatomic gases, which is treated as transformation of electron energy into vibrational. Thus for instance, extinguishing of D-fluorescence of sodium with nitrogen can hardly be interpreted otherwise.[1]

In view of the ease of transition of energy of electron excitation into electron energy during collisions of atoms and molecules (especially in the presence of resonance), it is possible that it is necessary to connect with electron transitions certain cases of dissociation during collisions of electron-excited atoms and molecules.

Transformation of vibrational energy in a molecular complex obviously should be represented as transition of system from one potential energy surface to another. Probability of this process should depend on forces of interaction between particles forming the complex, on energy of these particles and on lifetime of the complex.

One of the strongest interactions of colliding particles is interaction observed in chemical reactions. Together with that, a characteristic peculiarity of chemical reactions is ease transformations and exchange of vibrational energy. Chemical interaction undoubtedly plays large role also in physical processes of transformations and exchange of energy, which pertains, in particular, to processes connected with transformations of large portions of internal energy during collisions of molecules [2].

As an example it is possible to indicate the ability of vibrationally excited molecules of nitrogen (N_2^*) appearing during interaction of N and NO to split molecule of ozone [3]. The measured large probability of this process can be explained by the strong chemical interaction of N_2^* and O_3 and ease of transformation of vibrational energy in the complex $(N_2 \cdot O_3)^*$ caused by this. It is interesting that vibrationally excited molecules formed during interaction of O and O_3, in distinction from molecules of N_2, are not able to split ozone [4]. The absence or the negligibly small probability of process $O_2^* + O_3 = O_2 + O_2 + O$, must apparently be explained by weak interaction of O_2 with O_3 (unobservability of O_5 in distinction from N_2O_3).

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[1] There were expressed assumptions about large role of resonance between electron and vibrational energy during transformations of one form of energy into another. Against this witness data about extinguishing of fluorescence of thallium by hydrogen, where, in spite of sharp resonance, extinction practically does not occur [1].

It is also possible to assume that with large reserves of vibrational energy, its transformations are realized with greater ease, the more probable the chemical process becomes — for instance $HX^* + XX = HX + XX^*$ (as compared to physical process $HX^* + XX = HX + XX^*$). This transformation apparently occurs in the complex $(HX \cdot XX)^*$.

Literature

1. N. A. Prilezhayeva. ZhFKh (Journal of Physical Chemistry), 5, 1239 (1934).
2. J. Franck and A. Eucken. Z. phys. Chem., B20, 460 (1933).
3. L. F. Phillips and H. J. Schiff. J. Chem. Phys., 36, 3283 (1962).
4. D. J. McKenney and K. J. Laidler. Can. J. Chem., 40, 539 (1962).

Discussion

A. Ye. Shilov. It is known that with increase of vibrational quantum number there is increased probability of inter-transformation of translational and vibrational energy. What causes this — anharmonicity or something else?

V. N. Kondrat'yev. Matter not only concerns the magnitude of vibrational quantum, since even for a harmonic oscillator, where vibrational quanta are identical, probability of transformation of energy grows with increase of vibrational quantum number v according to the law

$$P_{v \to v-1} = (v+1) P_{1 \to 0}$$

Ye. Ye. Nikitin. Increase of probability of transformation of vibrational energy of a molecule into translational with increase of vibrational quantum number is due to several causes. For diatomic molecules in which redistribution of energy during the time between collisions is impossible, probability of transition is proportional in the first place to reserve of vibrational energy, i.e., $P_{v,v-1} \sim \sim B \cdot v$. This dependence (linear in v) is simply due to the fact that magnitude of intermolecular interaction responsible for energy transfer increases with increase of amplitude of vibrations. Factor B also depends on v; however, this dependence is considerable only with sufficiently great anharmonicity, and it leads to growth of B with increase of v. This effect is connected with decrease of period of oscillation as a result of anharmonicity with increase of v; therefore, collisions become less and less adiabatic. In other words, rate of interaction characterized by time of collision expressed in units of period of oscillations increases with growth of v.

Regarding dependence of probability of energy exchange for polyatomic molecules, in this case, apparently, it is necessary to consider in explicit form not only decrease of magnitude of vibrational quanta with increase of oscillatory quantum number, but also the possibility of energy exchange between normal oscillations as a result of anharmonicity in time of collision. Qualitative discussion of this question can be found in work [1].

M. A. Yel'yashevich. Are there direct experimental proofs of transition of energy of electron excitation into large portions of vibrational energy with considerable probability?

V. N. Kondrat'yev. Here there are very few reliable data. Interesting from this point of view is the work of Sher and Fayn [2], where it is quite clearly shown that high effectiveness of extinction of fluorescence of mercury by carbon monoxide (20 times larger than effectiveness of extinction by nitrogen) can be explained only by transformation of considerable part of energy of electron excitation into vibrational energy. Of course, direct proof would be direct detection of this process.

R. F. Vasil'yev. In the report were given examples of transformation of vibrational energy into energy of electron excitation, as a result of which there will be formed unstable molecule which then dissociates. Do there exist similar transitions in stable electron-excited state which, radiating light, would go to the ground state?

V. N. Kondrat'yev. To this question it is possible to give the following answer. For any process, according to the principle of microscopic reversibility, it is possible to suppose a reverse process. For instance, if above the discussion centered around transition of electron excitation of mercury into vibrational energy of CO during collision, then it is possible to present the reverse process, when strongly vibrating molecule of CO collides with atom Hg, transmits energy of its vibrational excitation to atom of mercury and excites it.

R. F. Vasil'yev. Are there experimental data on such processes?

V. N. Kondrat'yev. If there occurs a chemical process, i.e., transition to a new (from the point of view of potential surfaces) state, then such transition does not differ from transition to any other surface, in particular to a surface which corresponds to electron excitation. For instance, during collision of vibrationally excited molecule H_2^* with atom Na, there are formed sodium hydride and atom H, but if energy is sufficient, Na atom can also appear in electron-excited state. But this is also only indirect proof.

It is necessary, certainly, to obtain direct answers to all questions appearing here. The purpose of my report is to pose such problems to experiment and theoreticians.

Ye. Ye. Nikitin. Is it impossible to repeat what the sign of defect of resonance during interaction of hydrogen and thallium is?

V. N. Kondrat'yev. Energy of H_2^* (v = 8) is greater than energy of electronic excitation of atom of thallium by 0.03 ev. The question, why H_2 extinguishes fluorescence of Na and does not extinguish fluorescence of thallium was discussed at the Congress.[1] There was advanced the following explanation: in formation of complex of excited atom and NaH_2 molecule, there participate only s- and p-electrons, whereas in formation of a complex in the case of thallium, there participate d-electrons.

Ye. Ye. Nikitin. I would like to express certain considerations about resonance exchange of energy during atom-molecule collisions, in particular about transformation of electron energy of atom into vibrational energy of a molecule. In such a nonadiabatic electronic-vibrational transition, probability of exchange of energy as a function of resonance defect is asymmetric relative to the position of exact resonance, so that the question about sign of resonance defect is very significiant.

During approach to resonance from one side, there is possible intersection of two adiabatic electronic-vibrational terms, whereas from the other side, intersection may not occur. An example of the first process is one of the mechanisms of extinction of fluorescence of mercury caused by nonradiative transition [3]:

$$Hg(^3P_1) + X_2(v = 0) \rightarrow Hg(^3P_0) + X_2(v = 1).$$

Second question which I would want here to touch upon concerns multiquantum vibrational excitation, when electron energy becomes vibrational energy. A well-known example is interaction of excited state of sodium with a molecule of hydrogen. Curves on energy diagram corresponding to states $Na^* + H_2$, $Na + H_2$ intersect the curve of the ionic state, where nonadiabatic transition occurs at points of quasiintersection. Hence it would follow that all excitation energy is turned into vibrational energy of H_2. But the fact is that due to very strong interactions, the terms in reality do not intersect, and thus energy here is not turned into kinetic.

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[1] Transfer d'Energie dans les gaz. Institut International de Chimie, douzieme conseil de chimie tenu à l'Université Libre de Bruxelles du 5 au 10 novembre 1962, Interscience Publ, N. Y., p. 472-480.

Literature

1. Ye. Ye. Nikitin. Contemporary theories of thermal disintegration and isomerization of molecules in the gas phase. Moscow, Publishing House of Academy of Sciences of USSR, 1964.

2. M. D. Scheer and I. Fine. J. Chem. Phys., 36, 1264 (1962).

3. V. K. Bykhovskiy and Ye. Ye. Nikitin. Optics and spectroscopy, 16, 201 (1964).

PULSE APPROXIMATION IN THEORY OF ATOMIC AND ATOMIC-MOLECULAR COLLISIONS[1]

G. K. Ivanov and Yu. S. Sayasov

Pulse approximation is based on the following assumptions about nature of interaction of incident particle (considered as a structureless particle) with a complicated system of bound particles. First it is assumed that wavelength of incident particle λ_a and its effective radius of interaction with particles of a scattering system A are less than average distance between them R, so that $A\lambda_a/R^2 \ll 1$. Thus, potential v of interaction of the particle with the system can be considered to be paired: $V = \Sigma v_{a\nu}$, and processes of multiple scattering can be disregarded. Another assumption is that the time of paired interaction τ is much less than time of essential change of state of the scattering system $\hbar/\Delta E$: $\tau \ll \hbar/\Delta E$. Thus, as it turns out, as τ it is possible to take $\tau = \hbar d \ln F_{a\nu}/dE$ ($F_{a\nu}$ is scattering amplitude of free colliding particles, E is their relative energy). Condition $\Delta E \ll \left|\frac{d \ln F}{dE}\right|^{-1}$ can also be rewritten in the form $\frac{\Delta EA}{\hbar v_{OTH}} \ll 1$, where v_{OTH} is average relative velocity of colliding particles. Thus, the pulse approximation is essentially anti-adiabatic.

During the analysis of processes of collisions in the pulse approximation, it is convenient to transform initial expressions for differential cross sections so that they do not explicitly contain wave functions of final states, because the latter in most cases are complicated, and are not always known. This is attained

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[1] This work was presented at the symposium, but was not reported read.

by means of effective summation of partial cross sections and integration over variables of the incident particle, and gives a whole series of advantages in the analysis of inelastic processes. Initial expression for differential scattering cross section which is used by us subsequently has the form

$$\sigma = \Sigma_{\rho_i} (\Phi_i, T^{имп}\Phi_i),$$

where Φ_1 are wave functions of initial states of scattering system; ρ_1 – weighting factors; $T^{имп}$ – a certain operator, constructed in terms of scattering amplitudes of free particles and the Hamiltonian of the scattering system.

Ionization During Atomic Collisions

There was performed calculation of probabilities of ionization during collision of excited atom with atom in the ground state. Thus energy of excited atom was assumed to be so great that it is possible to consider it to be hydrogen-like, i.e., ionizing energy is $Q = 1/2n^2$ (in atomic units) where $n^2 \gg 1$. In this case the atom can be considered as consisting of singly charged case and an election located from it at a distance of the order of $10^{-8}n^2$ (the latter interacting with the other atom gives a decisive contribution to ionization). Conditions of applicability of the pulse approximation turn out to be satisfied (into condition $\frac{\Delta E \cdot A}{\hbar v} \ll 1$ there enters velocity of electron $v \sim 1/n$) at $n^2 \gg 1$, i.e., at ionizing energies $Q \lesssim 1$ ev. It is remarkable that total cross section of ionization is obtained to be of the order of σ_0/β^4 (σ_0 is cross section of elastic scattering of atom and electron, $\beta = \Delta A/\hbar v_a$ is adiabatic parameter of Messi) instead of exponentially small $\sigma_0 e^{-\beta}$, as this is considered in the case of $\beta \gg 1$. This is due to the fact that in spite of satisfaction of condition $\Delta A/\hbar v_a \gg 1$, process of interaction of incident atom has not an adiabatic, but a sudden, pulse character.

Scattering of Fast Atoms on Molecules

Despite the fact that the state of a molecular bond concerns the structure of atoms, law of interaction (potential V) of fast atom possessing energy $E_a \gtrsim 10$ ev with molecule can be considered to be paired $V = \Sigma v_{av}$ and not to depend on character of molecular bond. This assumption was used, for instance, by Magee[1] during classical calculation of dissociation of molecules, and it actually is true, inasmuch

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[1] L. Monchick, K. Funabashi and J. Magee. J. Chem. Phys., 27, 734 (1957).

as interaction of fast atoms occurring during their strong approach to each other is determined by participation of electrons of inner shells, whereas interaction of atoms in a molecule is carried out basically by orbital electrons, and this is carried out better, the greater the energy of incident atoms is and the heavier atoms in the molecule are.

Other assumptions of the pulse approximation in the range of energies $E_a \gtrsim 10$ ev are fulfilled with good accuracy. We will note only that for amplitudes of atomic scattering $\frac{d \ln F}{dE} \sim \frac{1}{E_a}$. Scattering of atoms by molecules can most simply be considered in the case when $|\varepsilon - R| \ll E_a$ ($R = \varkappa^2/2M_\nu$, ϵ – transmitted energy, $\varkappa$ – transmitted momentum, M_ν – masses of scattering atoms), when we arrive at a result equivalent to the Born results with the distinction that Born factors, equal to

$$F_B = -\frac{1}{2\pi\hbar^2}\frac{M_a M_\nu}{M_a + M_\nu}\int e^{i\vec{\varkappa}\vec{\rho}}\, v(\vec{\rho})\, d\vec{\rho},$$

are replaced by amplitudes of elastic scattering of free atoms $F_{a\nu}$ (E', $\varkappa$), where $E' = M_\nu E_a/(M_\nu + M_a)$. At $|\varepsilon - R| \sim E_a$, changeability of amplitudes $F_{a\nu}$ depending upon E introduces a whole series of additional peculiarities, and essentially affects final results.

CONCERNING THE RELATION BETWEEN CROSS SECTIONS OF ELASTIC AND INELASTIC PROCESSES DURING NONADIABATIC ATOMIC COLLISIONS

M. A. Kozhushner and Yu. S. Sayasov

It is known that during atomic collisions accompanied by change of internal state of particles, the presence of inelastic process can greatly affect cross section of elastic scattering. Such influence appears, in particular, in that the cross sections undergo unique breaks at the energy thresholds of corresponding inelastic processes. Presence of such threshold singularities is used with success at present time in nuclear physics for investigation of different characteristics of colliding particles, for instance in reactions of the type $X + Y \rightarrow X' + Y'$ [1, 2].

Investigation of relation between cross sections of elastic and inelastic processes is also important for physics of atomic and molecular collisions, all the more so because at present time there has been developed the technology of atomic and molecular beams with the sufficient intensity and monochromaticity necessary for observation of such a relation.

In this report are expounded results of work [3], in which there is given full analysis of relation between cross sections of elastic and inelastic processes occurring with participation of two atoms under the following assumptions:

1) all interactions are centrally symmetric;

2) there are only two interacting states;

3) energy terms of initial V_i and final V_f states intersect;

4) point of intersection of terms lies lower than energy threshold of reaction.

It is shown that in this case relation between total cross sections of elastic σ_y and inelastic σ_H processes has the form

$$\sigma_y = \sigma_p - \sigma_{н}. \qquad (1)$$

where σ_p is cross section of potential scattering in the term disturbed as a result of interaction W_{if}, which causes the transition

$$W_{if} = \frac{1}{2}(\bar{V}_i + V_f) + \sqrt{\frac{1}{4}(V_i - V_f)^2 + V_{if}^2}$$

and becoming as distance between particles $r \rightarrow \infty$ the undisturbed term V_i; σ_H is cross section of nonadiabatic transition (excitation, charge exchange and others), given by the known Landau formulas.

According to [1] total cross section σ_t coincides with σ_p. When interaction between particles in initial state V_i is short-range, σ_p in quasi-classical case, as it is known, is constant. Therefore, for typical inelastic processes, which have an almost adiabatic region (i.e., exponential growth with energy of colliding particles, and then a slow drop after the maximum), in the energy dependence of σ_y there should be observed a minimum, after which there follows a gradual increase. It is possible that observation of such energy dependences in elastic cross sections can be used for determination of cross sections of inelastic transitions. Such a method, which at present has not yet been applied, can in our opinion serve as an alternative to the usually utilized methods of determination of cross section of inelastic processes (for instance by de-excitation of excited atoms), especially in those cases when excited states are rapidly destroyed as a result of side processes.

Near the energy threshold E_{Π} of inelastic reaction there are possible two types of energy dependence of σ_y.

1. If particles in final state have Coulomb interaction (for instance $Na + Cl \rightarrow Na^+ + Cl^-$), then formula (1) is valid strictly near the threshold. Since σ_H in (1) is constant near the threshold at $E > E_{\Pi}$ and $\sigma_{\Pi} = 0$ at $E < E_{\Pi}$, then this means that σ_y undergoes in this case a finite jump equal to $\sigma_H(E_H)$ near the energy threshold, whereas total cross section $\sigma_t = \sigma_p$ remains constant in region $E \overset{\sim}{\gtrless} E_{\Pi}$, in accordance with the general theorem [2]. This jump in certain cases can be very considerable (as in the example $Na + Cl \rightarrow Na^+ + Cl^-$) and is easily observed experimentally. Therefore it seems to us that observation of such threshold singularities in elastic cross sections for the considered case can be used for determination of σ_H near the threshold.

2. If V_f falls off at large distances faster than $1/r^2$, then near energy threshold there occurs the following threshold singularity:

$$\sigma_y = \sigma_y(E_n) - 2C\sqrt{E - E_n}\cdot\sin^2\delta_0;\ E > E_n;$$
$$\sigma_y = \sigma_y(E_n) - C\sqrt{E_n - E}\cdot\sin 2\delta_0;\ E < E_n \qquad (2)$$

(δ_0 - phase of s-scattering in term V_i); i.e., in this case σ_y has near E_n a unique break, which in certain cases (in particular if $V_f \sim 1/r^3$, i.e., in the final state, two identical atoms in different states interact) can be very noticeable and attain several percent of the gas-kinetic value.

To us, further theoretical investigation of the relation between cross sections of elastic and inelastic processes during collisions with participation of molecules and electrons and in photochemical reactions seems desirable.

Literature

1. A. I. Baz'. ZhETF (Journal of Experimental and Theoretical Physics), 33, 923 (1957).

2. A. I. Baz'. ZhETF, 36, 1762 (1959).

3. M. A. Kozhushner and Yu. S. Sayasov. Optics and spectroscopy, 15, 577 (1963).

Discussion

V. I. Gol'danskiy. What is the width of the peaks (singularities) which were mentioned in the report?

M. A. Kozhushner. This width is small (~10^{-2} ev), inasmuch as it is caused by inapplicability of the quasi-classical approximation for heavy particles near the threshold which was utilized here. For this reason it is difficult to rely on the fact that this width will be detected in experiment.

V. I. Gol'danskiy. How does formation of bound state during collision influence behavior of singularities of cross section?

M. A. Kozhushner. This question was not considered by us. It is possible, however, to express the following assertion. If term of final state is characterized by presence of a bound state lying sufficiently close to the continuum, then cross sections of the considered inelastic processes should have near the threshold a resonance of Breit-Wigner character. Accordingly the form of singularities in elastic cross sections near the threshold in these cases undoubtedly differs from that given by the formula (2).

Question. Total cross section obtained by you behaves smoothly near the threshold. Does this not contradict the known results of Wigner, Newton, Baz' and others?

M. A. Kozhushner. If reaction products interact according to a Coulomb law, smooth behavior is not strange, inasmuch as we talk about a cross section averaged over all resonances appearing in this case. This result in particular was obtained by A. I. Baz'. Regarding behavior of the cross section when products of reaction are neutral, I spoke only of cross section of inelastic processes, and not about total cross section, which indeed changes abruptly.

ON THE THEORY OF INELASTIC ATOMIC COLLISIONS IN THE ADIABATIC REGION

L. I. Podlubnyy

In the two-level approximation, the probability of transition from state 1 to state 2 is determined by asymptotic behavior of system of equations:

$$i\hbar\dot{C}_1 = V_{12}C_2\exp\left\{-\frac{i}{\hbar}\Delta Et - \frac{i}{\hbar}\int_{-\infty}^{t}\Delta V\,dt'\right\};$$
$$i\hbar\dot{C}_2 = V_{21}C_1\exp\left\{\frac{i}{\hbar}\Delta Et + \frac{i}{\hbar}\int_{-\infty}^{t}\Delta V\,dt'\right\}. \qquad (1)$$

Here $\Delta E = E_2 - E_1$; $\Delta V = V_{22} - V_{11}$; V_{11}, V_{12}, V_{22} are matrix elements of perturbation.

If potential curves intersect, integration in formulas (1) leads to the known Landau-Zener formula. Form of curves of P(V) and $\sigma(E)$ is determined to a considerable degree not by the pressure of a point of intersection, but by the character of the approximation, so that for approximation of the data of experiment it is possible to use corresponding formulas without analyzing in detail peculiarities of behavior of the potential curves.

In particular, if there exists a well-defined region of maximum approach of potential curves to each other, for probability of transition P(v) in the first perturbation-theory approximation

$$P = \frac{1}{\hbar^2}\left|\int_{-\infty}^{\infty} dt V_{12}\exp\left\{\frac{i}{\hbar}\Delta Et + \frac{i}{\hbar}\int_{-\infty}^{t}\Delta V\,dt\right\}\right|^2 \qquad (2)$$

we have

$$P(v) = 4\pi\left|\frac{V_{12}}{\Delta}\right|^2\left(\frac{E_0}{\varepsilon}\right)^{1/2}\left[\Phi\left(\sqrt[3]{\frac{E_0}{\varepsilon}}\right)\right]^2,\ \varepsilon = \frac{Mv^2}{2}. \qquad (3)$$

Here $\Lambda = \Delta E + \Delta V$ and V_{12} are calculated at the point R_0 for which $\Delta V' = 0$;

$E_0 = \frac{M\Lambda^3}{\hbar^2 \Delta V''}$; M is reduced mass, Φ is Airy [illegible].

It is possible to go from (2) to (3) if we assume that the main contribution to integral (2) is introduced by the region in which phase is changed the most slowly of all (it is assumed that point of intersection of potential curves is absent). Putting in formula (2) the expansion

$$\Delta V(R) = \Delta V(R_0) + \frac{1}{2}\Delta V''(R_0)(R - R_0)^2 + \ldots \tag{2a}$$

and taking from this decomposition only the first two terms, we arrive at (3).

Thus behavior of transition probability as a function of speed of relative motion depends on minimum distance between potential curves and their curvature.

Partial summation of the perturbation-theory series leads to a result more accurate than (2)(for instance, see [1]):

$$P = \frac{1}{\hbar^2}\left|\int_{-\infty}^{\infty} dt\, V_{12} \cos\left\{\frac{1}{\hbar}\int_0^t dt' \sqrt{\Delta^2 + 4V_{12}^2}\right\}\right|^2. \tag{4}$$

It is easy to show that (3) also remains valid in this case; it is necessary only to replace Λ by $\sqrt{\Lambda^2 + 4V_{12}^2}$ and R_0 by R_1, where R_1 is determined from the condition of a minimum of the expression under the radical.

For cross section $\sigma(E)$, from (3) we find

$$\sigma = 12\pi^2 R_0^2 \left|\frac{V_{12}}{\Delta}\right|^2 E_0^{2/3} \frac{(E - U_0)^{1/3}}{E} \int_0^1 dx \left[\Phi\left(\frac{1}{x}\sqrt[3]{\frac{E_0}{E - U_0}}\right)\right]^2, \tag{5}$$

where U_0 corresponds to the larger of potential curves at point R_0.

In order to estimate E_0, we will set $M = 10$, $\Lambda = 1$ ev, $\Delta V'' = 1$ ev/Å^2. Then $E_0 \approx 10^3_{\text{ev}}$ and in the region $E \ll E_0$ we obtain from (5)

$$\sigma = \frac{3}{2}\pi^2 R_0^2 \left|\frac{V_{12}}{\Delta}\right|^2 \frac{E - U_0}{E} e^{-\frac{B}{\sqrt{E - U_0}}},\quad B = \frac{4}{3}\sqrt{E_0}. \tag{6}$$

Expression (5) was used as an approximating formula for description of reaction $Ar + Ar \rightarrow Ar + Ar^+ + e$, where it was considered that $u_0 \approx I$, where I is ionization energy of argon. Probability of transition to the continuous spectrum is obtained from (3) by integration over momenta of the knocked-out electron. $0 \leq \frac{p^2}{2m} \leq E - I$. In work [2] there was approximately calculated matrix element $V_{12}(P)$; electron was described by a plane wave. Near threshold of reaction, it is necessary to replace plane wave with a Coulomb function. Then (6) becomes

$$\sigma(E) = A' \cdot \frac{(E-I)^2}{E} e^{-\frac{B}{\sqrt{E-I}}}. \qquad (7)$$

It turned out that in region E > 40 ev, cross section depends on energy similarly to (5). Normalizing σ(E) with respect to two points (150 and 250 ev) of the experimental curve [3], we obtain

$$\sigma = A\frac{E_0}{E}\int_0^{x_0} dx\Phi^2\left(\frac{1}{x}\right);\ x_0 = \sqrt{\frac{E-I}{E_0}};\ E_0 = 450 \text{ эв } A = 9{,}2\cdot 10^{-18} \text{ см}^2. \qquad (8)$$

Equations (7) and (8) fairly well describe experimental data in a wide region of energies, from threshold to ~10^4 ev. So, for E = 10 Kev, $\sigma_T = 1.4\cdot 10^{-16}$ cm^2, while according to [4], $\sigma_э = 1.6\cdot 10^{-16}$ cm^2, and according to data of [5], $\sigma_э = 0.7\cdot 10^{-16}$ cm^2.

In the near-threshold region, absolute values of σ are unknown. According to data of [6], at points E = 26, 28, 30, 32, 24 ev $\sigma_1:\sigma_2:\sigma_3:\sigma_4:\sigma_5$ = 1:3:6:12:27. According to formula (7), this ratio is equal to 1:2, 9:6, 6:12, 8:24.

From (7) it ensues that the approximation of σ(E) near the threshold as a straight line $\sigma_П = a(E - I)$ for the purpose of calculation, for instance, of $z_П$ (the number of ionizing collisions) for temperatures kT ~ 1 ev gives greatly exaggerated results.

In work [7] it was noted that at the point E-24 ev, $\sigma \leqslant 10^{-19}$ cm^2. Considering that σ(24) = 10^{-19} cm^2, for $z_П/z$ (z is number of collisions accompanied by ionization, calculated according to (7)), we obtain

$$\frac{z_П}{z} = 1{,}1\cdot 10^{-4}\left(1+\frac{I}{2kT}\right)\left(\frac{4kT}{B^2}\right)^{1/6} e^{3\sqrt[3]{\frac{B^2}{4kT}}}. \qquad (9)$$

If kT = 1 ev, $z_П/z \approx 230$; for kT = 1.5 ev $z_П/z \approx 52$.

For processes $Ar + Ar \rightarrow Ar_2^+ + e$, electron energy changes within the limits $E - I \leq P^2/2m \leq E - I + D$, where D is binding energy of molecular ion. Therefore, in (7) we should replace $(E - I)^2$ by D(E - I). Such a rough estimate of relative role of processes of associative ionization gives

$$\frac{z}{z'} = \frac{kT}{D}\sqrt[3]{\frac{B^2}{4kT}} \qquad (10)$$

(z' is number of collisions accompanied by formation of molecular ion). For instance, taking kT = 1 ev and D = 0.5 ev, we will obtain z/z' = 12.

Literature

1. L. Vaynshteyn, L. Presnyakov and I. Sobel'man. ZhETF, 43, 518 (1962).
2. P. Rosen. Phys. Rev., 109, 348 (1958).
3. Rostagni. Nuovo Cimento, 13, 389 (1935).
4. T. J. M. Sluyters, E. De Haas and J. Kistemaker. Physica, 25, 1376 (1959).
5. H. F. Batho. Phys. Rev., 42, 753 (1932).
6. H. Wayland. Phys. Rev., 52, 31 (1937).
7. R. Varney. Phys. Rev., 53, 732 (1938).

Discussion

V. N. Kondrat'yev. Can you depict the potential energy curves which were mentioned in the report?

L. I. Podlubnyy. The curves can be different. Of interest to me is that case when potential curves approach sufficiently close to each other.

V. L. Tal'roze. Will you more precisely define what the conditions and temparature are for the ratio $z/z' = 6$?

L. I. Podlubnyy. During finding of the obtained estimate $z/z' = 6$, it was assumed that $kT \approx 1$ ev $\approx D$.

V. L. Tal'roze. To what will the ratio z/z' be equal if we consider that $D = 4$ ev?

L. I. Podlubnyy. Ratio $\frac{z'}{z} = \frac{kT}{D}\sqrt[3]{4\frac{B^2}{kT}}$ is simply inversely proportional to D. If $D = 4$ ev, then the probability of formation of a molecular ion will be considerable.

V. L. Tal'roze. I would like to turn attention to the fact that calculations according to source material give $D = 4.3$ ev.

L. I. Podlubnyy. There exist other data according to which magnitude D is equal to approximately 0.5 ev.

V. L. Tal'roze. I think that these data are incorrect.

V. L. Granovskiy. Can you write the absolute value of cross section of ionization at comparatively low energies?

L. I. Podlubnyy. In principle, this can be done. For this it is necessary to make the corresponding calculations, which was not done by us.

Ye. Ye. Nikitin. According to what law does cross section grow near the threshold?

L. I. Podlubnyy. Cross section of simple ionization increases according to the law $\sigma \sim (E - I)^2 e^{-\frac{B}{E-I}}$; for formation of molecular ion, i.e., in case of associative ionization, according to the law $\sigma \sim \frac{D(E - I)}{E} e^{-\frac{B}{E-I}}$, i.e., dependence on energy in second case is weaker. These formulas do not hold near threshold, since during their derivation there was used classical approach for atoms, and also because near threshold the reversal point will be close to the point of closest approach.

Yu. N. Demkov. I have two questions: 1) We certainly know little about electron terms, but does this mean that it is possible to sketch them however desired? 2) To what extent is your two-level approximation legal if one of states lies in continuous spectrum?

L. I. Podlubnyy. It seems to me that the most probable is the following assumption: the transition from behavior of potential curves in accordance with the Landau-Zener formula to any other is gradual, and if curves approach each other, then an absolute boundary between processes of first and second types does not exist. Regarding the second question, it is always difficult to substantiate the two-level approximation. In this case, as a certain substantiation can serve the following consideration: probability of ionization from ground level is considerably less than probability of ionization from excited levels.

GENERAL DISCUSSION

V. N. Kondrat'yev. There are a number of questions of the program which were not answered in the reports. I will name by turn some of them. Maybe someone has ideas concerning them. It is possible to start for instance with the question: "What is energy spectrum of secondary electrons appearing during ionization of O, O_2, N_2 by electrons with energy from 0.1 to 40 Kev?"

Yu. I. Gal'perin. This question pertains to the aurore polaris. In spectra of aurore polaris, there occurs glow under the action of electrons and also protons with energy in just that range which was indicated. It would be interesting to find out what causes this glow: primary beams which, in being decelerated, will finally have the appropriate energy, or is this glow caused by secondary electrons. Secondary electron under these conditions will surely "work," since under conditions of upper atmosphere, it cannot be "lost on the walls". Inasmuch as secondary electrons have less energy, character of spectrum should be different than that of spectrum obtained at energies ~Kev. In connection with this, it would be interesting to obtain the energy spectrum of secondary electrons, especially in that energy range where these electrons can cause electronic excitation of atoms and molecules, i.e., not in the 1-2 ev range, but noticeably higher.

V. N. Kondrat'yev. The following question of the program: "What is the probability of direct formation of alkyl radical under action of electron impact (dissociation into radicals)?"

V. L. Tal'roze. Certain answers to question of dissociation into neutral fragments are found in works of the West German mass-spectroscopial Oberghaus [1], which not very long ago was able for the first time to investigate experimentally the path of dissociation of a complicated molecule into neutral particles during electron impact. Basic result is natural from the point of view of investigations in region of radiation chemistry. It is that dissociation into neutral fragments, i.e., dissociation without ionization, has approximately the same probability as the total processes of ionization. This answer apparently is given with an accuracy up to the coefficient 2-3.

V. N. Kondrat'yev. But, after all, this should depend on energy of electron. If its energy is lower than ionizing energy, then ionization will not occur at all.

V. L. Tal'roze. You are absolutely right, but radiation chemistry usually is not very interested in electrons with energies lower than ionization threshold. Such electrons apparently give a contribution which in order of magnitude is not very great. Radiation chemistry is more interested in electrons with energies of order of tens and hundreds of ev. Results about which I spoke pertain to just such electron energies. It is necessary to note that in this energy range, dependence of ratios of cross sections of various processes on electron energy exists, but as a rule is very weak.

V. N. Kondrat'yev. The following question: "What is probability of dissociation of molecules during transmission of energy directly to vibrational levels by slow electrons?" It is known that electron with low energy can transmit vibrational energy to a molecule, where this does not occur according to law of elastic spheres. Cross section of such a process is greater than cross section of process proceeding according to the law of elastic spheres.

V. K. Potapov. Recently there have appeared works in particular the work of Schulz [2], in which it has been shown that during bombardment with electrons with energy of 2-3 ev, there can be excited vibrational levels of molecules. I hesitate to specify the value of cross section for such a process; apparently it is approximately one and a half orders less than the gas-kinetic value. It is assumed that in this case there will be formed a complex - a "negative ion." For instance, for nitrogen it is possible to depict the reaction as

$$N_2 + e \rightarrow N_2^{-*} \rightarrow N_2^{*} \text{ (vibrational) } + e.$$

In the mentioned work, author measured energy distribution of slow secondary electrons.

V. N. Kondrat'yev. Of the most interest for chemist is the possibility of dissociation which is the result of excitation of vibrational levels by electrons. Electrons can successively excite all higher vibrations. It would be desirable to answer the question: What is the probability of such dissociation in systems important in practice. In the majority of real systems, the most probable apparently is dissociation during electron impact, which proceeds through excitation of electronic level.

Literature

1. D. Beck and O. Osberghaus. Z. Phys., 160, 406 (1960).
2. G. I. Schulz. Phys. Rev., 112, 151 (1958).

4. REACTIONS IN IONOSPHERE

ROLE OF PROCESSES OF TYPE $X^+ + YZ \rightarrow XY^+ + Z$ IN TERRESTRIAL IONOSPHERE

A. D. Danilov

At present, the question of role of different chemical processes in upper atmosphere sharply stands out. Rate of processes of dissociative recombination determines effective recombination coefficient in ionosphere, knowledge of which is necessary for exact calculation of ionization balance in atmosphere. Laboratory data available at present on magnitude of rate constant of dissociative recombination α^* indicate [1] a high value of α^*:

$$\alpha^* = 3 \cdot 10^{-7} \sqrt{\frac{300}{T}} \quad \text{cm}^3 \cdot \text{sec}^{-1}, \qquad (1)$$

where T is temperature of gas. However, in laboratory experiments up til now the effect of diffusion has not been satisfactorily taken into account. Comparision of the most reliable data on magnitude of effective coefficient of recombination in ionosphere α' with experimental data on ionic composition of ionosphere leads [2] to lower values of α^*, which constitute at temperatures of the order of 1000°K about $3 \cdot 10^{-8}$ $\text{cm}^3 \cdot \text{sec}^{-1}$.

At present there is essential uncertainty in the question of effectiveness of various ion-exchange reactions occurring in the ionosphere. At the same time, role of similar reactions in the ionization-recombination cycle of processes is very great, since they lead to transformation of atomic ions formed as a result of primary ionization into molecular ions, which rapidly as a result of dissociative recombination [3]. Experimental investigation of changes of concentration of different ions in ionosphere with altitude permits us to distinguish ion-exchange process in ionosphere which are the most important.

Comparison of experimentally observed and theoretical change of ratio of concentrations $[NO^+]/[O^+]$ [4] indicates predominant role in formation of NO^+ ions of the process

$$N_2 + O^+ \rightarrow NO^+ + N. \qquad (2)$$

Thus, ionospheric data give for ratio of constants $\gamma_2/\alpha^*_{NO^+}$ the magnitude $(5\text{-}10)\cdot 10^{-5}$ [4, 5]. For the value of $\alpha^*_{NO^+}$ determined according to formula (1), the value of γ_2 at ionospheric temperatures is obtained to be equal to $(5\text{-}10)\cdot 10^{-12}$ $cm^3\cdot sec^{-1}$. If, however, we take for $\alpha^*_{NO^+}$ the value obtained from ionospheric data on α' (see above), the magnitude of γ_2 in ionosphere will be equal to $(1.5\text{-}3)\cdot 10^{-12}$ $cm^3\cdot sec^{-1}$.

At present there are two experiments on determination of magnitude γ_2. Experiment of V. L. Tal'roze with colleagues [6] gives for magnitude γ_2 an estimate $\gamma_2 \leq 7\cdot 10^{-11}$ $cm^3\cdot sec^{-1}$. According to data of Langstroth and Hasted [7], this magnitude is equal to $5\cdot 10^{-12}$ $cm^3\cdot sec^{-1}$. Thus, laboratory determinations of magnitudes γ_2 and α^* and the ratio γ_2/α^*_{NO}, obtained from ionospheric data will fully agree with each other.

Formation of O_2^+ ions in terrestrial ionosphere to altitudes of about 160 km is explained well by the reaction

$$O^+ + O_2 \rightarrow O_2^+ + O. \qquad (3)$$

Ratio of constants $\gamma_3/\alpha^*_{O_2^+}$ is obtained from ionospheric data [8] to be equal to 10^{-4}. For value of $\alpha^*_{O_2^+}$ equal, according to [1], at altitudes of 100-150 km to approximately $3\cdot 10^{-7}$ $cm^3\cdot sec^{-1}$, magnitude γ_3 will be obtained to be equal to $3\cdot 10^{-11}$ $cm^3\cdot sec^{-1}$.

This agrees well with experiment of Dickinson and Sayers [9], according to which $\gamma_3 = 2.5\cdot 10^{-11}$ $cm^3\cdot sec^{-1}$; however, it exceeds the magnitude $1.8\cdot 10^{-12}$ $cm^3\cdot sec^{-1}$ obtained by Langstroth and Hasted [7]. Above 160 km for explanation of formation of O_2^+ ions there is required a mechanism not connected with O_2 molecules, since their concentration sharply drops with altitude due to dissociation.

Investigation of distribution of ratio of concentrations of ions N_2^+ and N^+ with respect to altitude led the author to the conclusion [10], that the process

$$N^+ + N_2 \rightarrow N_2^+ + N \qquad (4)$$

also explains distribution of N_2^+ ions at altitudes greater than 250-300 km. However, the necessary magnitudes $\gamma_4 \approx 10^{-11}$ $cm^3 \cdot sec^{-1}$ is several orders higher than possible; therefore, reaction (4) is apparently not important in the ionosphere.

Of interest is the question of ion-exchange processes in ionosphere leading to disappearance of argon ions. Comparison of concentrations of neutral atoms of argon and estimates of concentrations of Ar^+ ions obtained experimentally shows [11] that Ar^+ ions have to disappear at altitudes of 100-200 km as a result of ion-exchange reactions with molecules of the atmosphere having rate constant not less than 10^{-11} $cm^{-3} \cdot sec^{-1}$, which is much higher than the magnitudes which Bates and Nicolet assumed [12].

The exact value of rate constants of basic ion-exchange processes is very important for explanation of a whole series of questions connected with distribution of ionic components of the ionosphere and also neutral atoms of the atmosphere [13].

Literature

1. G. S. Ivanov-Kholodnyy. Geomagnetism and aeronomy, 2, 377 (1962).

2. A. D. Danilov and G. S. Ivanov-Kholodnyy. Geomagnetism and aeronomy, 3, No. 5 (1963).

3. A. D. Danilov. Reports of AS USSR, 137, 1098 (1961).

4. A. D. Danilov. In the collection: Artificial earth satellites, Issue 5, Moscow, Publishing House of Academy of Sciences (AS) of the USSR, 1960, p. 60.

5. G. S. Ivanov-Kholodnyy. Reports of AS USSR, 137, 327 (1961).

6. V. L. Tal'roze, I. K. Larin and M. I. Markin. Report at II-nd All-Union Conference on Physics of Collisions, Uzhgorod, 1962.

7. G. F. O. Langstroth and J. B. Hasted. Disc. Faraday Soc., 33, 298 (1962).

8. A. D. Danilov. In the collection: Artificial earth satellites, Issue 7, Moscow, Publishing House of Academy of Sciences of USSR, 1961, p. 56.

9. P. H. D. Dickinson and J. Sayers. Proc. Phys. Soc., 76, 137 (1960).

10. A. D. Danilov. In the collection: Artificial earth satellites, Issue 8, Moscow, Publishing House of Academy of Sciences of USSR, 1961, p. 72.

11. A. D. Danilov. Space investigations, 1, No. 2 (1963).

12. D. R. Bates and M. Nicolet. J. Atm. Terrestr. Phys., 18, 65 (1960).

13. A. D. Danilov. Geomagnetism and aeronomy, 1, 20 (1961).

Discussion

N. A. Bakh. In radiation chemistry of gaseous mixture of N_2 and O_2, basic role is played by the reaction $N_2^+ + O_2 \rightarrow NO^+ + NO$. Why isn't this reaction also decisive under the conditions of the upper atmosphere?

A. D. Danilov. The answer is that concentration of parent substances of this reaction is very low as compared to concentrations of O^+ and N_2, and therefore it is not decisive, although it probably occurs. Calculations based on the assumption that reaction $O^+ + N_2$ has the main role gives agreement with experiment.

L. M. Biberman. Did you assume that between the components there exists so to speak, photochemical equilibrium, and if you did, on what basis?

A. D. Danilov. We assumed that rates of formation of NO^+ by the reaction $N_2 + O^+$ and disappearance of NO^+ by means of dissociative recombination are equal.

L. M. Biberman. And on what basis?

A. D. Danilov. Your question as I understand it is as follows: Is there some unaccounted for process? If we did not err in the chemical mechanism then the only such process is diffusion. However, estimates have shown that up to altitudes of about 350 km its influence is immaterial.

L. M. Biberman. In what temperature interval is it possible to use expressions for constants obtained by you?

A. D. Danilov. Obtained ratios of constants remain unchanges with the range of 100-400 km for O_2^+ and NO^+ and from 200 to 50 km for N_2^+, i.e., in the whole region of existence of these ions. This corresponds to temperatures from 400 to 1500°C. Regarding, however, α^*, in this case everything depends on preservation of temperature dependence of magnitude α^* during transition from laboratory conditions to conditions of the upper atmosphere.

Yu. I. Gal'perin. What is the rate of chemical reactions in upper atmosphere, and what is total heat emission?

A. D. Danilov. Reaction rate changes with altitude. Integral value of flux of ionizing radiation is 3-10 ergs/cm^2·sec. The fraction of ionizing radiation which passes into heat has as yet not been sufficiently exactly determined.

V. N. Kondrat'yev. Processes considered by you are bimolecular. Is it possible to disregard reactions with participation of three particles and radiative recombination under these conditions?

A. D. Danilov. Consideration of processes more complicated than bimolecular should be conducted at altitudes less then 80 km, where the quantity of neutral particles is large, although for collisions $O + O_2$, it is necessary to consider this even higher. For ion collisions, I made an attempt to consider the reaction $O^+ + O \rightarrow O_2 + h\nu$, which caused serious objections, although I assume that some similar processes, for instance N + N → N_2 + hν, will have to be used in order to explain the disappearance of atomic nitrogen.

V. L. Tal'roze. From the obtained values of constants and coefficients of diffusion, it has followed that diffusion does not have time to interfere. It is possible that more exact values of constants will require consideration of diffusion at least for altitudes from 30-500 km.

INVESTIGATION OF DISSOCIATIVE RECOMBINATION OF ATMOSPHERIC IONS N_2^+, O_2^+ AND NO^+

G. S. Ivanov-Kholodnyy

Discussion of the question of rate of dissociative recombination of ions at present in the literature can be considered to be completed. It has been established that the reaction of dissociative recombination of molecular ions indeed possesses a high rate. There are, however, large difference between laboratory data on the magnitude of rate, although the most reliable determinations differ from each other by not more than an order of magnitude.

New data obtained with help of rockets and satellites, on density and electron concentration in upper atmosphere, intensity and spectrum of shortwave ionizing solar radiation, and especially data on ionic composition, which indicate the high concentration of molecular ions at different altitudes, shows that in the main part of ionosphere higher than ~100 km, neutralization is determined mainly by the reaction of dissociative recombination. Analysis of different ionospheric data permits us to estimate order of magnitude of rate of this reaction for different molecular ions. Although these estimates possess great uncertainty, they are close to values obtained in recent laboratory experiments. Further refinement of these magnitudes has great value for selection of ideas of the nature of basic elementary processes occurring in the ionosphere, about the magnitude of energy balance, and so forth.

It is necessary to conduct laboratory measurements of magnitudes of rate constant of dissociative recombination with accuracy up to the factor 1.5-2, which requires setting up very thorough and well thought out experiments; in particular, it is important to correctly consider the disturbing effect of ambipolar diffusion of ions to walls of chamber in the laboratory installation. It is important to determine rate of reaction of dissociative recombination for atmospheric ions N_2^+, O_2^+, and especially NO^+, and also to investigate dependence of this process on temperature. Consideration of available geophysical data on the reaction of dissociative recombination is interesting for clarification of various peculiarities of this process and formulation of the most important laboratory experiments.

Discussion

V. L. Tal'roze. May I ask you to name facts for whose explanation there is required use of the hypothesis of existence of a source of night ionization?

G. S. Ivanov-Kholodnyy. Besides a day source of ionization (shortwave solar radiation), in upper layers of atmosphere there is another source of ionization — corpuscular radiation, which constitutes a flux of electron with energy of about 1 Kev. The very existence of the ionosphere at night, and also nightglow (red oxygen line 6300 A), which is connected with dissociative recombination, are impossible without the presence of ionization. Furthermore, there are a set of other processes in upper layers of ionosphere which indicate presence of corpuscular radiation. There has already been started investigation of "soft" electrons (with energy of 1-10 Kev) on rockets and satellites, and quantities of such electrons agree with other data.

Yu. I. Gal'perin. What is magnitude of flux of electrons with energy of 1 Kev which is necessary for explanation of night ionization, if we assume available effective recombination cross sections?

G. S. Ivanov-Kholodnyy. There is necessary a flux of approximately 1 erg/cm^2·sec if we assume for recombination coefficient a magnitude of $\simeq 3\cdot 10^{-7}\cdot\sqrt{\frac{300}{T}}$ cm^3·sec^{-1}.

I would like to emphasize that at the present time energy balance in atmosphere has begun to be examined very seriously. Earlier it was assumed that energy flux by day was 0.1-0.3 erg/cm^2·sec, but now this magnitude has increased to 3-10 erg/cm^2·sec. It depends on solar activity. Power of night flux differs from power of day shortwave solar radiation by 3-10 times, which has been confirmed by high-altitude temperature distribution; it is known that at great heights, temperature has value of 1500-2000°C during the day as well as at night. For this there is necessary a source of heating at night. Works conducted recently confirm that flux of electrons of

1 erg/cm^2·sec could give this effect. However, it is necessary to know what fraction of energy of electrons goes to heating, ionization and other processes.

D. P. Rayzer. How do you explain the fact that laboratory and ionospheric measurements of values of rate constant of dissociative recombination differ by 30 times?

G. S. Ivanov-Kholodnyy. Ionospheric measurements give magnitudes of rate constant of recombination of the order of 10^{-7}-10^{-9} cm^3·sec^{-1}, and in certain cases they are too low, whereas laboratory data are too high. Understating of data in ionospheric measurements obtained according to 24-hour changes of electron concentration can be explained by the influence of change of density in the upper layers, which is asymmetric with respect to noon. Exact analysis leads to the fact that there remains a disagreement between ionospheric and laboratory data of approximately 3 times.

Yu. M. Yemel'yanov. What are the concentrations of O_3^+ ions in the atmosphere, and how are they formed?

G. S. Ivanov-Kholodnyy. These ions have not been detected in upper layers of atmosphere. They have been observed only in laboratory experiments.

ON THE INVESTIGATION OF CHEMICAL PROCESSES IN THE IONOSPHERE

S. P. Yatsenko

With development of rocket technology, there has appeared the possibility of study of chemical processes occurring in the upper atmosphere. Thus there are considered processes including participation of atmospheric ions, since first of all, ionic concentrations are easier to measure than concentrations of neutral components, and, secondly, distribution of ionic concentrations with respect to altitude is determined basically by chemical processes, whereas distribution of neutral particles is greatly influenced by diffusion, which hampers investigation of chemical processes.

Chemical investigations in the ionosphere can be approached from two points of view. On the one hand, chemical processes determine the most important properties of the ionosphere, and therefore for study of ionosphere it is necessary to develop investigation of elementary chemical processes. On the other hand, in the upper layers of atmosphere chemical processes flow in the most "pure" form; here there are absent walls and other factors distorting flow of the process. Therefore, study of ionosphere can give valuable information about laws determining rates of elementary chemical processes. Thus chemistry of ionosphere and investigation of elementary chemical processes are intimately related from the point of view of experimental possibilities.

The basic means of study of chemical composition of ionosphere at present is the radio frequency mass-spectrometer [RMS] (PMC) [1]. Contemporary RMS[1] have sensitivity

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[1] To avoid confusion in terminology, we should consider that the same abbreviation is sometimes used for mass-spectrometers intended for determination of free radicals. (Ed. note).

during "ionic" analysis of 10^2-10^3 ions/cm^3, and during "neutral" analysis — up to 10^{-10} mm Hg. Weight of instrument is about 2 kilograms. Further improvement of RMS goes along the line of increase of sensitivity with simultaneous decrease of dimensions.

In investigation of neutral composition of atmosphere, there have so far been made only the first steps [2-5]. Basic difficulty here is recombination of atomic components on walls of instrument [6, 7]. Concerning ionic composition, valuable information has been obtained by V. G. Istomin with the third artificial earth satellite and in a number of rocket experiments and also by Johnson (USA) by means of rockets [5, 8, 9]. During ionic analysis, the main difficulty is discrimination with respect to masses, which has an especially strong effect during measurements on a satellite.

The nearer the mass numbers of investigated components are, the higher the accuracy of determination the ratio of their concentrations. For finding absolute concentrations there are used data on electron density. In principle it is possible to measure absolute concentrations directly with the help of RMS, but for this it is necessary to conduct much preliminary work.

Data on the high-altitude change of relative concentrations of ions allowed A. D. Danilov to investigate the role of ion-exchange reactions in the ionosphere [10]. No less value in study of ionosphere can have experimental investigation of high-altitude change of absolute concentrations of different ions. It is possible to show that ions disappearing as a result of recombination with electrons and ions disappearing as a result of interaction with neutral components of the atmosphere must have sharply different variation of ion concentrations with altitude [11]. Experimental data of V. G. Istomin [12, 13] confirm this conclusion.

If there are known basic chemical reactions determining composition of ionosphere, there can also be found relationship between concentrations of ions, which must remain constants with change of altitude, geomagnetic or geographic latitude, time of day or other parameters. Investigation of such "chemical invariants" can give valuable information about properties of ionosphere [14].

Besides measurement of chemical composition, it is possible to study chemical processes in ionosphere by releasing in ionosphere different gases and observing the occurring reactions with the help of RMS.

In launching of geophysical rockets, the container with mass-spectrometer on descending branch of trajectory passes through a cloud of gases released by the rocket. Then there are recorded ions of the contaminating materials [9]. Processing of data on contamination could probably give interesting results. It is possible to imagine setting up a special experiment: a container with mass-spectrometer passes through an artificially created cloud of gas (for instance molecular nitrogen) and reports about change of chemical composition of ions in cloud as compared to that in the undisturbed atmosphere.

Instead of creation of an artificial cloud, it is possible also to install on the container next to the RMS a device for ejection of small portions of gas [15]. Calculation shows that sensitivity of RMS is sufficiently high for detection of products of interaction of released gas with ions of the atmosphere. It is interesting to note that on the third artificial earth satellite there were recorded up to the third orbit ions of contaminating substances released by surface of the satellite. The time variation of concentration of these ions shows that they were formed as a result of interaction with ions of the atmosphere.

The radiofrequency mass-spectrometer presents great possibilities for chemical investigations in the ionosphere. It is obviously time to ask the question concerning wide use of these possibilities.

Literature

1. V. G. Istomin. Mass-spectrometric investigations of composition of ionosphere of earth. Candidates dissertation, Moscow, 1961.

2. A. A. Pokhunkov. In the collection: Artificial earth satellites, Issue 13, Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 110.

3. A. A. Pokhunkov. In the collection: Artificial earth satellites, Issue 7, Moscow, Publishing House of Academy of Sciences of USSR, 1961, p. 89.

4. E. B. Meadows and J. W. Townsend. Space Research Amsterdam. 1960, p. 175-198.

5. C. J. Johnson. Ann. geophysique, 17, 100 (1961).

6. V. G. Istomin. Geomagnetism and aeronomy, 1, 359 (1961).

7. A. A. Pokhunkov. Geomagnetism and aeronomy, 3, 252 (1963).

8. V. G. Istomin. In the collection: Artificial earth satellites, Issue 4, Moscow, Publishing House of Academy of Sciences of USSR, 1960, p. 171.

9. V. G. Istomin. In the collection: Artificial earth satellites, Issue 7, Moscow, Publishing House of Academy of Sciences of USSR, 1961, p. 64.

10. A. D. Danilov. Reports of the AS USSR, 137, 1098 (1961).

11. S. P. Yatsenko. Geomagnetism and aeronomy, 2, 873 (1962).

12. V. G. Istomin. Reports of the AS USSR, 137, 1102 (1961).

13. V. G. Istomin. In the collection: Artificial earth satellites, Issue 6, Moscow, Publishing House of Academy of Sciences of USSR, 1961, p. 127.

14. S. P. Yatsenko. Report at the I-st All-Union Conference on results of the IG.

15. A. D. Danilov and S. P. Yatsenko. Space investigations, 2, No. 2 (1964).

GENERAL DISCUSSION

Yu. I. Gal'perin. The importance of chemical processes in upper atmosphere in principle is well established. I want to give several examples of how part of problems of upper atmosphere would already be solved today if certain of our data has been considered in detail by specialists of that type which is represented at this symposium.

At present, processes determining formation and destruction of the ionosphere, i.e., processes of ionization and recombination, have been very thoroughly discussed. A large role here is played by the no longer new conception which was presented here by A. D. Danilov and G. S. Ivanov-Kholodnyy about the role of molecular ions opening the way for fast recombination in the ionosphere. The thought about the large role of molecular ions was for the first time expressed by Bates [1]. He considered that in ionosphere there are fast recombining particles, which are formed directly under action of an ionizing agent and rapidly disappear, and there are also those particles which we are able to observe in a certain stationary concentration – these are products of chemical reactions. If we consider that there occur the reactions about which A. D. Danilov spoke here (i.e., reactions of type $X^+ + YZ \rightarrow XY^+ + Z$, which have rate constants $\sim 10^{-10}$ cm^3/sec), that flux of solar radiation ~10-100 erg/cm^2·sec (these magnitudes are accepted in works of A. D. Danilov and G. S. Ivanov-Kholodnyy, although recently they lowered somewhat the required energy fluxes), that the ionosphere basically consists of molecules, and finally, if we take effective recombination coefficients equal to 10^{-7}-10^{-6} cm^3/sec, then we can explain magnitude of concentrations of charged particles during the day.

Then, however, due to high effective coefficients of recombination, the ionosphere would have to disappear rapidly at night. In order to explain existence of ionosphere at night, A. D. Danilov and G. S. Ivanov-Kholodnyy have to introduce yet another ionizing factor, which is, they assume, corpuscular. Recently there have been obtained data about rate constants of ion-molecule reactions, about the intensity about intensity of solar radiation and about values of effective recombination coefficients. If we compare these data with data on corpuscular ionizing agent, then there appears a contradiction. It was established [2] that flux of corpuscular ionizing radiation at night time, which obviously must cause the glow which is characteristic for aurore polaris, does not exceed $3 \cdot 10^{-2}$ erg/cm^2·sec, i.e., it is almost two orders less than the magnitude about which G. S. Ivanov-Kholodnyy spoke. Thus corpuscular night ionization at low and average latitudes is practically absent.

The way out of this situation which has been created is not clear, but possibly can be found if we consider that composition of ionosphere is not molecular. Molecular ions which are revealed there would have recombine rapidly with dissociation, and in the ionosphere there would have to be few molecules. There are other possibilities for preservation of the night ionosphere. Therefore, we should examine all these conceptions anew. According to recent data [3], the ionosphere at the considered heights consists almost completely of products of dissociation of molecules. Basically these are atoms of oxygen and helium (inasmuch as reliable data on concentration of atomic nitrogen are still absent, its existence is nevertheless probable).

V. L. Tal'roze. Consideration of ionospheric processes which were discussed in these reports is an important achievement in the region of understanding of what occurs in the ionosphere. Apparently it is impossible to imagine another way of recombination of charged particles besides recombination through the stage of formation of a molecular ion. On the other hand, the character of fall of concentration of ions at night also is strange: quite rapid fall of concentration after sunset, and then practically constancy. This, as I understand it, has induced the thought about existence of a constant source of ionization. However, in examining these questions, usually no attention is paid to other chemical consequences which will be worked by processes of dissociative recombination. To what do processes of recombination through the stage of formation of a molecular ion lead?

Process $O^+ + N_2 \rightarrow NO^+ + N$ obviously will lead to a case in which after dissociative recombination of NO^+ there will be obtained atoms of N and O, i.e., as a result of this process there will occur destruction of molecules. Any processes of dissociative recombination lead to destruction of molecules. In the end, in the ionosphere there will be destroyed all molecules. Necessarily there appears the assumption which Yu. I. Gal'perin expressed here: does not the entire ionosphere consist of atoms, although this is contradicted by information about composition of the upper ionosphere which has lately become canonical. Simple calculation shows that time of recombination of atoms formed in ionsophere is from 10^9 to 10^{14} sec. As a result, there would have to occur destruction of the "molecular" ionosphere and replacement of it by an "atomic" atmosphere (night will practically not introduce any changes), where there would remain so few molecules that effective recombination rates of ions calculated on the basis of highest possible rate constants of dissociative recombination would still be exceptionally low.

In light of this, I have advanced a hypothesis, which is that the basic process determining recombination rate in ionosphere in the regions of the F-layer most interesting to us is diffusion ("fall") of atoms formed as a result of ion-molecule and other processes in lower layers of ionosphere and reverse diffusion of molecular nitrogen. Preliminary rough calculations show that the characteristic diffusion time which is necessary to provide the observed coefficients of effective recombination is $\sim 10^5$ sec. Solution of the problem, which simultaneously takes into account kinetics of chemical reactions and diffusion in the field of gravitation is very complicated. A. S. Kompaneyets recently considered the simpler problem of diffusion in a gravitational field without taking into account kinetics, and is now seeking approaches to the whole problem. In light of the hypothesis proposed by us, the picture of the process of ionization and recombination in ionosphere is the following:

By day, under action of solar radiation, there is established a certain stationary concentration of ions, which are destroyed by means of dissociative recombination; this concentration is controlled by supply of molecules from lower layers by means of diffusion, as the slowest process.

After sunset there occurs fast drop of the concentration of ions which was under ionizing factor of the sun, and then the process of recombination again starts to be controlled by the slow process of diffusion. Process of drop of concentration, as rough estimates show, should occur slowly in this case. After sunrise, starts again ionization, which is "constructed" under diffusion and is established day concentration of ions.

It seems to me that the hypothesis about such flow of processes makes it possible to avoid introduction into consideration the idea of a night ionizing factor and gives a logical explanation of the entire set of known facts and processes leading to that stationary concentration of electrons in the ionosphere which determines its basic properties.

In conclusion, I should apologize before my comrades studying questions of the ionosphere for the fact that in my work with M. I. Markin and I. K. Larin [4], there was an unfortunate misprint in the value of the upper limit of rate constant of the reaction $O^+ + N_2 \rightarrow NO^+ + N$. It is written that $k \leq 7 \cdot 10^{-12}$ cm^3/sec. This should read $k \leq 7 \cdot 10^{-11}$ cm^3/sec. This does not at all change the present situation, inasmuch as there exist data of Hasted [5], according to which $k = 5 \cdot 10^{-12}$ cm^3/sec. At present we are developing a method with the help of which we hope to obtain no longer an estimate, but a more exact value of this constant.

Yu. I. Gal'perin. I agree with the fact that it is necessary to consider the role of diffusion. The necessity of such a consideration, in particular in the case of the night ionosphere, was indicated long ago [6], but unfortunately a quantitative theory of such diffusion, which for understandable reasons is very complicated, does not exist. The important role of diffusion is indicated by a whole series of experimental data, in particular data about equatorial anomaly in ionosphere, about distribution of concentration according to altitude and about dynamics of this distribution at night, which, I would note, absolutely do not correspond to the assumption about a new ionizing factor. It is very good that now there will appear ways to create a quantitative theory of the ionosphere taking into account diffusion.

A. D. Danilov (to Tal'roze). I do not understand how the process of supply of neutral molecules at heights where recombination occurs will change the whole recombination cycle. Should removal of atoms of nitrogen and delivery of molecules of nitrogen be included in the recombination cycle? After all, we rely on the concentration of N_2 measured, for instance, with the help of a mass-spectrometer to heights of about 500 km (data indicate that there is much molecular nitrogen to heights of about 400 km). Is it impossible to consider that the recombination cycle is one problem and the providing of the concentration of molecular nitrogen is a different problem? The second problem is exactly connected with the diffusion proposed by you.

V. L. Tal'roze. I should repeat. As a result of recombination reactions there are formed atoms. If we calculate how fast they have to disappear in the absence of diffusion, then it will appear that they do not disappear for, let us say, 10^5 years. Consequently it is necessary to look for a molecular replacement for them. We established that the process of recombination is such a slow process that it explains nothing. In chemistry I do not find other processes which could be sufficiently fast to determine rate of the process of ionization. Therefore, we are forced to assume that the source of molecules is lower layers, and that the process determining effective recombination rate of ions is diffusion. If you will, this signifies that I include diffusion in the total recombination cycle, where I include it as the main controlling process.

G. S. Ivanov-Kholodnyy (to Tal'roze). What processes of diffusion do you have in mind?

V. L. Tal'roze. We consider diffusion of neutral molecules from below and, naturally, reverse diffusion, or fall of atoms and other particles. The total picture should certainly also take into account diffusion of ions, although by introduction of diffusion we wanted to turn attention for the time being only to the fact that as soon as we include in our consideration ion-molecule processes which "convert" molecules into atoms, the process which controls the concentration of ions in the ionosphere becomes diffusion, and not the ion-molecule reactions, although everything occurs through them.

Yu. I. Gal'perin. Important is the fact that at night it is necessary to consider diffusion of ions and electrons from above-lying layers, inasmuch as there recombination does not occur, due to the low concentration. Therefore, at night there mainly occurs recombination in the lower ionosphere, and in the upper ionosphere recombination is practically absent. The "middle" is supported by diffusion.

V. L. Tal'roze. It would be interesting to establish what "fall" of ions downward not only from upper layers of the ionosphere, but, we will say, from the radiation belts can contribute to night ionization. It seems to me that magnetic fields permit such a fall. At one time I considered that this fall could be just the ionizing agent which G. S. Ivanov-Kholodnyy discusses, until I began to consider diffusion as the basic regulating mechanism explaining the stationary concentrations of ions without a night ionizing factor.

G. S. Ivanov-Kholodnyy. The hypothesis of V. L. Tal'roze about the role of diffusion is undoubtedly of interest and can sufficiently well explain a number of questions. However, diffusion processes do not eliminate the possibility of presence of a night source of ionization.

A. D. Danilov. It is necessary to consider how diffusion processes are superimposed on ion-molecule reactions and recombination processes. Furthermore, it is necessary to know the true concentration of N_2. Usually the fraction of N_2 was taken by us to be constant to heights of 400 km. Under such an assumption, all our subsequent reasonings are accurate. But is it correct to choose such a concentration of N_2? The hypothesis of V. L. Tal'roze pertains, it seems to me first of all to the question of concentration of N_2. If consideration of diffusion leads to data agreeing with presently known concentrations of N_2 in the ionosphere, then all that was reported by G. S. Ivanov-Kholodnyy and I will completely agree with the hypothesis concerning the role of diffusion.

V. L. Tal'roze. I agree with such a formulation of the problem. If night ionization does not exist, then it is necessary to look for error in measurements of concentration. If, however, a source of night ionization does exist, higher concentrations of N_2 can occur. Quantitative data on calculations of diffusion will help to clarify this. And, conversely, if it turns out that a large quantity of N_2 can be supplied by diffusion, it is necessary to look for a night source of ionization. If not, diffusion is the controlling process in ionization.

Literature

1. D. R. Bates. Proc. Roy. Soc., A196, 562 (1949).

2. Yu. I. Gal'perin. News of AS USSR, physics series, No. 2, 252 (1962).

3. I. Harris and W. Priester. NASA TN 1443 (1961); J. Geophys. Res., 68, 5891 (1963).

4. V. L. Tal'roze, M. I. Markin and I. K. Larin. Disc. Faraday. Soc., 33, 257 (1962).

5. G. F. O. Langstroth and J. B. Hasted. Disc. Faraday Soc., 33, 298 (1962).

6. G. A. Radcliff and C. Weeks. In the collection: Physics of the upper atmosphere. Ed: G. A. Radcliff. Moscow, IL, 1963; Ya. L. Al'pert. Propagation of radio waves in the ionosphere. Moscow, Fizmatgiz, 1962.

5. MECHANISM OF CERTAIN COMPLICATED PROCESSES AT HIGH TEMPERATURES AND IN A PLASMA

THE ROLE OF HEAVY IONS IN THERMAL EQUILIBRIUM IONIZATION OF GASES

V. L. Tal'roze and I. K. Larin

The authors[1] calculated equilibrium concentrations of ions formed during thermal ionization of water vapor, hydrogen and argon, taking into account processes of formation of H_3O^+, H_3^+ and Ar_2^+ ions. Calculations showed that for H_2O and H_2 up to 4000°K, and for Ar, up to 6000°K, ionization is caused by formation of H_3O^+, H_3^+ and Ar_2^+ ions respectively, where concentration of heavy ions exceeds concentration of positive ions calculated without taking into account the former, in the region of 2000°K for water by three orders of magnitude, for hydrogen by two orders and for argon by four orders. This result is consequence of the large value of affinity of protons for water (169 kcal/mole) and hydrogen (70 kcal/mole) and of the Ar^+ ion to Ar($\approx$99.3 kcal/mole). At the same time, from the entropy point of view, processes of formation of heavy ions

$$2M \rightleftarrows M_2^+ + e \qquad (I)$$

are less suitable than processes of direct ionization:

$$M \rightleftarrows M^+ + e. \qquad (II)$$

Therefore, with increase of temperature, when influence of heats of corresponding processes on degree of ionization decreases, and role of entropy factor increases, equilibria of type (II) become decisive, the degree of ionization of which is calculated by the Saha formula.

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[1] I. K. Larin and V. L. Tal'roze. Kinetics and catalysis, 3, 305 (1962).

At present the authors have considered question about influence of pressure on role of heavy ions in equilibrium ionization. It is clear that with decrease of pressure, the role of heavy ions in equilibrium ionization should decrease in importance.

As an example, for argon and hydrogen there were calculated pressures at which $P_{Ar_2^+} = P_{Ar^+}$ and $P_{H_3^+} = P_{H_2^+} + P_{H^+}$.

For argon there was considered the system of equations:

$$2Ar \overset{K_1}{\rightleftarrows} Ar_2^+ + e; \quad K_1 = \frac{P_{Ar_2^+}P_e}{P_{Ar}^2}; \; Q_1 = 265 \text{ kcal/mole}; \qquad (1)$$

$$Ar \overset{K_2}{\rightleftarrows} Ar^+ + e; \quad K_2 = \frac{P_{Ar^+}P_e}{P_{Ar}}; \quad Q_2 = 364 \text{ kcal/mole}; \qquad (2)$$

$$P_{Ar} = P_{Ar}^0; \quad P_e = P_{Ar^+} + P_{Ar_2^+}. \qquad (3)$$

From (1) and (2) it follows that

$$\frac{P_{Ar_2^+}}{P_{Ar_2^+} + P_{Ar^+}} = \frac{K_1 \cdot P_{Ar}^0}{K_1 P_{Ar}^0 + K_2},$$

i.e., the contribution of Ar_2^+ to ionization in the beginning increases proportionally to pressure, and then asymptotically tends to unity, where at $T = 2000^\circ K$ $\frac{P_{Ar_2^+}}{P_{Ar_2^+} + P_{Ar^+}} \approx 0.5$ if $P_{Ar}^0 \approx 1.6 \cdot 10^{-8}$ atm. Thus, heavy ions predominate starting at insignificantly low pressures.

In the case of hydrogen, there was calculated $\frac{P_{H_3^+}}{P_{H_3^+} + P_{H_2^+} + P_{H^+}} = f(P_{H_2}^0)$. There was considered the following system of equations:

$$2H_2 \overset{K_3}{\rightleftarrows} H_3^+ + H + e; \quad K_3 = \frac{P_{H_3^+}P_H P_e}{P_{H_2}^2}; \; Q_3 = 348 \text{ kcal/mole}; \qquad (4)$$

$$H_2 \overset{K_4}{\rightleftarrows} H_2^+ + e; \quad K_4 = \frac{P_{H_2^+}P_e}{P_{H_2}}; \quad Q_4 = 355.7 \text{ kcal/mole}; \qquad (5)$$

$$H \overset{K_5}{\rightleftarrows} H^+ + e; \quad K_5 = \frac{P_{H^+}P_e}{P_H}; \quad Q_5 = 313 \text{ kcal/mole}; \qquad (6)$$

$$H_2 \overset{K_6}{\rightleftarrows} 2H; \quad K_6 = \frac{P_H^2}{P_{H_2}}; \quad Q_6 = 103.2 \text{ kcal/mole}; \qquad (7)$$

$$P^0_{H_2} = P_H + P_{H_2}; \qquad (8)$$

$$P_e = P_{H_3^+} + P_{H^+} + P_{H_2^+} \qquad (9)$$

(it is possible to disregard the role of OH^- since it is small, and at P = 1 atm and T = 2000°K it will decrease with pressure).

From (4)-(8) it follows that

$$\frac{P_{H_3^+}}{P_{H_3^+} + P_{H_2^+} + P_{H^+}} = \frac{K_3 P^0_{H_2}}{K_3 P^0_{H_2} + K_2 K_4}$$

and at T = 2000°K $\frac{P_{H_3^+}}{P_{H_3^+} + P_{H_2^+} + P_{H^+}} \approx 0.5$ if $P^0_{H_2} \approx 2.9 \cdot 10^{-5}$ atm.

Discussion

L. N. Gorokhov. What molecular constants are used by you in calculations for heavy ions?

I. I. Larin. It was necessary to know moments of inertia and frequencies of vibrations, which for H_3O^+ are taken to be the same as for the analogous molecule NH_3. Distance between nuclei H_3^+ is taken proceeding from the work of Hirschfelder.[1] For Ar_2^+ frequencies of vibrations were calculated proceeding from the assumption that its anharmonicity is the same as for HCl. Distance between nuclei is arbitrarily taken equal to 2A. Possible error as a result of this should not exceed a factor of 2.

V. L. Tal'roze. Now for calculation of concentrations there is not required in practice an accuracy better than a factor of 1.5-2, and therefore accuracy of selected constants was sufficient.

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[1] J. O. Hirschfelder. J. Chem. Phys., 6, 795 (1938).

ESTIMATION OF RELATIONSHIP BETWEEN KINETIC CONSTANTS OF ELEMENTARY PROCESSES ACCORDING TO THE ARCING VOLTAGE OF AN ELECTRIC DISCHARGE

Yu. V. Filippov, Yu. M. Yemel'yanov and V. G. Samoylovich

Among elementary processes occurring in the zone of an electric discharge, a large role is played by processes occurring during collisions of molecules of gas with electrons.

Direct determination of kinetic constants of such reactions is very complicated, especially in the case of reactions in the zone of a discharge at high pressures. One of the possible methods of estimation of kinetic constants or their ratio can be the method of total determination of inelastic losses according to arcing voltages of a discharge.

In a positive column of unlimited cross section, gradient of potential replenishes only the energy loss of electrons which is connected with elastic and inelastic collisions, since ambipolar diffusion in such a column is absent. Thus, the potential gradient can serve as a criterion of energy losses of electrons. One of forms of inelastic energy losses is electron excitation and the chemical reaction following it.

Consequently, for estimation of intensity of chemical processes, it is possible to use magnitude of reduced field E/p in positive column of discharge.

This method was applied for estimation of ratio of kinetic constants of two reactions: $O_3 + e$ and $O_2 + e$. Magnitude E/p was determined according to arcing voltage of discharge in a special discharger with dielectric electrodes at pressure of gas from 10 mm Hg to 1 atm and with discharge gaps in the range from 0.25 to 4 mm.

For checking of correctness of the method, at first there was investigated discharge in helium. For helium in region of small E/p in positive column, it is possible to consider only elastic collisions of electrons with molecules. (Radiation losses were not taken into account, since in applied form of discharge radiation has low intensity). In this case, it is possible to represent balance of energy in positive column in the form

$$\frac{E}{p}=\frac{T_e\sqrt{2\varkappa}}{\lambda_1},$$

where T_e is electron temperature; $\varkappa$ is fraction of energy of electron lost during collision; λ_1 is mean free path of electron at p = 1 mm Hg. T_e found thus corresponds to 2.9 ev, which is very close to the source material.

During discharge in oxygen-ozone mixtures, arcing voltage of discharge is linearly related to concentration of ozone (to 7% volume of ozone in mixture). Extrapolation of experimental data permits us to determine E/p for pure oxygen and for ozone in oxygen-ozone mixtures. Magnitude E/p in positive column during discharge in oxygen constitutes 21 v/cm·mm Hg, and for ozone 100 v/cm·mm Hg. If we disregard losses of energy during elastic collisions and consider that basic nonelastic processes are the following:

$$O_3+e\rightarrow O+O_2+e \qquad (1)$$

and

$$O_2+e\rightarrow O+O+e, \qquad (2)$$

then ratio of magnitudes of reduced fields in ozone and oxygen will be equal to ratio of products of number of corresponding elementary wants and energy loss of electrons in every event. This permits us to estimate ratio of kinetic constants of processes (1) and (2). Ratio turns out to be equal approximately to 5.

This magnitude will agree satisfactorily with ratio of kinetic constants of processes (1) and (2) obtained from data on kinetics of formation of ozone during discharge in an ozonizer.

Discussion

Question: In your consideration photons do not participate. How do inelastic losses "leave" the volume and why then is the Maxwellian distribution disturbed?

V. G. Samoylovich. The question pertains to ways of consumption of total energy, and all reasonings given in the report concern only an electron gas. Plasma of investigated discharge is nonisothermal, and energy of electrons during inelastic processes becomes energy of neutral gas; subsequently this energy of neutral gas can go to chemical reaction and to be released in the form of heat on the electrodes.

CONCERNING THE QUESTION OF STATIONARY STATES OF A GAS SYSTEM ESTABLISHED UNDER THE ACTION OF SOURCES OF FAST PARTICLES

Ye. V. Stupochenko and A. I. Osipov

We will consider a gas system under the influence of a source of fast particles. These particles have a certain initial kinetic energy E_0 considerably exceeding average thermal energies. During direct influence of particles, in the system there can occur processes with activation energy less than or near to E_0. However, this is not the only possibility. Action of particles causes disturbance in Maxwellian distribution of particles of gas, which propagates (for comparable masses) far into the region of energies greater than E_0. Energy distribution of bombarding particles also changes as a result of their elastic scattering in the gas. In such a way there is realized the mechanism by means of which source of particles with energy E_0 can lead to processes with activation energy considerably exceeding E_0. Below there are considered two simplified models of such a mechanism.

Let us assume that in a monatomic gas with small impurity of diatomic molecules there acts a source creating per unit volume per unit time N of the same monatomic particles with kinetic energy E_0, where $e^{-\frac{E_0}{kT}} \ll 1$. Considering molecules as harmonic oscillators with frequency $\omega > E_0/\hbar$, we will find the stationary distribution of molecules with respect to vibrational levels. Let mass m of atom be small as compared to mass M of molecule. Then kinetic energy distribution of molecules practically remains Maxwellian. Distribution function of light component coincides with distribution of single-component system disturbed by a source of particles, and in the region $x > x^0 = E_0/kT$ has the form

$$f_+(x)dx = \left[\rho + C\left(x - \frac{3}{2}\right)\right] f^{(0)}(x)dx, \qquad (1)$$

where x = $mv^2/2KT$; ρ is density of number of particles, $f^{(0)}(x)dx$ is Maxwellian rmalized distribution;

$$C = \frac{N}{\sqrt{\pi}}\sqrt{\frac{m}{2\pi kT}} \cdot \frac{1}{d^2\rho} \cdot \frac{u_2(z_0)}{z_0\Delta(z_0)},$$

where d is particle diameter;

$$z_0 = x^* + \frac{1}{2}; \quad \Delta(z) = u_1(z)u_2'(z) - u_1'(z)u_2(z);$$

$$u_1(z) = (z^2 - 2z)e^{-z}; \; u_2(z) = z^{-3}G(3, 2, z); \; G(\alpha, \beta, z) -$$

is a function for which the following asymptotic distribution holds

$$G(\alpha, \beta, z) = 1 + \frac{\alpha\beta}{1!z} + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!z^2} + \dots$$

In the region of thermal energies, distribution of the light component practically remains Maxwellian. Designating by symbol x_n the concentration of molecules on the n-th vibrational level and by the symbol P_{mn} – the probability of transition m → n referred to one collision, for stationary distribution we have (single-quantum transitions) [3], [4]:

$$\frac{x_n}{x_{n+1}} = \frac{P_{n+1,n}}{P_{n,n+1}}. \qquad (2)$$

Deactivation occurs mainly during collisions in the region of average thermal velocities; therefore, $P_{n+1,n} = (P_{n+1,n})_{\text{равн}}$. Calculating $P_{n,n+1}$ with the help of (1), we will obtain in the adiabatic approximation

$$P_{n,n+1} = (1 + \alpha)(P_{n,n+1})_{\text{равн}}, \quad \alpha = \frac{C(x^* - {}^3/_2)}{\rho}, \qquad (3)$$

where x^* is that value of x, the neighborhood of which is essential for excitation of vibrational levels [3]. Substituting these results in (2), on the basis of the equality

$$(P_{n,n+1})_{\text{равн}} e^{-\frac{\varepsilon_{n+1}}{kT}} = (P_{n,n+1})_{\text{равн}} e^{-\frac{\varepsilon_n}{kT}}$$

we obtain for the stationary distribution the Boltzmann distribution with temperature θ, determined by the equality

$$\frac{1}{\theta} = \frac{1}{T}\left[1 - \frac{kT}{\hbar\omega}\ln(1 + \alpha)\right]. \qquad (4)$$

In equation (1), N is taken to be small as compared to the total number of collisions per unit volume per unit time. However, the method does not assume smallness of perturbation in region of high energies, and equation (1) also describes finite perturbations in the tail of the distribution. Therefore, equation (4) is also valid when difference between θ and T is considerable.

The second example is displacement of chemical equilibrium in a system analogous to the one considered. We will take the following simplified scheme of vibrational levels of molecules of impurity dissociating according to equation $2A - A_2 = 0$. The first m + 1 levels (0, 1, 2, ..., m) we consider to be equidistant levels of harmonic oscillator with frequency $\omega(\hbar\omega > E_0)$ and corresponding transition probabilities. The upper l levels (not necessarily equidistant) are characterized by such small values of $\hbar\omega_{s,s+1}$ $(m \leq s \leq m + l - 1)$ that transition between them (forward and reverse), just as transition from upper levels to the continuous spectrum (dissociation), are connected basically with collisions in the region of thermal velocities. Equilibrium values of concentrations C_1 of atoms A and C_2 of molecules A_2 are related by the law of mass action:

$$\frac{C_1^2}{C_2} = \varkappa(T); \varkappa(T) = C(T)\frac{e^{-\frac{E_d}{kT}}}{r(T)q(T)}, \tag{5}$$

where C(T) is determined by statistical sums of translational motion; r(T) is rotational and q(T) is vibrational statistical sum; E_d is dissociation energy.

During perturbation by sources of particles according to equation (4), for populations x_s of vibrational levels we have:

$$x_s = ae^{-\frac{E_s}{k\theta}} (0 < s < m); \tag{6}$$

$$x_s = be^{-\frac{E_s}{kT}} (s > m) \tag{6'}$$

and

$$ae^{-\frac{E_m}{k\theta}} = be^{-\frac{E_m}{kT}}. \tag{7}$$

Let us assume that C_1^* and C_2^* are stationary concentrations. Concentration C_1^* is in equilibrium with upper levels (6'). Therefore, on the basis of the approximate equality

$$\sum_{m}^{m+l-1} be^{-\frac{E_s}{kT}} \approx b \quad \text{we have} \quad \frac{C_1^{*2}}{b} = \varkappa(T). \tag{8}$$

Assuming that $C_2^* \approx \sum_0^m ae^{-\frac{E_s}{k\theta}}$, from (7) and (8) we obtain

$$\frac{C_1^{*2}}{C_2^*} = \varkappa^*(T, \theta). \tag{9}$$

If we assume that $E_m \approx E_d$ and $q(T) = 1$, then

$$\varkappa^*(T, \theta) = C(T) \frac{e^{-\frac{E_d}{k\theta}}}{r(T)q(\theta)} \qquad (10)$$

(compare with formula (5)). On the basis of (4), and considering that $q(\theta) \approx 1$,

$$\varkappa^* = (1+\alpha)^m \varkappa(T). \qquad (11)$$

Taking for m a value of the order of 10, we see that $\varkappa^*$ is very sensitive to perturbation in the tail of the Maxwellian distribution (influence of magnitude α).

Literature

1. Ye. V. Stupochenko. Reports of the AS USSR, 67, 635 (1949).
2. Ye. V. Stupochenko. Moscow State University Herald, No. 8, 57 (1953).
3. A. I. Osipov and Ye. V. Stupochenko. UFN, 79, 81 (1963).
4. G. Messi and Ye. Barkhop. Electron and ion collisions. Moscow, IL, 1958.

CONCERNING DIRECT MOLECULAR DISINTEGRATION OF HYDROCARBONS

R. A. Kalinenko and A. M. Brodskiy

In high-energy chemistry (radiation chemistry, photolysis, decomposition at high temperatures), an essential role has begun to be played by processes of direct molecular disintegration. By direct molecular disintegration we mean processes in which in a single event there occurs breaking of more than one bond in the molecule. Breaking of several bonds in molecule without its preliminary intramolecular reconstruction (for instance detachment simultaneously of two H atoms with formation of hydrogen or a CH_3 radical and H with formation of methane) is extremely difficult energetically. Such processes have activation energy of about 160-180 kcal/mole and are unrealizable in thermal processes at temperatures of 1000-2000°. Meanwhile, in experiments on cracking of ethane with additions of tagged methane $C^{14}H_4$ at 800-890°C and pressure of 90 mm Hg in a reactor with complete mixing, we found [1] that formation of ethylene occurs basically by a molecular mechanism with activation energy of 82 ± 2 kcal/mole, which corresponds to energy of 3.5 ev.

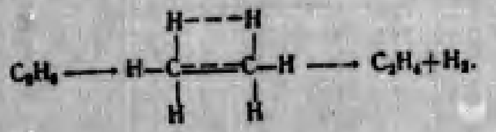
As the reaction of chain formation of C_2H_4 there was considered the reaction of disintegration of ethyl radical; the constant of chain formation of C_2H_4 was defined as

$$k_1 = \frac{k_4[C_2H_5]}{[C_2H_6]} = \frac{k_4 k_2 [R] t}{1 + k_{2(C_2H_5,M)}[M] t + k_3 [R] t + k_4 t}, \qquad (1)$$

and the fraction of chain formation of C_2H_4 was defined as the ratio of k_1/k, where k is total rate constant of the process of formation of C_2H_4 from C_2H_6. In formula (1): k_2 – rate constant of reactions of substitution of any radicals with C_2H_6; $k_{2(C_2H_5,M)}$ – rate constant of reactions of substitution of C_2H_5 radicals with any molecules; k_3 — rate constant of reactions of recombination of radicals; k_4 — rate constant of disintegration of C_2H_5 into C_2H_4 and H; [R] and [M] are respectively concentrations of radicals and molecules in the system; t is stay time in the reaction zone.

Calculation according to formula (1) has shown that $k_1/k = 0.1$; i.e., at 800-900°C by means of the chain mechanism there will be formed not more than 10% ethylene. The value of k_1 is obtained to be small, mainly due to the small value of k_2 because of the presence in substitution reactions of a steric factor of the order of 10^{-4}. The fact that substitution reactions have a steric factor of the order of 10^{-4} was repeatedly noted in the literature, and at present apparently causes no doubts. Thus, in the chain scheme of formation of olefins from paraffin hydrocarbons, the rate of basic reaction of continuation of the chain turns out to be very small, which creates the possibility for the molecular process of decomposition to compete with the chain process.

Question about nature of the actual elementary event of molecular disintegration is not fully clear. It is only clear that it does not occur by means of successive breaking of several bonds. It is probable that direct molecular disintegration is preceded by an elementary act of intramolecular reconstruction, as a result of which there are formed structures whose disintegration is facilitated, for instance;



$$C_2H_6 \longrightarrow H-\underset{H}{\overset{H}{C}}=\!=\!=\underset{H}{\overset{H}{C}}-H \longrightarrow C_2H_4+H_2.$$

Formation of such structures is an energetically difficult process and is the limiting stage of the entire reaction. Their further disintegration however, apparently occurs with relatively high rate. Confirmation of the fact that direct molecular disintegration of hydrocarbons can pass without simultaneous breaking of two bonds can be found in works on photolysis of hydrocarbons during action of light with wavelengths in the region of hard ultraviolet. In these works it was shown that during irradiation of hydrocarbons by light with wavelength of 2537 A (~5 ev), there occurs only detachment of prepared molecules, for instance H_2 [2]. During transition to irradiation by light with wavelengths of 1470 A (8.43 ev) and 1239 A (10.02 ev) [3], there increases the role of simultaneous detachment of 2H from one molecule. Consequently, when energy of irradiation becomes sufficient for breaking of two bonds, then these processes really begin to be detected.

At lower energies (photosensitized irradiation by light of 2537 A (~5 ev)), there are observed molecular processes of detachment of H_2 and CH_4; processes of simultaneous breaking of two bonds still do not occur. Thus, there is determined a lower threshold of energies, starting at which there appear reactions flowing with simultaneous breaking of two bonds: this is approximately 7-8 ev or 160-190 kcal/mole. In the region of energy 3.5-5 ev, however, (lower threshold is determined from our experiments on decomposition of C_2H_6), processes of molecular disintegration of hydrocarbons occur by another mechanism, omitting the stage of simultaneous breaking of two bonds.

Let us note that there are essential differences between mechanisms of occurrence of molecular processes above and below 7 ev. Thus, during photosensitized photolysis of ethylene in the excited state, there is realized internal exchange of hydrogen atoms (relationship H_2:HD:D_2 is approximately identical during photolysis of CH_2CD_2 and cis-CHD—CHD). During photolysis by light with wavelengths in the region of vacuum ultraviolet, such exchange in the excited state is absent (relationship H_2:HD:D_2 is equal to 2:8:1 during photolysis of trans-CHDCHD and 2:2:1 during photolysis of CH_2CD_2). During photosensitized decomposition of hydrocarbons, there occurs the isotope effect. During photolysis by light with wavelengths in the region of vacuum ultraviolet of mixtures $C_2H_4 + C_2D_4$, $C_2H_6 + C_2D_6$, $C_3H_8 + C_3D_8$, the isotope effect is absent, and during decomposition under these conditions of CHDCHD, CH_2CD_2, CH_3CD_3, the isotope effect occurs.

Literature

1. A. M. Brodskiy, R. A. Kalinenko, K. P. Lavrovskiy and V. B. Titov. Journal of Physical Chemistry, 33, 2457 (1959).

2. R. J. Cvetanovic and A. B. Callear. J. Chem. Phys., 23, 1182 (1955).

3. H. Okabe and I. R. McNesby. J. Chem. Phys., 36, 601 (1962).

Discussion

A. Ye. Shilov. You give for activation energy of molecular disintegration of ethane the magnitude of 82 Kcal/mole, which is approximately equal to binding energy of C — C in ethane. How do you explain the fact that radical disintegration $C_2H_6 \rightarrow 2CH_3$, activation energy of which is equal to binding energy of C — C, occurs much more slowly?

R. A. Kalinenko. During comparison of rates of molecular disintegration of ethane and disintegration of it into two CH_3 radicals, one should consider not only activation energy of these reactions, but also pre-exponential factors of rate constants.

Question: What is activation energy of development of a chain?

R. A. Kalinenko. 12 kcal/mole.

V. V. Voyevodskiy. Concerning the question of the first event: If 10% of substance is formed by the chain scheme, then this should signify that rate of primary process of disintegration into radicals is more than 10 times less than rate of molecular disintegration, since there are several monomer units. How is it possible then to say that disintegration into 2 methyl radicals is considerably slower than molecular disintegration? After all, this disintegration occurs with normal rates.

R. A. Kalinenko. According to our data, rate constant of molecular disintegration of C_2H_6 has a pre-exponential which is two orders greater than the rate constant of disintegration into two CH_3 radicals.

A. Ye. Shilov. Considering the change of entropy of the reaction, we had to make the opposite conclusion: formation of a four-membered ring is less probable than simply stretching of the bond.

R. A. Kalinenko. The event of molecular disintegration is unknown.

V. V. Voyevodskiy. It is surprising how at 900°C there could be obtained a strongly excited molecule.

R. A. Kalinenko. This is experimental fact.

V. V. Voyevodskiy. Sensitized photolysis (reactions during the interaction $Hg^* + RH$) cannot be considered from the point of view of the same mechanism as photolysis of an isolated molecule under the action of a shortwave quantum.

R. A. Kalinenko. During sensitized photolysis there occurs complete exchange of hydrogen atoms.

V. V. Voyevodskiy. Once again I recall that this process occurs in the presence of an Hg^* atom; this constitutes sensitization. There appears the complex $(RH \cdot Hg^*)$.

V. N. Kondrat'yev. At what pressures were experiments carried out? Could there not be influence of wall?

T. A. Kalinenko. Pressure was 90 mm Hg. Experiments were carried out on corundum and quartz, and results in both cases coincide.

A. M. [illegible]. There is a whole series of experimental data from which it follows that with increase of temperature there are increased activation energy and pre-exponential factor. Experiments show that there exists a molecular process with pre-exponential factor which is two orders larger than the time of the usual electron transition. It is possible to express two hypotheses: 1) there occurs a preliminary event of intramolecular reconstruction, where there will be formed a state of rotational excitation with subsequent disintegration, and 2) there occurs increase of activation energy in a narrow range of temperatures; activation energy of 82 kcal/mole is a quantity which does not accidentally coincide with energy of breaking of C — C bond. Maybe there occurs something like a cellular effect.

GENERAL DISCUSSION

N. D. Sokolov. I wanted to discuss briefly the question of reactivity of molecules in the triplet state. This question, in general, is very important, inasmuch as chemistry of molecules in the triplet state constitutes an independent region. I will dwell only on qualitative characteristics of activation energy of reaction in which molecules in the triplet state participate. How does such a molecule differ from a radical? The simplest example is an O_2 molecule, for which triplet state is ground state. We will consider at first the interaction of O_2 molecule with an H atom, which leads to formation of O_2H radical. In the given case, obviously, there is no activation energy.

From consideration of the three-electron problem, one may see that energy of system $H + O_2$ within the framework of the London method is equal to

$$\varepsilon = Q - \sqrt{\alpha^2 + \beta^2 - \alpha\beta}. \qquad (1)$$

where Q is Coulomb interval, α is "intermolecular" exchange integral of 1s-orbit of H atom and $2p_z\pi$-orbit of molecule $O_2 (\alpha < 0)$, β is intramolecular exchange integral between $2p_z\pi$- and $2p_x\pi$-orbits of molecule $O_2 (\beta > 0,\ \beta \sim 1.5$ ev).

It is assumed that H atom is located in plane of orbit $2p_z\pi$ on a straight line perpendicular to axis of molecule (direction Oy) and passing through one of atoms O. With such a location, exchange integral between orbit of atom H and $2p_x\pi$-orbit of atom O is equal to zero. For large distances between H and O_2, when $|\alpha| \ll \beta$, equation (1) gives

$$\varepsilon = Q - \beta + \frac{1}{2}\alpha. \qquad (2)$$

If we disregard quantity Q, then under the indicated conditions energy of attraction between H and O_2, which is equal to $\Delta\varepsilon = 1/2\alpha$, is 2 times less than energy of attraction of atom H to radical having only one uncoupled electron; this energy is equal simply to α. Such a conclusion is qualitatively confirmed by experimental data. It is known that binding energy of atom H with molecule of oxygen is about 50 kcal/mole, and with radical HO_2 – about 90 kcal/mole. Similar results should also be expected for case when molecule in triplet state interacts not with an atom, but with a saturated molecule. Activity of molecules in triplet state will be less than that of radicals, due to the fact that for the former, height of potential barrier is, roughly speaking, 2 times higher than for the latter. The cause of this is the following: 1) second electron of molecule, which has spin of the same direction as the first, "interferes" with the first, and 2) uncoupled electrons in molecule are "smeared out" on several atoms; the latter pertains also to radicals with conjugate bonds; the greater this "smearing," the less active is the radical, as well as the molecule in the triplet state.

For elementary reactions of saturated molecules with molecules in triplet state, nonadiabatic transitions are apparently very significant. In excited states of molecules there are usually many closely crowded located electronic levels, which intersect each other. Consideration of transitions between them is necessary for the entire chemistry of excited states.

V. N. Kondrat'yev. During the study of quenching of fluorescence of sodium vapor by different gases, it was possible for us to obtain smooth dependence between quenching cross sections and heats of the possible reactions of excited sodium with the quenching molecules. Possibly it is more correct to take activation energy or some quantity as a measure of chemical interaction. It is necessary that theoreticians understand this question.

L. M. Biberman. The problem of rate of radiative recombination for hydrogen is solved exactly. For more complicated atoms there are obtained good approximations. Rate constant depends on temperature as $\sqrt{T}$. If data on recombination obtained under conditions of upper layers of atmosphere differ from these values, this means that there is something unsatisfactory in other questions, and not in this one.

With respect to recombination of charged particles during triple collision, there is one essential difficulty. This is the question of cross sections of capture processes at some excited level. For hydrogen cross sections of ionization from the level with principle quantum number n increases in the case of the Born approximation as n^3, and in the case of the classical approximation as n^4. Inasmuch as cross section very sharply increases with principal quantum number, and level n = 10 is sometimes realizable, especially in upper layers of atmosphere where density is very low, then the difference can attain one order of magnitude, and it is necessary to take this note into account.

II. ELEMENTARY PROCESSES IN THE CONDENSED PHASE

1. TRANSMISSION OF ENERGY OF ELECTRON EXCITATION

COMPARATIVE ROLE OF POSSIBLE MECHANISMS OF ENERGY TRANSFER DURING RADIOLYSIS OF LIQUID DILUTE SOLUTIONS

I. G. Kaplan

I. One of the causes of deviation from additive law during radiolysis of mixtures[1] can be transfer of energy between separate components. Let us consider briefly possible mechanisms of transfer and criteria of their applicability.

1. Transfer of energy occurs during approach of donor molecule D to acceptor molecule A to distances of the order of kinetic radii. Rate of process is determined by diffusion rate. For molecules with identical diameter $k_{\text{диф}} = \frac{8RT}{3000\ \eta}$ liter/mole·sec, where η is viscosity of medium [1]. Number of encounters of excited molecule D^* with molecules A in 1 sec $z = k_{\text{диф}} C_A$, average interval of time between encounters $\Delta t = 1/z$. Necessary condition for efficiency of transfer process is $\Delta t < \tau$, where τ is lifetime of D^*. For benzene at 25°C, $k_{\text{диф}} = 10^{10}$ liter/mole·sec. Therefore, at $C_A = 10^{-3}$ mole/liter we should have $\tau > 10^{-7}$ sec. As a result of this, at small concentrations of acceptor, diffusion plays a role basically for transfer of energy through triplet levels due to their large life time. In the presence of considerable difference in height of triplet levels, rate constant of such transfer can approach the diffusion rate constant [2-3].

2. Resonance transfer of electron excitation energy from low singlet excited level D to singlet excited level A. Probability of transfer $W = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6$, where R_0 is

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[1] Primary chemical change of component becomes not proportional to fraction of energy absorbed by it.

effective distance at which probability of transfer is equal to probability of spontaneous deactivation [4]. Formula for W is derived under the condition of immobility of molecules and validity of the Boltzmann distribution. For solutions with low viscosity, when diffusion displacement $\sqrt{\overline{r^2}} = \sqrt{6D\tau}$ (D is diffusion coefficient) becomes of the same order as R_0, there is necessary joint consideration of diffusion and resonance transfer. Such a problem was correctly formulated in work [5] and solved in limiting cases of viscous ($D\tau << 8R_0^2$) and low viscosity ($\sqrt{D\tau} > 30R_0$) solutions.[1]

3. Diffusion of excitation between molecules D, until D^* is sufficiently close to A for transfer to be possible (diffusion of "localized exciton"). According to Förster [6], diffusion coefficient $D_e \approx R_0^6/\tau L^4$, where L is distance between molecules D. At $R_0 = 25\text{Å}$ (for dyes $R_0 \approx 40\text{Å}$) $C_A \approx 10^{-1}$ mole/liter, $\tau_D \approx 10^{-9}$ sec, we obtain $D_e \approx 6 \cdot 10^{-5}$ cm^2/sec, which somewhat exceeds diffusion rate of molecules in low viscosity solutions. For instance, for pure benzene, as a result of calculation [7], we have $D_e \approx 2 \cdot 10^{-7}$ cm^2/sec. However, this is only a rough estimate, since for closely crowded molecules Försters formula ceases to be valid.

4. Resonance transfer of energy through upper singlet levels. Usually it has not been considered due to smallness of lifetime of molecule in upper state (according to Kasha [8], $\tau \approx 10^{-13}$ sec). There is reason to consider that this is the lower limit, and we will consider $\tau \approx 10^{-12}$ sec. In such a short time thermal equilibrium does not have time to be established. During exact resonance between defined vibrational levels, excitation oscillates between D and A, where probability of transfer $\sim 1/R^3$. As follows from Försters calculations [9], for intense transitions $W = 10^{12}$ sec^{-1}. For $C_A > 10^{-1}$ mole/liter this corresponds to energy of interaction ~100 cm^{-1}. However, due to diffusivity of bands for upper levels, it is possible to consider such transitions as transitions in a constant spectrum, when exact resonance is absent. This leads to faster growth of W with decrease of $R (\sim 1/R^6)$. And since oscillator strengths of transitions into upper states for the majority of complex molecules ~1, then it is possible to expect that transfer of energy through

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[1] See also reports of N. N. Tunitskiy, Kh. S. Bagdasar'yan, V. A. Krongauz, I. N. Vasil'yev, and B. P. Kirsanov in the present collection.

upper levels in favorable cases will compete with internal conversion even at $C_A > 10^{-2}$ mole/liter.

5. Transfer of charge $D^+ + A \rightarrow D + A^+$. Necessary condition is $I_D > I_A$, cross section is maximum at $I_D \approx I_A$ (I is ionization potential). Transfer is efficient if τ_{D^+} is larger than interval of time between encounters. For $C_A \approx 10^{-1}$ mole/liter, there should be satisfied $\tau_{D^+} > 10^{-9}$ sec. Reliable information about lifetime of ions in liquids are absent.

6. Selectivity in absorption of energy by components of the solution can also lead to disturbance of additivity. A characteristic example is dissociative capture of thermal electrons by molecules of an additive. This process is more efficient, the greater the affinity to an electron and the less the appearance (occurence) potential of a negative ion. Such conditions are satisfied by halides, for instance CH_3Br, CCl_4, and so forth.

II. Experiments indicating deviation from additivity during radiolysis of solutions can be divided into two large groups.

1. Sensitized radiolysis. In a number of works of Krongauz and Bagdasar'yan [10] there was revealed sensitized disintegration in benzene of a number of peroxides, disulfides and also compounds under the action of γ-radiation. Radiation yield G of process of disintegration at $C_A = 10^{-2}$ mole/liter attained values of 3; at $C_A > 10^{-2}$ mole/liter there was observed deceleration of growth of G with increase of C_A. Such high values of G cannot be explained by resonance transfer through lower singlet levels, since $G(^2B_{2u}) < 0.5$ for benzene (see p. 323). Against dissociative capture of electrons witnesses the fact that in cyclohexane, sensitization of disintegration of benzoyl peroxide did not occur. We consider that the kinetic behavior obtained by the authors can be satisfactorily explained if we assume that at $C_A < 10^{-2}$ mole/liter, the basic contribution is given by triplet-triplet transfer of energy, and at $C_A > 10^{-2}$ mole/liter transfer through upper levels starts to give a contribution. Unfortunately, it still is not possible to estimate stationary concentration of molecules in triplet state during γ-irradiation.

In other works, for instance [11], where there was observed sensitization of disintegration of halides in benzene, the contributions of different mechanisms of transfer change. Triplet level of molecules of the majority of additives lies higher than for benzene. Therefore, here the main contribution is given by dissociative capture of electrons; this is all the more favorable for this class of substances. There is not excluded transfer through upper excited levels at $C_A > 10^{-1}$ mole/liter. Direct experimental proof of insignificance of participation of first level of benzene in process of transfer is given in work [12].

2. Radiation shielding. The requirement that transfer of energy have time to occur during the lifetime of the state from which disintegration of the molecule occurs (10^{-10}-10^{-13} sec) is decisive. Disintegration of aromatic molecules occurs during their excitation to upper levels; therefore, attempts to inhibit radiolysis of benzene by addition of 10^{-3}-10^{-2} mole/liter of anthracene and terphenyl did not give results [13]. The most thoroughly studied is radiation shielding of cyclohexane by addition of benzene. Decrease of $G(H_2)$ begins at $C_A = 10^{-3}$ mole/liter. However, here there still exists confusion in the question of capture of H radicals with formation of C_6H_7 (compare [14] and [15]).

The mechanism of charge transfer advanced by Burton requires a lifetime of $C_6H_{12}^+$ of the order of 10^{-7}-10^{-8} sec. It is possible that the controlling process is transfer through triplet levels. However, information about lifetime and position of triplet level of cyclohexance is absent in the literature. Thus, the mechanism of protection of saturated hydrocarbons by aromatic additives remains vague in many respects.

Literature

1. J. Q. Umberger and V. K. LaMer. J. Am. Chem. Soc., 67, 1099 (1945).
2. K. Sandros and H. Bäckström. Acta Chem. Scand., 16, 958 (1962).
3. G. Porter and F. Wilkinson. Proc. Roy. Soc., A264, 1 (1961).
4. T. Förster. Disc. Faraday Soc., 27, 7 (1959).
5. Yu. A. Kurskiy and A. S. Selivanenko. Journal of General Chemistry, 8, 643 (1960).
6. T. Förster. Ann. Phys., 2, 55 (1948).
7. S. Lipsky and M. Burton. J. Chem. Phys., 31, 1221 (1959).
8. M. Kasha. Disc. Faraday Soc., 9, 14 (1950).
9. T. Förster. In: Comparative Effects of Radiation. Ed. M. Burton etc. New York, London, Wiley, 1960, p. 300.
10. V. A. Krongauz and Kh. S. Bagdasar'yan. Reports of Academy of Sciences of USSR, 116, 837 (1957); 127, 1047 (1959); 132, 1136 (1960).
11. W. Van Dusen, Jr. and W. H. Hamill. J. Am. Chem. Soc., 84, 3648 (1962).
12. G. Kallmann Oster and H. P. Kallmann. Nature, 194, 1033 (1962).

13. M. Burton and W. Patric. J. Chem. Phys., 22, 1150 (1954).
14. G. R. Freeman. J. Chem. Phys., 33, 71 (1962).
15. M. Stone and P. J. Dyne. Radiation Res., 17, 353 (1962).

Discussion

V. V. Voyevodskiy. In your report there were discussed several different mechanisms of energy transfer. What are criteria of selection of the mechanism in each specific case?

I. G. Kaplan. In every given case it is necessary to consider a specific system. And therefore, as I have already said, in the case when there is an addition with great election affinity, capture of thermal electrons is very probable. In cases, when there is not, it is necessary to consider, in the first place, the position of triplet levels. If triplet level of donor molecule is higher than triplet level of acceptor molecule, then probability of transmission through triplet levels with subsequent disintegration of acceptor molecule is very great.

N. N. Tunitskiy. How is the situation with dissipation of energy? Will energy of electron excitation be "pumped" over into vibrational excitation in the process which you considered?

I. G. Kaplan. During estimation of efficiency of transfer we require only that time of energy transfer be less then quenching time. It is important how processes of quenching occur – they may be completely different mechanisms. If there occurs nonradiative conversion to the ground state, then energy doubtlessly is converted to vibrational energy.

V. L. Yermolayev. Did you calculate the coefficient of exciton diffusion in benzene using Förster's theory?

I. G. Kaplan. In this case I gave data of Lirsky and Burton.

V. L. Yermolayev. First of all, at such distances Forster's theory is not applicable, and secondly, at such distances it is necessary to consider resonance exchange transfer according to Dexter.

I. G. Kaplan. This remark is correct.

EXCITONS IN THE LIQUID PHASE AND STRUCTURE OF LIQUIDS

Kh. V. Protopopov

In condensed molecular systems, including liquids, it is possible to distinguish strong, average and weak bonds between excited and unexcited molecules [1, 2]. In the case of strong bond in domains [3, 4] of molecular liquids with high short-range order, there can appear free excitons with lifetimes of $\tau_c^* < \tau_2/n$. Here $\tau_2 \approx 10^{-11}$ sec is the time of orientational relaxation; n is number of molecules in the domain.

During interaction of domain with defects, free exciton is localized. Local exciton corresponding to average bond embraces several neighboring molecules of liquid and combines them in an excited aggregate – an eximer. As a result of resonance interaction of the eximer with surrounding unexcited molecules in its vicinity, there is increased orientational short-range order. Motion of local exciton represents a consecutive transition of state of eximer to the nearest neighboring molecules. Together with local exciton, in liquid there is propagated also the state of local ordering – orienton [5], which protects the exciton from extinguishing thermal collisions.

Directivity of resonance forces and the plane or prolate form of molecules of liquid promote reconstruction of the eximer along a definite axis. Furthermore, for a not too weak bond, excitons themselves have the tendency to move in a directed manner [6]. Therefore, there is not excluded a certain directivity of displacement of local exciton in liquid at distances of the order of several molecular diameters.

Both free and local excitons apparently exist in aromatic liquids and solutions. Independence of "α/β-ratio" on state of aggregation of organic scintillators and the independence of fast components of de-excitation times in them on dE/dx (linear energy transfer of radiation) indicate the great similarity of processes of excitation and fast quenching in liquid and solid organic scintillators [7] and also the relation between these processes and fast excitons. Sharp drop of light yield with increase of dE/dx in all organic scintillators, accompanied by increase of contribution of the slow component of luminescence can be explained by exciton-exciton interactions in the region of the track, which lead, according to [8], to formation of ions.

Existence of sufficiently high short-range orders in aromatic liquids and solutions which are necessary for formation of free excitons has been indirectly confirmed by experiments with X-rays [9], by data on the large deviation of binary liquid systems of the type benzene-cyclohexane from idealness [10], and also by investigations of shift of nuclear magnetic resonance [NMR] (ЯМР) signals in such systems [11]. According to Burton and his colleagues [3, 4], large magnitudes of rate constants of quenching and energy transfer in liquid scintillators, and also the minima of luminescence in multicomponent scintillating systems containing a diluent and quenching agent are explained by the large contribution of excitons embracing domains of 10-15 molecules of solvent to energy transfer.

These peculiarities of processes in liquid scintillators cannot be explained by resonance energy transfer from solvent to activator or quenching agent. Resonance transfer here can probably not occur at distances exceeding molecular diameters. Since for molecules of aromatic solvents transitions of higher orders are characteristic, then values of R_0 [1] cannot be calculated by Förster's formula, which is useful only for dipole-dipole interaction [1]. The remaining possibility of energy transfer by means of diffusion of molecules does not explain either the high values of quenching constant and energy transfer constant or the proximity of these magnitudes for such substances as oxygen and n-terphenyl [3].

The domain hypothesis agrees well with direct data on high rates of energy transfer in solutions of anthracene in benzene [12] and in other liquid scintillators for average distances between excited molecule of solvent and molecule of activator not exceeding 15 Å. With increase of this distance to 50 Å duration of energy transfer is increased by many times, which indicates essential change of mechanism of energy transfer in the interval of 15-50 Å.

Recently it was shown that many aromatic molecules in solutions, and even in vapors, form excited dimers which represent simple eximers [13]. Binding energy of molecules in such eximers not infrequently exceeds kT [14]. Existence of eximers in liquid benzene and toluene is confirmed by recent work of Sveshnikov and others [15], in which there are revealed minima of quantum yield of luminescence and of de-excitation time of solutions of these substances in hexane at concentrations higher than 1 mole/liter, and also intense fluorescence in region of 320 mμ at concentrations exceeding 0.5 mole/liter.

The greatest resonance interaction between molecules of aromatic solvents is expected in that case when the edge of one ring is above the center of another (as in neighboring planes in graphite) [16]. Therefore, it is expected that the process of rearrangement of the eximer during transfer of the exciton should have noticeable directivity. Diffusion displacement of the orienton as a whole aggregate of molecules is obviously still less important for transfer of energy than diffusion of excited molecules. Directivity of motion of orientons at distances of 4-5 molecular diameters is possibly explained by existence of gently sloping (approximately linear) segments of dependences of scintillation light yields on average distance between molecules of activator in liquid scintillators in the range of concentrations 1-0.1 gm/liter [5, 7]. It is essential that molecules of activator, before obtaining excitation energy from solvent, be drawn into the orientons and, then be "built into" eximers due to resonance forces.

Transfer of local state of ordering, which is similar to motion of orienton, should take place in associated liquids during exchange of protons or during transfer of electrons in biologically active materials.

It is interesting that an orienton represents an elementary self-organized system, which exists in motion, resists dissipation of energy of electron excitation, and promotes conservation and transfer of this "high-quality" energy to the place of its use in the chemical or optical process.

Literature

1. T. Förster. Comparative Effects of Radiation. Ed. M. Burton etc. New York — London, Wiley, 1960, p. 300.

2. R. M. Hochstrasser. Revs. Modern Phys., 34, 531 (1962).

3. S. Lipsky and M. Burton. J. Chem. Phys., 31, 1221 (1959).

4. J. M. Nosworthy, J. L. Magee and M. Burton. J. Chem. Phys., 34, 83 (1961).

5. Kh. V. Protopopov. Author's abstract, Leningrad, 1951.

6. J. L. Magee. Comparative Effects of Radiation. Ed. M. Burton etc., New York — London, Wiley, 1960, p. 130; J. L. Magee and K. Funabashi. J. Chem. Phys., 34, 1715 (1961); J. C. Lorquest, S. G. Elkomoss and J. L. Magee. J. Chem. Phys., 37, 1991 (1962).

7. V. O. Vyazemskiy, A. N. Pisarevskiy, Kh. V. Protopopov and others. Scintillation method in radiometry. Moscow, Atomizdat, 1961.

8. Sang-il Choj and S. A. Rise. Phys. Rev. Letters, 8, 410 (1962); M. Silver, D. Olness, M. Swicord and R. C. Jarnagin. Phys. Rev. Letters, 10, 12 (1963).

9. P. H. Bell and W. P. Davey. J. Chem. Phys., 9, 441 (1941).

10. G. A. Bottomby and I. H. Coopers. Nature, 193, 268 (1962); S. E. Wood. J. Chem. Phys., 15, 385 (1947); A. Münster. Trans. Faraday Soc., 46, 165 (1950).

11. J. Polp, V. Schneider and G. Bernstein. Nuclear magnetic resonance spectra of high resolution. Moscow, IL, 1962, p. 592.

12. H. Z. Knau. Z. Naturforsch., 12a, 881 (1957).

13. B. Stevens. Nature, 192, 725 (1961).

14. G. J. Hoijtink. Z. Elektrochem., 64, 156 (1960).

15. T. V. Ivanova, G. A. Mokeyeva and B. Ya. Sveshnikov. Optics and spectroscopy, 12, 586 (1962).

16. R. S. Malliken. J. Am. Chem. Soc., 74, 811 (1952).

Discussion

A. Ya. Temkin. In examining excitons in crystals, we usually consider a crystal of sufficiently large dimensions. Was there considered in your case the proximity effect of boundaries of local regions to one another? Were there considered conditions on boundary of local region? In particular, how large is the ratio of volume of local region to its surface?

Kh. V. Protopopov. Even in crystals, at first there occurs a non-stationary process — the exciton is formed in a small region and then spreads apart. In the case of a liquid we can speak only about such a process. Full formation of exciton apparently does not have time to occur. Boundary conditions are exactly those conditions which lead to localization of the exciton. The question of localization of excitons on defects is considered in detail in the survey of Hochstrasser.[1]

A. T. Koritskiy. Is it possible to apply the model considered by your to vitrified media?

Kh. V. Protopopov. In vitrified media it is difficult to talk about any ordering during excitation, since for this, apparently, there is not sufficient energy.

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[1] R. M. Hochstrasser. Revs. Modern Phys., 34, 531 (1962).

Yu. L. Khait. It is known that in examining excitons in crystals, the structure of crystal is assumed to be fixed. How is it possible, in connection with this, to consider excitons and orientons in liquids?

Kh. V. Protopopov. An exciton will be formed during a time at least an order of magnitude less than the relaxation time of volume and shear viscosity. Therefore, everything occurs as in a solid, but not very ordered medium. However, in the work there are considered liquids with sufficiently high short-range order. Regarding the orienton, that as soon as there exist some additional forces, the system will tend to a minimum of potential energy by means of ordering, and it will be realized if interaction energy exceeds kT.

Yu. L. Khait. How did you obtain the estimate of 10^{-12} sec for the lifetime of the exciton?

Kh. V. Protopopov. We have data only about the fact that for $\bar{R} < 15$ Å, de-excitation times during excitation of solvent (medium) or only of the activator coincide within the limits of $2 \cdot 10^{-10}$ sec. Regarding $\tau_c^* \leq 10^{-12}$ sec, condition shows only how much the lifetime of the exciton depends on mobility of short-range order in the liquid.

L. S. Polak. What energy can be transferred during migration of a free exciton?

Kh. V. Protopopov. Several electron-volts.

A. Ya. Rozovskiy. Self-adjusting systems have to be characterized by the presence of feedback. How is feedback carried out in your case?

Kh. V. Protopopov. The report concerned not a self-adjusting, but a self-organized system, i.e., a system which is fully open from the point of view of thermodynamics, and which possesses the rudaments of self-organization.

Yu. L. Khait. Even if it is a self-organized system there still shou[illegible]ist feedback: otherwise there will not be self-organization.

V. K. Lykhovskiy. What is the nature of forces which prevent fast removal of excitation energy from the orienton? Since in the system there are low-lying energy levels, cannot it happen that energy will disperse throughout the medium and the exciton will rapidly disintegrate?

Kh. V. Protopopov. It is possible to show that for average binding energy, the wave packet exactly should be extended to cover several molecules. This question is considered in detail in work [1].

L. S. Polak. On how many molecules is the exciton localized in the beginning of its formation?

Kh. V. Protopopov. The exciton is localized on a group of the order of tens of molecules. If in some region there fluctuatingly appears short-range order, then during the time of existence of this region, in the absence of defect in it, the exciton will spread out through it to the boundaries and then recombine nonradiatively or luminesce, or will be localized.

V. L. Tal'roze. What is the time of spontaneous decay of excitation in the solution?

Kh. V. Protopopov. 10^{-9} - 10^{-8} sec.

V. L. Tal'roze. Should energy transfer then occur more rapidly?

Kh. V. Protopopov. Duration of transfer should be included in this time, apparently, as a small component (about $2 \cdot 10^{-10}$ sec). In those cases when duration of transfer is large, de-excitation time will be changed.

Yu. L. Khait. How is it possible to consider the existence of the ordered region in the liquid for 10^{-9} sec?

Kh. V. Protopopov. Region of ordering is considered not as stationary but in motion. During energy transfer, the region of ordering around the excited molecule is reconstructed - it, as it were, "goes" after excitation.

DIFFERENT TYPES OF NONRADIATIVE ENERGY TRANSFER FROM TRIPLET MOLECULES OF AROMATIC COMPOUNDS

V. L. Yermolayev

In works [1-3] it is shown that in solid solutions there can be carried out two types of nonradiative transfer (migration) of energy from triplet molecules of organic compounds. First type of transfer appears in the phenomenon of sensitized phosphorescence of organic compounds in vitreous solutions at low temperatures, which was discovered in 1952 [1]. Deactivation of triplet molecules of donor in this case is accompanied by excitation of molecules of acceptor directly into the triplet state, i.e., transfer occurs according to the scheme ${}^3\Gamma_Д + {}^1\Gamma_A \rightarrow {}^1\Gamma_Д + {}^3\Gamma_A$. The diagram of electron levels for this case is shown in Fig. 1.

Quantitative relations in triplet-triplet transfer sharply differ from relations observed in the earlier investigated singlet-singlet transfer [4]. Dependence of efficiency of quenching of donor of energy q_0/q on concentration of acceptor C in this case is described by Perrin's formula [5, 6]: $q_0/q = \exp(VN'C)$, which testifies to the sharply limited sphere of action of quenching V. Magnitudes of V for different combinations of donor and acceptor, determined from experiments on quenching, are equal to $(5-14)\cdot 10^3$ Å^3, which corresponds to distances between centers of interacting molecules of 10-15 Å [6]. It was shown that the probability of triplet-triplet transfer does not depend on probability of intercombination singlet-triplet transition in the molecule of the acceptor of energy [7, 8]. These and other observed facts testify to the fact that the phenomenon of nonradiative transfer of energy through triplet levels is caused by exchange-resonance interactions of excited donor molecule and unexcited acceptor molecule which appear

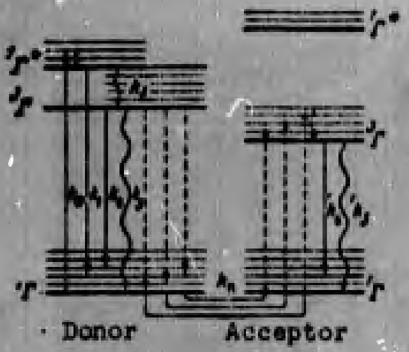

Fig. 1. Diagram of electronic-vibrational levels of molecules in the phenomenon of nonradiative energy transfer through triplet levels: $^1\Gamma$, $^1\Gamma^*$ – ground and excited singlet, $^3\Gamma$ – triplet levels. Straight arrows designate radiative transitions, wavy arrows designate internal processes of nonradiative degradation, and dotted arrows designate transitions accompanying nonradiative electron excitation energy transfer. k_0-k_5, k_{11} are rate constant of the corresponding processes.

during superposition of peripheral parts of electron shells of the interacting molecules [7, 8]. Exchange-resonance transfer is permitted if there is observed Wigner's rule of conservation of total spin of donor and acceptor during transfer.

In 1961 [3], it was experimentally shown that triplet molecules can also give up electron excitation energy with the help of nonradiative transfer through the usual inductive-resonance mechanism. As a result of transfer, the acceptor molecule is excited into the singlet excited state, i.e., $^3\Gamma_{\text{Д}} + {}^1\Gamma_{A} \rightarrow {}^1\Gamma_{\text{Д}} + {}^1\Gamma_{A}^*$. The phenomenon of triplet-singlet transfer was observed both by reduction of τ and quenching of phosphorescence of the donor, and by the appearance of sensitized afterglow of the acceptor. For this type of transfer it is necessary that spectrum of phosphorescence of the donor overlap the intense absorption spectrum of the acceptor. Quantitative relations and distances of transfer (25-55 Å) are close to those observed for singlet-singlet transfer [4]. Diagram of levels for triplet-singlet transfer is shown in Fig. 2. This type of transfer does not require superposition of electron shells of interacting molecules and obeying of Wigner's rule.

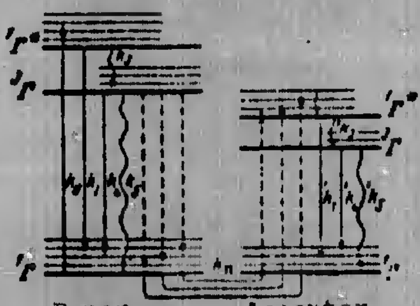

Fig. 2. Energy level diagram of molecules for nonradiative transfer of energy from triplet to singlet level. See designations in Fig. 1.

Both effects were used by us for the study of intramolecular nonradiative degradation of electron-excited molecules in solid solutions at low temperatures [9]. These investigations showed that in the absence of photochemical reactions, internal degradation of energy of electron excitation of aromatic molecules is carried out through the triplet state. The actual processes of nonradiative transfer of energy of both types are not accompanied by transition of all energy of electron excitation into heat.

Literature

1. V. L. Yermolayev and A. N. Terenin. Collection: "Memoirs of S. I. Vavilov," Moscow, Publishing House of Academy of Sciences of USSR, 1952, p. 137.

2. A. N. Terenin and V. L. Yermolayev. News of Academy of Science of USSR, physics series 26, 21 (1962); V. L. Yermolayev. UFN (Progress in Physical Sciences), 80, 3 (1963).

3. V. L. Yermolayev and Ye. B. Sveshnikova. News of Academy of Sciences of USSR, physics series 26, 29 (1962).

4. M. D. Galanin. Transactions of Physics Institute of Academy of Sciences of USSR, 12, 3 (1960).

5. F. Perrin. C. r. Acad. Sci., 178, 1978 (1924).

6. V. L. Yermolayev. Reports of AS (Academy of Sciences) USSR, 139, 348 (1961).

7. V. L. Yermolayev and A. N. Terenin. Journal of Chemical Physics, 55, 698 (1958).

8. V. L. Yermolayev. Optics and spectroscopy, 6, 642 (1959).

9. V. L. Yermolayev and Ye. B. Sveshnikova. Report on XI-th conference on luminescence. Minsk, 1962. Theses of reports, Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 26; Reports of AS USSR, 149, 1295 (1963).

Discussion

N. D. Sokolov. What is the mechanism of triplet-singlet energy transfer?

V. L. Yermolayev. This is the usual mechanism of inductive-resonance transfer. It is completely analogous to the mechanism of singlet-singlet transfer, with the difference that everything occurs in another region of times.

Ye. Ye. Nikitin. When singlet-singlet energy transfer occur, then the measure of intermolecular interaction in molecular crystals is dipole-dipole splitting of terms (Davydov splitting of terms). Is it possible from experimental data to find a quantity characterizing inductive-resonance interaction?

V. L. Yermolayev. Inductive-resonance interaction is weak, and splitting of terms is not observed for molecules separated by a distance of 30-40 Å. In particular, such an interaction does not affect optical characteristics of donor or acceptor molecules.

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I. G. Kaplan. From experimental data it follows that during excitation of molecules of benzophenone, phosphorescence composes 100% of the radiation. This signifies that excited molecule passes from singlet state into triplet state in a time of about 10^{-10} sec, since de-excitation time of singlet level can attain 10^{-9} sec. How do you explain such fast transition of excited molecule into triplet state?

V. L. Yermolayev. This question has still not been answered. It is necessary to note that the time 10^{-10} sec is too low an estimate. Radiative transition of a molecule of benzophenone from singlet into ground occurs not in 10^{-9} sec, but in 10^{-6} sec. Consequently, so that there will be revealed only phosphorescence, it is sufficient to have a time of transition to the triplet state of 10^{-8} sec.

V. V. Voyevodskiy. Your method of calculation pertains only to the mechanism of transfer of energy from donor molecule to acceptor molecule. And do you not consider the mechanism of transfer from donor molecule to donor molecule through triplet levels?

V. L. Yermolayev. Apparently it is not necessary to take this into account, since there is no dependence of probability of transfer on concentration of donor (in the region $C_{\text{Д}} = 10^{-3} - 10^{-1}$ mole/liter); if there were such a transfer, then there would be a dependence of probability of transfer on concentration of donor.[1]

Question: At what concentrations does there appear action of the acceptor?

V. L. Yermolayev. By certain methods it is possible to observe influence of acceptor starting at concentrations of 10^{-2}-10^{-3} mole/liter; by other methods, for instance according to quenching – at $5 \cdot 10^{-2}$ mole/liter. In experiments of Sandros and Bäckström,[2] where transfer of energy through triplet levels was observed in liquid solutions, very low concentrations of acceptor are sufficient (10^{-4}-10^{-5} mole/liter).

Question: Is it possible to explain self-quenching of molecules of donor by triplet-triplet transfer?

V. L. Yermolayev. Self-quenching for aromatic molecules in solid solutions is not observed up to a concentration of ~1 mole/liter. Self-quenching occurs for molecules of the type of dyes, where spectra of radiation and absorption strongly overlap. For aromatic molecules, this effect is practically not observed up to very high concentrations.

Question: Is it possible to say that if there is experimentally observed transfer of excitation to large distances for aromatic molecules in the solid phase at concentration of the order of 10^{-3}-10^{-4} mole/liter, that this is not transfer through triplet levels?

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[1] At very high concentrations in solid solution at 77°K (0.3-1.2 mole/liter), there was revealed triplet-triplet transfer of energy between donor molecules [V. L. Yermolayev. Optics and spectroscopy, 16, 548 (1964)].

[2] K. Sandros and H. L. J. Bäckström. Acta Chem. Scand., 16, 958 (1962).

V. L. Yermolayev. Yes, for solid solutions it is possible to assert this quite definitely.

V. M. Agranovich. If there occurs induced resonance, then for probability of triplet-singlet transfer, the dependence on distance r should be $1/r^6$. Then in the case of good overlapping you would obtain transfer at 100 Å. Are there known experimental data of such kind?

V. L. Yermolayev. We estimated the distance of singlet-triplet transfer. It was shown that for different combinations of donor and acceptor, they compose from 25 to 55 Å; i.e., this is the usual distance observed for singlet-singlet transfer. Therefore, there is not contradiction here with singlet-singlet transfer.

R. N. Nurmukhametov. How do you explain invariability of spectrum during sensitized luminiscence? Since according to you there is formed something like an eximer, then the spectrum should be characteristic for an eximer.

V. L. Yermolayev. The question of eximers drops out, since they are formed in liquid solutions, where there is possible regrouping of interacting molecules after excitation of one of them. In solid matrices, molecules after excitation remain in the same places. After energy transfer from donor to acceptor, molecule of donor does not interact with acceptor because triplet level of donor is higher.

Question: Efficiency of transfer should depend on overlapping of π-electron shells. Did you observe a dependence of efficiency of transfer on structure of donor and acceptor and on the introduction of interlocking substitutes?

V. L. Yermolayev. Efficiency of transfer should be somewhat higher for donor molecules, which have a stronger prohibition of intercombination for transitions in the molecule itself. This tendency indeed appears, but it is necessary to make such a conclusion with certain caution, since it is difficult to estimate and to compare dimensions of different molecules.

R. N. Nurmukhametov. You investigated carbazole and diphenylamine, which in the excited state enter into interaction with molecules of the matrix. Could it be that the formed radicals of alcohol quench excited molecules?

V. L. Yermolayev. The yield of photochemical processes is small. Inasmuch as in our case for excitation there were used low intensities, it is apparently possible to disregard photochemical processes.

V. V. Voyevodskiy. How is there ensured homogeneity of impurity in the medium?

V. L. Yermolayev. In polar solvents (mixture of ether and alcohol), both introduced components combine more quickly with molecules of solvent than with each other. Therefore, we exclude the association effect; it does not appear either spectroscopically or otherwise.

PROCESSES OF ENERGY TRANSFER IN CONDENSED SYSTEMS

N. N. Tunitskiy and Kh. S. Bagdasar'yan

For explanation of many phenomena of luminescence photochemistry and radiation chemistry, there are widely used the concepts of "energy transfer" from some molecules to others [1, 2]. By this idea embraces processes whose physical mechanisms are very different, and in certain cases possibly even unknown. From this point of view, of doubtless interest is establishment of a region in which concepts of the "resonance" mechanism of transfer of energy of electron excitation are valid. Probability of energy transfer per unit of time from excited molecule B to molecule A in the case of dipole transitions is equal to

$$p = \frac{\alpha}{r^6}, \qquad (1)$$

where r is distance between molecules; α is energy transfer constant (depending also on their orientation).

Theory of resonance transfer permits us to determine α from electronic spectra of donor and acceptor molecules. On the other hand, α can be determined by experimental means according to some process which is a result of energy transfer. Such processes can be quenching of fluorescence of B^* by molecules A, sensitized fluorescence of A, "protection" of molecules B^* from chemical decomposition and sensitized photolysis or radiolysis of molecules A. Comparison of experimental and theoretical values of magnitudes α can serve as the most convincing argument in favor of resonance mechanism of transfer. In connection with this, in this work there is given exact solution of problem about transfer of excitation energy from molecules B to molecule A with consideration of diffusion. Approximate solutions of this problem are given in works [3, 4].

We will consider change of concentration of excited molecules B* in vicinity of molecule A. Let us assume that initial concentration of excited molecules is constant over the volume, and that new molecules will not be formed. After a certain time, near each of molecules A, on the average, there will be established a region with lowered concentration of excited molecules B*, since molecules B* located close to A will lose excitation faster. Furthermore, near every molecule A there will be disturbed the equilibrium distribution of molecules B* with respect to their orientations. We, however, due to the great complexity, will not begin to consider orientational effects, and will use values obtained by averaging over all possible orientations, which is permissible during sufficiently fast rotation of molecules.

Average concentration n of excited molecules B* in neighborhood of A will be described in such a case by the equation

$$\frac{\partial n}{\partial t} = \frac{D}{r}\frac{\partial^2 (rn)}{\partial r^2} - kn - \frac{\alpha n}{r^6}, \qquad (2)$$

where k is probability of spontaneous deactivation of molecule B* per unit of time; D is diffusion coefficient.

As additional conditions we have:

$$\text{at } t = 0, \quad r > R_0 \quad n = n_0;$$

$$\text{at } t > 0, \quad r = R_0 \quad \frac{\partial n}{\partial r} = 0. \qquad (3)$$

Here R_0 is distance of minimum approach of molecules A and B. Sometimes, instead of the second condition we use: at $r = R_0$, $n = 0$, which contains the assertion of an additional mechanism of energy transfer during approach of molecules to each other. Number of molecules B* losing excitation near molecules A per unit time will be equal to

$$N = 4\pi\alpha \int_{R_0}^{\infty} \frac{n}{r^6}\, dr. \qquad (4)$$

For t = 0 or for any t, in the limiting case when D → ∞, we have

$$N(0) = \frac{4\pi\alpha n_0}{3} \cdot \frac{1}{R_0^3}.$$

In order to find value of N for later moments of time with finite D it is necessary to solve equation (2). At $t > t_1$ (t_1 will be estimated below) solution has the form

$$n = n_0 e^{-kt} C(z) = n(r = \infty) c(z), \qquad (5)$$

where

$$c(z) = z^{1/4}\frac{\Gamma\left(\frac{3}{4}\right)}{2^{1/4}}\left[I_{-1/4}(z) - \frac{I_{+1/4}\left(\frac{\sqrt{b}}{2}\right)}{I_{-1/4}\left(\frac{\sqrt{b}}{2}\right)}I_{+1/4}(z)\right];$$

$$b = \frac{\alpha}{DR_0^4}; \quad z = \frac{\sqrt{b}}{2}\cdot\frac{R_0}{r};$$

I_p – Bessel function of index p.

From (4) and (5) we find

$$N = 8\pi\alpha n(r = \infty)\left(\frac{1}{b}\right)^{3/4}\frac{\Gamma(3/4)}{\Gamma(1/4)}\cdot\frac{I_{+3/4}\left(\frac{\sqrt{b}}{2}\right)}{I_{-3/4}\left(\frac{\sqrt{b}}{2}\right)}. \qquad (6)$$

At large values of b we have

$$N(b) = \frac{8\pi}{3}\cdot\frac{\alpha}{R_0^3}\left(\frac{1}{b}\right)^{3/4}n(r = \infty). \qquad (7)$$

Using Smolukhovskiy's formula for rate of coagulation of colloidal particles, we can introduce the idea of radius of equivalent absorbing sphere R, determined by the relation

$$N = 4\pi DRn(r = \infty).$$

We have

$$R = \frac{2}{3}b^{1/4}R_0 = \frac{2}{3}\left(\frac{\alpha}{D}\right)^{1/4}. \qquad (8)$$

Time of establishment of stationary distribution for function C is determined by following relationship:

$$t_1 \approx b^{1/2}\cdot\frac{R_0^2}{D} = \frac{\alpha^{1/2}}{D^{3/2}}. \qquad (9)$$

We see that during strong resonance transfer of excitation energy, R does not depend on dimensions of molecules, but only on magnitudes α and D. Thus, dependence of R on α and D is weak. Usually values of α lie within limits 10^{-33} - 10^{-31} cm^6/sec; D ≈ 10^{-5} cm^2/sec. Therefore, R should have the order of 10^{-7} cm.

The found value of effective radius can be used for approximate consideration of stationary process.

If transfer of excitation energy from molecule B^* to molecule A necessarily leads to chemical transformation of A, then concentration of molecules A will be determined by the equation

$$\frac{dv}{dt} = -Nv. \qquad (10)$$

The above relationships are valid if concentration of molecules A is sufficiently small.

Literature

1. Kh. S. Bagdasar'yan. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 52.

2. V. A Krongauz. Progress in chemistry, 31, 222 (1962).

3. G. P. Belikova and M. D. Galanin. Optics and spectroscopy, 1, 168 (1956).

4. V. A. Krongauz, I. N. Vasil'yev and B. P. Kirsanov. Present collection, p. 145.

Discussion

A. M. Brodskiy. What excitations are being considered here, and what are the lifetimes of excited states with respect to chemical disintegration and luminiscence What concentrations does the theory consider?

N. N. Tunitskiy. Lifetimes of excited molecules can be various. It is necessary to make only one limitation: concentration of molecules A should be low enough that there is not much overlapping of zones with impoverished concentrations. This reduces to the following concentration of molecules A should be less than $10^{20} - 10^{19}$ molecules/cm^3 (depending upon magnitude of constants).

V. V. Voyevodskiy. You wrote boundary conditions. The first condition $\left(\frac{dn}{dr}\right)_{R_0} = 0$. In the presence of a diffusion flux it apparently is not satisfied and, in any case, this condition is impossible to introduce with additional substantiation. The second alternative condition proposed by you, $n = 0$ at $r = R_0$, assumes that basically the process is limited by diffusion. Thus you use boundary conditions for the diffusion region without conducting a general solution in order to clarify relationship between diffusion and other processes. It would be more correct, I think, to take the usual conditions, when concentration is not equated to zero on the boundary, but when there are equated flux and rates of process at the wall. Then you indeed obtain general conditions, which in the extreme diffusion case lead to the conditions $n = 0$.

N. N. Tunitskiy. In this problem, if we do not assume some new mechanisms, it is necessary to have the boundary condition - diffusion flux is equal to zero. Then loss of excitation by molecule is determined by the accepted law $1/r^6$.

If in the usual diffusion equation we set flux equal to zero, then there will not be disappearance of particles. In this complicated equation, flux is equal to zero, and disappearance of particles is considered by the term $\alpha n/r^6$.

A. Ya. Temkin. You said that particle density of $B^* \approx 10^{19}$ 1/cm^3. Is it possible in such a case to write equation of diffusion in differential form? It seems to me that in this case it is necessary to write integral kinetic equation and not differential equation of diffusion. Concentration of molecules is too small, whereas diffusion equation pertains to physically small element of volume containing a large number of particles.

N. N. Tunitskiy. In our case it is possible to write the equation of diffusion. Diffusion approximations are justified here.

A. Ya. Temkin. You consider molecule A to be secured at a point, but it, after all, accomplishes random walks, which in general lead to the result that it can depart from the zone of the excited molecule B^* and arrive at a zone where such excitation is absent. Qualitatively this effect is the same as diffusion of molecules B^*, but quantitatively it can be absolutely different. What is your opinion concerning the role of random wals of molecules A?

N. N. Tunitskiy. It is sufficient to refer on Smolukhovskiy, who considered relative Brownian motion and showed that during relative Brownian motion diffusion coefficients are added. Here we understand by D the coefficient of relative Brownian motion.

I. G. Kaplan. If lifetime of excited state is such that diffusion displacement will be small compared to radius R_0, then it is not necessary to consider diffusion at all. For instance, for highly excited molecules (lifetime ~10^{-12} sec), it is possible not to consider diffusion.

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INVESTIGATION OF MECHANISM OF INTERMOLECULAR ENERGY TRANSFER IN ORGANIC SOLUTIONS. THE INFLUENCE OF DIFFUSION

V. A. Krongauz, I. N. Vasil'yev
and B. P. Kirsanov

During sensitized luminescence of liquid organic scintillators and also during certain sensitized radiation and photochemical reactions, transfer of excitation energy from solvent to solute occurs apparently by means of resonance interaction of excited molecules of energy donor and molecules of acceptor [1-3]. In liquid solutions, a considerable role in energy transfer is played by diffusion motion of interacting molecules.

Dependence of relative intensity (1) of luminescence of solution DPO (ДФО) (0.005 mole/liter) in IPD (ИПД) — cyclohexane mixtures on magnitude of reverse viscosity of the solvent. Point A — solution of DPO in vitreous IPD at -78°C.

As an example of influence of diffusion, in the figure there is shown change of intensity of sensitized luminescence of 2,5-diphenyloxazole [DPO] (ДФО) dissolved in mixtures of isopropyldiphenyl [IPD] (ИПД) and cyclohexane be under action of light absorbed by IPD. Decrease of viscosity was attained by increase of content of cyclohexane.

It is possible to consider the influence of diffusion in the following way: In the steady state, at small concentrations of energy acceptor B, distribution function $n(r)$ of excited molecules of energy donor A^* near the molecule B in the presence of resonance interaction and diffusion is determined by the equation

$$D\Delta n(r) - W(r)n(r) - \frac{n(r)}{\tau_0} + \beta = 0; \qquad (1)$$

under the conditions: $n(R_{12}) = 0$; $n(\infty) = \beta\tau_0$, where

$$W(r) = \frac{1}{\tau_0}\left(\frac{r_0}{r}\right)^6. \qquad (1a)$$

D is diffusion coefficient; W(r) is probability of resonance interaction of A^* and B; τ_0 is lifetime of excited molecules A^*; r_0 is "critical distance" of resonance energy transfer; β is concentration of A^* formed per unit time; R_{12} is sum of kinetic radii of A and B.

We will formulate the following principle of equivalence: number of molecules deactivated during collision with a "sphere" of radius r_1, which instantaneously quenches every molecule A^* colliding with it. Criterion of applicability of this principle is

$$\frac{r_1^2}{6D\tau_0} \ll 1. \qquad (2)$$

On the basis of the formulated principle, it is possible to write equation (1) without the second term with the boundary conditions:

$$n(r_1) = 0, \qquad n(\infty) = \beta\tau_0. \qquad (3)$$

Solution of such an equation leads, as is known [4], to the following expression for rate constant of energy transfer (k_{AB}):

$$k_{AB} = 4\pi Dr_1 N\left(1 + \frac{r_1}{\sqrt{D\tau_0}}\right). \qquad (4)$$

Magnitude r_1 is simple to determine by using the following simple method [5]. Let us consider deactivation of A^* by resonance means in accordance with equation

$$D\Delta n(r) - W(r)n(r) = 0 \qquad (5)$$

under the conditions

$$n(R_{12}) = 0, \quad n(\infty) = n_0.$$

Determining from (5) the value of dn/dr, we will find number of molecules A^* deactivated by particle B per unit time, which, according to principles of equivalence, should satisfy the equality

$$4\pi Dr_1^2 \left.\frac{dn}{dr}\right|_{r=\infty} = 4\pi Dr_1 n_0. \qquad (6)$$

Placing value of dn/dr found from (5) in (6), we will finally obtain

$$r_1 = \frac{\Gamma(3/4)}{2\Gamma(5/4)}\left(\frac{r_0^6}{D\tau_0}\right)^{1/4}\frac{I_{-1/4}(\omega)}{I_{1/4}(\omega)}, \qquad (7)$$

where $\Gamma(x)$ in gamma-function and $I_\nu(\omega)$ is Bessel function of 1-st kind,

$$\omega = \frac{r_0^2}{2(D\tau_0)^{1/2}R_{18}^3}.$$

A similar expression for equivalent radius is obtained in work [6].

If we consider that constant k_{AB} calculated according to the Stern-Volmer equation practically do not depend on concentration of acceptor and are kept in the region of very low concentrations, then values of k_{AB} calculated according to equation (4) can be compared with experimental values.

In the table there are compared values of k_{AB} for certain systems, which were determined from experiments on the kinetics of sensitized luminescence of DPO solutions and sensitized radiation decomposition of solutions of benzoyl peroxide [3], with values calculated by means of formula (4).

Comparison of Experimental and Calculated Values of k_{AB}

Solution	$k_{AB} = 10^{-10}$ liter/sec	
	Experimental	Calculated
Benzoly peroxide — toluene	2.5	1.6
DPO — toluene	7.7	3.2
DPO — IPD — cyclohexane	40	26

As can be seen from the table, calculated magnitudes of k_{AB} are less than experimental values. Possibly this is connected with the fact that dependence of probability of resonance interaction on distance between molecules, which is determined by expression (1a), is not retained during diffusion approach of A^* and B to small distances from each other.

Literature

1. T. P. Belikova and M. D. Galanin. Optics and spectroscopy, 1, 158 (1956).
2. A. Weinreb. J. Chem. Phys., 35, 91 (1961).
3. V. A. Krongauz and I. N. Vasil'yev. Kinetics and catalysis, 4, 76 (1963).
4. B. Y. Sveschnickov. Acta Physicochimica, 3, 257 (1935).
5. G. R. Khutsishvili. ZhETP (Journal of Experimental and Theoretical Physics), 42, 1321 (1962).
6. N. N. Tunitskiy and Kh. S. Bagdasar'yan. Present collection, p. 105.

Discussion

R. F. Vasil'yev. You said that it is necessary to consider diffusion if lifetime of excited state is sufficiently great. At what lifetimes does this phenomenon show up?

V. A. Krongauz. The criterion of applicability of our ideas is the condition

$$\frac{r_{eq}}{6D\tau_0} \ll 1,$$

where τ_0 is lifetime of excited molecules of solvent; i.e., the equivalent sphere is "skipped" without deactivation, and in the equivalent sphere particles are not generated. Only then can we apply the proposed considerations. Otherwise, the idea of equivalent sphere is not applicable. It is satisfied because $\tau_0 \approx 10^{-8}$ sec.

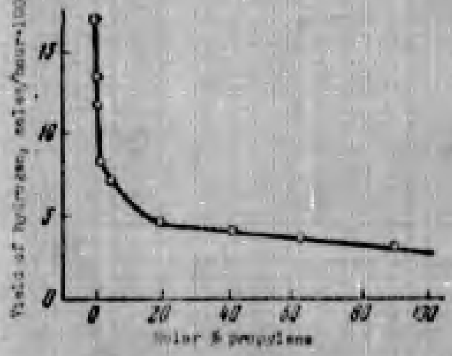
Question: And how is the matter at large τ_0?

V. A. Krongauz. Our approach is exactly justified at large τ_0. It is important that spontaneous deactivation not occur inside the sphere. If, however, deactivation occurs inside the sphere, then our consideration is not applicable. I want to add that the analogous idea about equivalent radius was used by M. D. Galanin and G. P. Belikova. However, magnitude of equivalent radius was taken by them to be equal to half the critical distance, which in our opinion is not fully justified.

ENERGY TRANSFER DURING RADIOLYSIS OF HYDROCARBONS

A. M. Brodskiy, Yu. A. Kolbanovskiy and L. S. Polak

Among problems of causing the greatest interest during the study of radiolysis of hydrocarbons at low and average temperatures are included characteristics of transfer of excitation energy during inhibiting. Experimental curves of inhibiting of formation of definite products of disintegration have in many cases the characteristic form represented schematically in the figure. As can be seen from the figure, there are two different intervals. In the first, inhibiting is accelerated very sharply with increase of concentration of the addition, and in the second it grows comparatively slowly. Moreover, in case of inhibiting in liquids, transition from one interval to the other occurs in region of relative molar concentrations 10^{-4}-10^{-6} or at average distances of about $5 \cdot 10^{-5}$-10^{-6} cm; in case of gases, however [1], the corresponding transition occurs at concentrations of altogether 10^{-2} mole/mole, but at the same distances. Let us note that curve of inhibiting of many usual gas reactions has analogous form, only the corresponding critical average distances are several times larger. On second interval magnitude $[G(\rho) - G(\infty)]^{-1}$ (G — radiation yield; ρ — concentration of inhibitor in mole/cm^3), which is a linear function of probability of transfer of excitation, is proportional to ρ^2; i.e., its behavior is analogous to behavior during inhibiting



Inhibiting of yield of hydrogen during radiolysis of propane by additions of propylene (according to work [1]).

of luminescence. At the same time, as analysis of experimental data made in work [2] and also analysis of subsequent more exact experiments from works [1, 3] showed, initial section of curve of inhibiting is characterized, with good accuracy, by proportionality of magnitude $[G(\rho) - G(\infty)]^{-1}$ to concentration $C^{2/3}$ which corresponds during "strong inhibiting" to proportionality to the mean square distance $\overline{R}^2$.

According to our works [4], the indicated distinction of the concentration dependence of inhibiting can be connected with transition from one region of variation of the dimensionless parameter.

$$\alpha = \frac{\hbar c}{\omega R} \simeq \frac{\hbar c \rho^{1/3}}{1.7\omega},$$

where ω is corresponding excitation energy, to the other. Magnitude ω during radiolysis of hydrocarbons can take values of the order of energies of electron excitation, i.e., approximately 5-7 ev. Then it is obtained that exactly at average distances of $5\cdot10^{-5}$-10^{-6} cm or at the above-indicated critical values of concentrations, parameter α passes from values smaller than unity to values larger than unity.

In connection with what was said above, we advanced the assumption that transfer of the considered comparatively high excitations with relaxation times $\sim10^{-15}$-10^{-14} sec occurs by means of direct electromagnetic transmission, where, in accordance with values of α at low concentrations, it is necessary to consider the time lag. In theoretical consideration [4] of the proposed mechanism of inhibiting, the problem was divided into two parts. At first there was considered the model quantum-mechanical problem of transfer of energy in vacuum from excited molecular system to molecule of inhibitor. Probability of such process when only dipole - dipole terms are retained turns out to be, with the most favorable location of dipoles, equal to

$$w_{if} = \frac{9\hbar}{2^7\cdot\pi}\alpha^6\left(1+\alpha^2+\frac{9}{4}\alpha^4\right)\rho(\omega)w_{I}w_{II}, \tag{1}$$

where w_I and w_{II} are probabilities of dipole radiation of excited molecule and inhibitor; $\rho(\omega)$ is probability density function of final states of inhibitor molecule. In the real problem, we have excited ions and molecules and molecules of inhibitor statistically distributed among them (usually aromatic compounds with complicated system of levels, iodine molecules, etc.).

In many cases during radiolysis of hydrocarbons, levels of excitation of chemically active molecular systems, in particular ions, lie below the first electronic level of the main part of the molecules, so that the medium is indeed transparent.

During strong absorption by inhibitors we, based on formula (1), obtain expression for dependence of probability of inhibiting on concentration:

$$w = A\rho^{2/3}\left(1+\beta_1\frac{(\hbar c)^2 p^{2/3}}{\omega^2}+\beta_2\frac{(\hbar c)^4 p^{4/3}}{\omega^4}\right), \qquad (2)$$

where β_1 and β_2 are constant coefficients of the order of unity depending on "strength of interaction." As it is easy to see, formula (2) permits the describing of the enumerated peculiarities of inhibiting phenomena.

Literature

1. R. A. Back. J. Phys. Chem., 64, 125 (1960).

2. Yu. A. Kolbanovskiy and L. S. Polak. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 64; Yu. A. Kolbanovskiy. Candidates dissertation, Moscow, 1961.

3. Radiolysis of hydrocarbons. Moscow, Publishing House of Academy of Sciences of USSR, 1962.

4. A. M. Brodskiy and Yu. A. Kolbanovskiy. Reports of Academy of Sciences of USSR, 139, 1081 (1961).

Discussion

I. G. Kaplan. Formulate, please, the cause of the difference of your conclusions from conclusions of Förster.

A. M. Brodskiy. The dependence on R according to us is the very same as for Förster at small R, but Förster considers mainly luminescence, i.e., the case when in reality, apparently, it is necessary to consider diffusion.

I. G. Kaplan. As far as I understood, your time of transfer of energy is the order of 10^{-12}-10^{-13} sec; i.e., it is comparable with decay time. Thus, in addition to that, according to your formula there is still necessary the condition of overlapping of spectra. If this is so, then how do you explain experimental data according to which with introduction of additions of terphenyl or anthracene into benzene with concentration of 10^{-2}-10^{-3} mole/liter, no protection of benzene by these additions is revealed, although their spectra apparently overlap sufficiently well. How do you explain this phenomenon?

A. M. Brodskiy. In order to explain behavior in every concrete case, there is necessary more careful examination.

We made a whole series of approximations. We considered a certain model. For instance, we consider that there exists only one excited level, which this usually can not be realized. Thus may be changeover between several levels. There may, conversely, be carried out sensitization – the transfer from one level to another. Furthermore, during inhibiting of radiolysis of aromatic hydrocarbons by aromatic hydrocarbons, it is impossible to expect considerable effects.

Yu. V. Konobeyev. Will you tell me, please, in detail how you obtained the concentration dependence?

A. M. Brodskiy. We have some excited system, and at a certain average distance from it there is a molecule of inhibitor. If inhibiting is sufficiently strong, and location of molecules is favorable, then inasmuch as in radiation chemistry the concentration of excitations is usually very small, it is possible simply to take the average distance to the nearest molecule of inhibitor. If, in fact, absorption on the first molecule does not occur, it is necessary to consider following molecules of inhibitor, but then it is necessary to consider the characteristic attenuation term, which cuts off the influence of very distant molecules of inhibitor.

V. A. Krongauz. It is impossible to pass from law of interaction between two molecules to average concentrations. From your method of consideration it follows that Förster's theory should give a dependence on C^2.

A. M. Brodskiy. Yes, in the limiting case of high concentrations and under conditions corresponding to radiolysis conditions, i.e., comparatively high excitation energies. There is a region of sharp drop of rate of radiolysis, which evidently falls in the range of concentrations less than $5 \cdot 10^{-4}$ mole/liter in the case of investigation of liquids. Thus, when $hc/\omega R$ is of the order of unity in general, as follows from the theory, it is impossible not to consider delay. Break of the inhibiting curve is found approximately in the region corresponding to $hc/\omega R \cong 1$. Apparently, at low concentrations, data are best of all described by a 2/3 power law, where the curve is drawn not directly through experimental points, but through initial point and in the direction of a straight line. Recently there have also appeared experimental data with points lying on a straight line constructed according to the 2/3 power law.

V. L. Tal'roze. I have a question for all comrades studying energy transfer in liquids. Recently there appeared the articles of Hardwick,[1] who found very strict

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[1] T. J. Hardwick, J. Phys. Chem., 66, 2132 (1962).

correlations between energy transfer in saturated hydrocarbons and ionization potentials of the corresponding substances. He made hence the conclusion that in saturated hydrocarbons there basically occurs charge transfer, and not transfer of excitation energy. This does not pertain to processes caused by the action of light, but should be considered in radiation processes. It is necessary to deal carefully with coincidences with formal-kinetic results, since very frequently very different kinetic schemes give very similar formal-kinetic equations. I would like to know the opinions of comrades of working in region of transfer of excitation on this subject.

A. M. Brodskiy. Dependence on $C^{2/3}$ can be obtained only from theory of electromagnetic transmission, taking into account time lag. If it were possible experimentally to prove the 2/3 law, then this would be a decisive argument. If the mechanism of inhibiting consisted of charge transfer, then the lifetime of excited state would be 10^{-13} sec, which corresponds to a very high rate of propagation of excitation (time $\sim 10^{-14}$ sec). I can not see how there can occur transmission of electrons with such speed.

V. L. Tal'roze. I did not understand what you said. After all, the rate of transfer is always measured in accordance with definite assumptions about competing loss processes. If you do not introduce such concepts, then you will obtain simply a formal-kinetic constant, which in direct form still does not express the rate of transfer.

A. M. Brodskiy. Transfer has time to occur before disintegration; decay time is 10^{-13}-10^{-14} sec; distance is 100 Å, we divide one by the other and obtain the rate of transfer.

INVESTIGATION OF ENERGY TRANSFER BY METHOD OF CHEMILUMINESCENCE

R. F. Vasil'yev

The fate of excited molecules should not depend on method of excitation. At the same time, every such method has its own peculiarities, and this can hamper interpretation of results. Therefore, during investigation of role of excited states during radiolysis, it is expedient to utilize other methods of excitation.

Chemiluminescence in cold and hot flames has been repeatedly used for excitation of simple molecules and investigation of their properties [1]. In the liquid phase, until recently, this method had not been used due to complexity and uncertainty of mechanism of reactions with bright chemiluminescence. Detection of glow in reactions with well studied mechanism [2] creates basis for application of chemical synthesis as a method of supplementing other methods of excitation.

Peculiarities of the method are: a) excited molecules are distributed evenly over volume of reaction vessel; b) there is absent background of source of excitation, and it is possible to record radiation with very low yields; c) effective portions of energy are small (2-4 ev); d) absorbing ability of other components of solution does not play a role; i.e., their presence does not affect excitation; e) there are not excited highly luminescent components (they can be excited only by energy transfer); f) excitation occurs by "dark" means; therefore, selection rules are not in effect, and there is possible effective population of "forbidden" levels.

As an example of application of this method of investigation, we will consider influence of spin-orbital interaction on intermolecular nonradiating transfer of excitation energy.

It was shown [3, 4] that in chemiluminescent reactions of oxidation of hydrocarbons, excited particles are carbonyl compounds in the triplet (${}^3T'_P$) state. With introduction in the solution of luminophors, as a rule there occurs amplification of chemiluminescence and change of its spectrum. It was established [5] that in the case of derivatives of anthracene (A), the phenomenon reduces to intermolecular nonradiating transfer of energy from ${}^3T'_P$ to the singlet excited level ${}^1T'_A$ (Fig. 1). Probability of transfer k_{PA} is low for alkyl- and phenylanthracenes, but is increased with the introduction of chlorine and bromine. It is remarkable that halogens also increase the probability k_1 of intramolecular nonradiating transition ${}^3T'_A \rightarrow {}^1T_A$, measured by the method of pulse photolysis [6]. It is not difficult to note that both processes are intercombinational, i.e., occurs with change of multiplicity. Influence of halogens on intercombination transitions is usually explained by spin-orbital interaction, which disturbs selection rules [7]. It is interesting to conduct quantitative comparison of this influence on inter- and intramolecular transitions. For the purpose of selection of a single "scale of spin-orbital interaction," we will consider characteristics of these transitions.

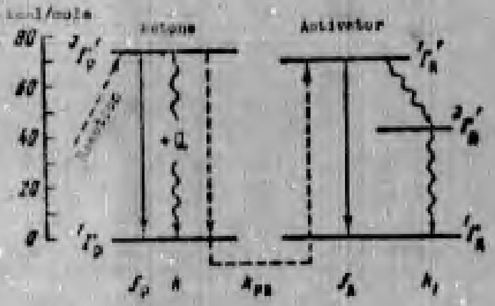

Fig. 1. Energy level diagram illustrating chemiluminescene in the reaction of oxidation of ethylenebenzene and transfer of energy to derivatives of anthracene. Rate constants of radiative (solid lines) and nonradiative transitions (wavy lines) and transfer (dotted lines) are designated.

If energy transfer occurs according to exchange mechanism (exchange of electrons during superposition of peripheral parts of electron shells in the state of collision),[1] its probability is proportional to square of matrix element of exchange interaction [9]:

$$k_{PA} \sim |\langle H_1 \rangle|^2 = \left| \int \psi_A^{**}(r_1, \sigma_1)\, \psi_A^{*}(r_2, \sigma_2) \frac{1}{r_{12}} \psi_A'(r_1, \sigma_1)\, \psi_A(r_2, \sigma_2)\, d\tau_{12} \right|^2.$$

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[1] Characteristics of energy transfer sharply differed [5] from those required by the theory of inductive-resonance or reabsorption transfer. Maximum value of k_{PA} (for dibromanthracene in benzene at 50°C) was one and a half orders lower than the gas-kinetic value ($1.6 \cdot 10^{11}$ liter/mole·sec), which agrees with the idea of energy transfer during collision of donor and acceptor. Apparently, in our systems there did not exist conditions for the inductive-resonance triplet-singlet transfer which was observed recently in solid solutions [8].

Wave functions have the form $\psi(r, \sigma) = \varphi(r)\cdot\chi(\sigma)$ and $\langle H_1\rangle$ is not equal to zero if there exist the following equalities for spin parts: $\chi'_{\text{Д}}(\sigma_1) = \chi'_A(\sigma_1)$ and $\chi_{\text{Д}}(\sigma_2) = \chi_A(\sigma_2)$. Obviously these selection rules are not obeyed for paired transition $|{}^3\Gamma'_P \rightarrow {}^1\Gamma_P| \rightarrow |{}^1\Gamma_A \rightarrow {}^1\Gamma'_A|$ (since $\chi'_{\text{Д}} \neq \chi'_A$), and $\langle H_1\rangle$ and k_{PA} turn out to be small. With introduction of halogens into their field, there is strengthened the interaction of spin and orbital magnetic moments, which leads to "mixing" of states of different multiplicity:

$$\psi_A = {}^1\psi_A + \lambda^3\psi_A.$$

Now it is possible to designate transfer of energy as a paired transition:

$$|{}^3\Gamma'_P \rightarrow {}^1\Gamma_P| \rightarrow |{}^1\Gamma_A \rightarrow {}^1\Gamma'_A + \lambda^3\Gamma'_A|;$$

it becomes to a certain degree allowed, and k_{PA} increases.

Probability of intramolecular transition ${}^3\Gamma'_A \rightarrow {}^1\Gamma_A$ is proportional to square of matrix element of the corresponding operator[1] H_2:

$$k_1 \sim |\int \psi_A^{*}(r,\sigma) H_2 \psi_A(r,\sigma)\,d\tau|^2.$$

Selection rule requires conservation of spin: $\chi'_A = \chi_A$; it is not obeyed for the transition ${}^3\Gamma'_A \rightarrow {}^1\Gamma_A$ and k_1 is small. Analogously to that which was mentioned above, introduction of halogens "permits" the transition ${}^3\Gamma'_A + \lambda^1\Gamma'_A \rightarrow {}^1\Gamma_A$ and k_1 increases.

Exact calculation of probabilities of transitions is difficult. For a series of halogen-substituted napthalenes, fairly good agreement with experiment was obtained on the assumption that $k_1 \sim \lambda^2 \sim \zeta^2$, where ζ is the radial part of the matrix element of the operator of the spin-orbital interaction for an isolated halogen atom [7]. Therefore, we decided to characterize position of compound in the "scale of spin-orbital interaction" by the quantity $\sum_i \zeta_i^2$, which is equivalent to introduction of a very rough model of the

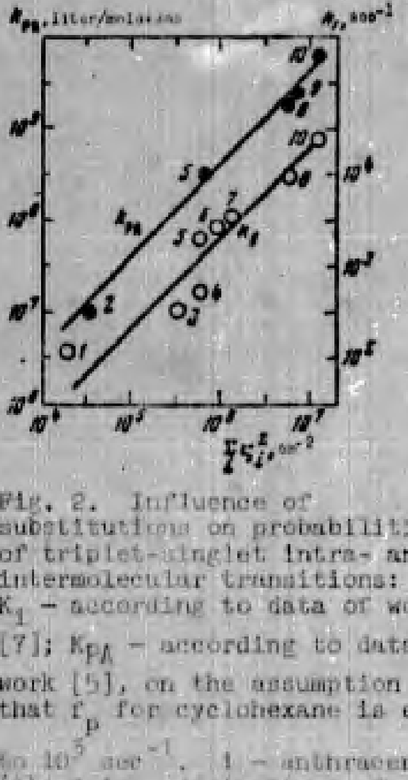

Fig. 2. Influence of substitutions on probabilities of triplet-singlet intra- and intermolecular transitions: K_1 – according to data of work [7]; K_{PA} – according to data of work [5], on the assumption that r_p for cyclohexane is equal to 10^5 sec^{-1}. 1 – anthracene (A); 2-10 – derivatives of anthracene: 2 – 9, 10-diphenyl; 3 – 1-chloro; 4 – 1, 5-dichloro; 5 – 9, 10-dichloro; 6 – 2, 9, 10-trichloro; 7 – 1, 5, 9, 10-tetrachloro; 8 – 9-bromo; 9 – 9-bromo; 10-phenyl; 10 – 9, 10-dibromo. Straight lines correspond to proportionality between abscissa and ordinate. There was investigated oxidation of cyclohexane in benzene at 50°C.

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[1] For radiative transition H_2 is the dipole moment operator; for nonradiative transition, it is the nonadiabaticity operator.

molecule as a system in which isolated atoms independently affect the excited electron. From Fig. 2 it follows that quantities k_{pA}, k_1 and even $\sum \zeta^2$ are approximately proportional to each other. This shows that, in accordance with the above ideas, the influence of halogens on inter- and intramolecular transitions is controlled by one and the same mechanism of mixing of states.

Another intermolecular process – deactivation of the triplet product by quenching agents Q (see Fig. 1) – is considered in work [4].

Literature

1. A. Geydon. Spectroscopy of flames. Moscow, IL, 1959.

2. V. Ya. Shlyapintokh, R. F. Vasil'yev, O. N. Karpukhin, L. M. Postnikov and I. V. Zakharov. Physical problems in spectroscopy. Materials of the XIII-th conference, 1960. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 317.

3. R. F. Vasil'yev and A. A. Vichutinskiy. News of the Academy of Sciences of the USSR, physics series, 27, 729 (1963).

4. R. F. Vasil'yev and I. F. Rusina. Reports of the Academy of Sciences of the USSR, 153, 1101 (1963).

5. R. F. Vasil'yev, A. A. Vichutinskiy and A. S. Cherkasov. Reports of Academy of Sciences of USSR, 149, 124 (1963).

6. M. Z. Hoffman and G. Porter. Proc. Roy. Soc., A268, 46 (1962).

7. D. S. McClure. J. Chem. Phys., 17, 905 (1949).

8. V. L. Yermolayev and Ye. B. Sveshnikov. Reports of Academy of Sciences of USSR, 149, 1295 (1963).

9. D. L. Dexter. J. Chem. Phys., 21, 836 (1953).

Discussion

S. S. Butsko. What experimental data confirm that fact that the formed excited molecule is in the triplet state?

R. F. Vasil'yev. We conducted much preliminary work in identification of excited states. This work included investigation of spectra (with help of a high-transmission spectrometer which was specially built for these purposes), measurement of lifetime of excited state (according to quenching of chemiluminescence), measurement of quantum yield of radiation (according to activation of chemiluminescence) with parallel careful control of reaction rate and with utilization of data on kinetics and the mechanism of the studied chemical reactions. As a result of this work, excited state was quantitatively characterized with highest possible completeness, and this permitted us to conduct its identification.

S. S. Butsko. Is it impossible to conclude that the activator with lower singlet level activates better?

R. F. Vasil'yev. No, we did not observe such a dependence. Here I can refer to data of Bäckström and Sandros[1] on triplet-triplet transfer. They showed that as soon as level of acceptor becomes lower than level of donor, then energy transfer occurs practically at every collision. In our experiments, levels of activators were always lower than levels of donor.

S. S. Butsko. Do you consider it possible at least partially to explain your data by formation of complex of activator with excited molecule of reaction product?

R. F. Vasil'yev. We studied the temperature dependence of activated chemiluminescence, from which it follows that if a complex is formed, then the energy of its formation in any case is less than 0.5 kcal/mole. Moreover, we did not observe the changes in spectra which usually accompany formation of complexes.

V. L. Yermolayev. Why don't you consider transfer to the triplet level of the activator. After all, triplet-triplet transfer in this case is permitted, in distinction from the type of transfer which you discuss in your report? Therefore, it is also necessary to introduce it into your scheme - in any case to take it into account. It can lead to processes of quenching, but not to that process which interests you.

R. F. Vasil'yev. I think that in the framework of that investigation which was conducted here, this would not affect results, inasmuch as triplet-triplet transfer occurs in parallel with triplet-singlet transfer. At the same time, we have indications that these processes can occur. For instance, certain luminophors in a number of reactions are quenching agents; probably in these cases there occur transfer of energy to their triplet level and deactivation of the latter.

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[1] K. Sandros and H. L. J. Bäckström. Acta chem. scand., 16, 958 (1962).

SPECIFIC QUENCHING OF LUMINESCENCE OF ORGANIC COMPOUNDS DURING EXCITATION BY FAST ELECTRONS

S. F. Kilin and I. M. Rozman

During excitation or ionization of one molecule of organic compound, there is expended the energy of the fast electron, which is about 10 ev. Therefore, limiting value of yield of radioluminescence could be ~0.1 η photon/ev (η_f – quantum yield of fluorescence). In reality, yield is 4 [1]-8 [2] times less. This can be due to either the absence (or low efficiency) of transition of excitation energy from "nonluminescent" to "luminescent" states of the molecule [3-5], or to the presence of additional quenching [6]. For the purpose of checking the last assumption, we measured yields and durations of luminescence of a series of different organic substances. Obtained results, part of which are presented in works [7-10], undoubtedly testify to presence of dynamic quenching during excitation by fast electrons. Let us consider some of these results.

Duration of glow was measured on phase fluorometer (frequency of modulation $\omega = 1.26 \cdot 10^8$ sec^{-1}). From Fig. 1 one may see that for plastic scintillators containing additions of 1, 3, 5-triphenyl-Δ^2-pyrazoline [3PP] (3ФП) or 1, 1, 4, 4-tetraphenyl-1, 3-butadiene [TPB] (TФБ), phase angle during X-ray excitation φ_S becomes less than the angle during optical excitation of the actual luminescent addition directly φ_0, if its concentration C_A exceeds 0.04 mole/liter. For a scintillator containing ~0.2 mole/liter of 3PP, corresponding fluorometric times are equal to $\theta = 4.6$ and $\theta_0 = 6.7$ Nsec. Analogous reduction of duration of excited state (d.e.s.) of molecules of energy acceptor is also observed in liquid solutions (for instance, 3PP in toluene).

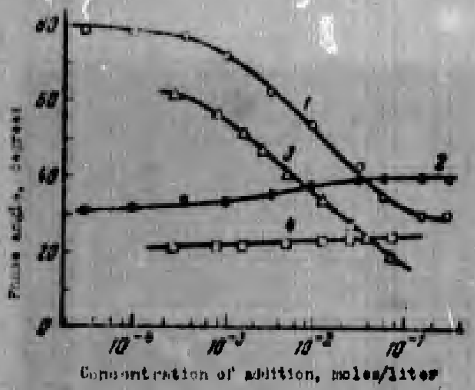

Fig. 1. Dependence of duration of glow of plastic scintillators on concentration of luminescent addition. Along the axis of ordinates is plotted phase angle of light of luminescence of addition. 1 and 2 – 1, 3, 5-triphenyl-Δ^2-pyrazoline (SPP) in polyvinyltoluene; 3 and 4 – 1, 1, 4, 4-tetraphenyl-1, 3-butadiene (TPB) in polystyrene. Curves 1 and 3 correspond to excitation by x-rays; 2 and 4 correspond to excitation by ultraviolet light (λ = 3200 Å – 3800 Å).

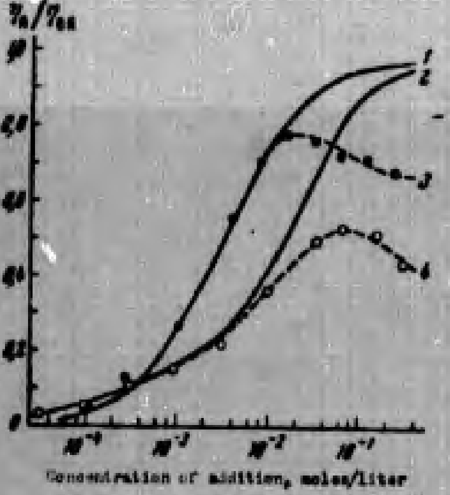

Fig. 2. Dependence of light yield of liquid (curves 1 and 3) and plastic (curves 2 and 4) scintillators on concentration of addition: 1, 2 – ratio of quantum yields of fluorescence of addition during optical excitation of solvent (λ = = 2652 Å) and of the addition directly (λ = 3650 Å) 3, 4 – ratio of luminous intensities during excitation by β-particles of preparation C^{14} and photons (λ = 3650 Å) (normalized to the region of low concentration).

The influence of specific quenching of acceptor on yield of luminescence during excitation by electrons may be seen from Fig. 2. This quenching greatly limits luminous efficiency of scintillators, since maximum output corresponds to a concentration of acceptor at which effectiveness of transfer of excitation energy to it is less than unity.

Thus, during excitation of plastic or liquid scintillators by fast electrons, there take place some processes able to cause deactivation of molecules of impurity which have obtained energy of electron excitation by means of transfer from the basic substance. Obviously these processes also have to quench excited state of molecules of energy donor. If for description of the phenomenon we use the Stern-Folmer equation with constant rate constants of the processes, then we will obtain the formula

$$\frac{I_{SA}}{\eta_{fA}} = \text{const}\,\frac{1 + \tau_{0Д} k_f C_A}{(1 + \tau_{0Д} k_{SД} + \tau_{0Д} k_f C_A)(1 + \tau_{0A} k_{SA})}. \qquad (1)$$

where $\tau_{0Д}$ and τ_{0A} are d.e.s. of molecules of donor and acceptor in the absence of transfer and specific quenching; k_t is specific rate constant of energy transfer; $k_{SД}$ and k_{SA} are rate constants of specific quenching of donor and acceptor. It is easy to see that this formula will not agree with experiment (Fig. 2).

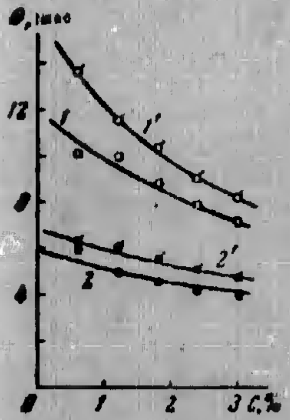

Fig. 3. Dependence of duration of glow of anthranilic acid in alcohol on concentration during optical (1 and 1') and X-ray (2 and 2') excitation. 1 and 2 – solutions saturated with air; 1' and 2' – the same solutions after bubbling with nitrogen.

Qualitative agreement with experiment is given by the following kinetic scheme. Processes of quenching act only for a certain time t_S and in a limited region of the solution V_S. They affect the yield of luminescence of acceptor in the following way: First they cause deactivation of part of excited donor molecules. This part decreases with growth of concentration of acceptor, since then rate of transfer of energy to it increases. Secondly, they cause deactivation of a certain part of acceptor molecules which obtain energy due to transfer. This part increases with increase of concentration due to growth of average duration of stay of excited acceptor molecules in the quenching zone. Considering also that donor molecules excited due to distant collisions are not subjected to the action of specific quenching (their fraction will be designated 1 - δ), it is possible to represent "quantum yield" of radioluminescence in the form

$$\frac{\eta_{SA}}{\eta_{0A}} = (1-\delta)\eta_{rt} + \delta(\eta_{St} - \gamma), \qquad (2)$$

where η_{rt} and η_{St} are efficiencies of transfer from donor to acceptor in absence of quenching of donor and in its presence; γ is efficiency of transfer with subsequent quenching of acceptor.

Quantities η_{rt}, η_{St} and γ can be calculated for different mechanisms of transfer and kinetics of quenching. However, the abundance of parameters whose numerical values are little known or quite unknown leaves great arbitrariness in quantitative comparison with experiment.

To obtain an estimate of parameters δ and k_S, there was conducted measurement of duration of glow of water and alcohol solutions in which transfer of energy from solvent was practically absent [7]. Duration of radioluminescence turned out to be considerably less than duration of fluorescence (Fig. 3). If we assume that quenching constant k_S is constant during t_S and is equal to zero at $t > t_S$, then for θ_S we will obtain the formula (Stern-Folmer kinetics, $\omega t_S << 1$)

$$\theta_S = \tau_f \frac{(1-\delta)(u^2+z^2)+\delta(1+u^2)+\delta(z-1)[z(1+\mu)+1-\mu u^2]\,e^{-\mu z}}{(1-\delta)(u^2+z^2)+\delta(1+u^2)z+\delta(z-1)[z(1-\mu u^2)-u^2(1+\mu)]\,e^{-\mu z}} \qquad (3)$$

where $u = \omega\tau_f$; $z = 1 + \tau_f k_S$; $u = t_S/\tau_f$; τ_f is the d.e.s. of molecules of dissolved compound. It contains three unknown parameters: δ, k_S, t_S. However, experimental data can be coordinated with dependence (3) only for values of δ satisfying inequality $\delta_{\text{мин}} \leq \delta \leq 1$. Numerical results for two values of t_S are given in the table. Selection t_S = 2 Nsec to a certain degree is justified by the idea of a "spreading apart" track. For values of parameters corresponding to t_S = 2 Nsec, the ratio of quantum yields of radio- and photoluminescence

$$\frac{\eta_s}{\eta_f} = 1 - \delta + \delta\,\frac{1+(z-1)\,e^{-\mu z}}{z} \qquad (4)$$

turns out to be equal to 0.17-0.20. In the case $t_S >> \tau_f$, it is equal to 0.40-0.50; i.e., specific quenching considerably weaker.

Values of Parameters δ and k_S Calculated by Means of the Formula (3)

Solvent	Luminescent compound	$t_S = \infty$			$t_S = 2 \cdot 10^{-9}$ sec			
		$\delta_{\text{мин}}$	k_S, 10^8 sec^{-1}		$\delta_{\text{мин}}$	k_S, 10^8 sec^{-1}		
			$\delta = 1$	$\delta = \delta_{\text{мин}}$		$\delta = 1$	$\delta = 0.94$	$\delta = 0.90$
Water	Quinine sulfate	0.65	0.62	2.5	0.92	9.8	13	–
Ethanol	Sodium salicylate....	0.84	1.4	4.2	0.94	9.3	16	–
Ethanol	β-Naphthylamine	0.66	0.63	2.6	0.90	10	13	18
Ethanol	Anthranilic acid.........	0.75	0.93	3.4	0.90	11	14	19

Thus, with certain selection of parameters t_S, δ and k_S, there can be obtained satisfactory agreement of ideas developed here, concerning specific quenching of radioluminescence, with experiment. In connection with this, it is of great interest to obtain values of these parameters both from independent experimental data and from theoretical estimates.

In conclusion, we will note one more important circumstance: Investigation of luminescence of alcohol solution of anthranilic acid containing quenching agent CCl_4 showed that in this region of the track where specific quenching acts, action of CCl_4 is strengthened. Rate constant of quenching here is equal to $k_q = 4.7 \cdot 10^9$ liter/mole·sec. For photoluminescence it is equal to $2.4 \cdot 10^9$ liter/mole·sec.

Literature

1. G. T. Wright. Proc. Phys. Soc., A68, 701 (1955).

2. Z. A. Chizhikova. Transactions of Physics Institute of Academy of Sciences of USSR, 15, 178 (1961).

3. M. D. Galanin and A. P. Grishin. Journal of Experimental and Theoretical Physics, 30, 33 (1956).

4. W. L. Buck. IRE Trans. on Nucl. Sci., NS-7, No. 2-3, 11 (1960).

5. J. B. Birks. Nuclear Electronics, Vol. 1, Vienna, 1962, p. 17.

6. S. F. Kilin and I. M. Rozman. Optics and spectroscopy, 6, 65 (1959).

7. K. A. Kovyrzina and I. M. Rozman. Optics and spectroscopy, 12, 248 (1962).

8. S. F. Kilin. Optics and spectroscopy, 12, 733 (1962).

9. S. F. Kilin, K. A. Kovyrzina and I. M. Rozman. Optics and spectroscopy. In the collection: Luminescence. Moscow, Publishing House of Academy of Sciences of USSR, 1963, p. 147.

10. S. F. Kilin and I. M. Rozman. Optics and spectroscopy, 15, 494 (1963).

TRANSMISSION OF ENERGY ABSORBED BY A SOLID BODY TO MOLECULES ON ITS SURFACE

Yu. A. Kolbanovskiy, Yu. V. Pepelyayev, L. S. Polak,
Yu. L. Khait and E. B. Shlikhter

There was studied gamma-radiolysis of n-heptane adsorbed on the following catalysts: γ-oxide of aluminum (I), aluminum-chromium, activated K_2O (II), aluminum-molybdenum (III), cobalt-aluminum-molybdenum (IV). Linear dependence of radiolysis rate (ΔP/gm C_7H_{16}·hr) on ratio of electronic fractions, catalyst II/heptane, in interval of values corresponding to the limiting cases of a monomolecular layer and a homogeneous system indicates that radiation energy transfer from catalyst to heptane occurs only in the monolayer. On the basis of formal-kinetic scheme there is conducted estimation of probability of transfer z, which strongly depends on preliminary conditioning of catalyst. With identical conditioning, separate values of $\Delta P = \varphi(z)$ for different catalysts lie on one straight line. The most active is the catalyst, irradiation of which together with the absorbed substance does not change the electron paramagnetic resonance [EPR] (ЭПР) spectrum as compared to the spectrum of the initial irradiated catalyst. The greater the change in spectrum (I < IV < II < III), the less active the catalyst is (I > IV > II > III). It has been established that the greater the electrical conductivity of the catalyst, the less the change of intensity of the EPR signal.

As one of the possible approaches for explanation of experimental results, there is proposed the so-called "activation model." Consideration is based on the fact that microcrystalline regions of a polycrystal during a short interval of time can be considered to be quasi-insulated, so that radiation energy absorbed inside microcrystal will leave time practically to reach equilibrium distribution inside it before energy is dissipated throughout the polycrystal. Then it is possible to consider the probability that radiation energy as a result of a random process, will be transmitted to the adsorbed molecule in a quantity sufficient for overcoming the activation barrier of the chemical process. It is clear that under the above made assumption it is possible to introduce idea about effective temperature, entropy, and so forth, and to obtain the following formula for probability of an elementary event:[1]

$$W = \frac{kT(a^{*}_{\text{эф}})}{h} \frac{d}{\Delta E^{*}} \theta S_V/V \exp\left\{-\frac{E}{kT_i}\right\},$$

which will agree qualitatively with experimental results.

During investigation of temperature dependence of rate of heterogeneous radiolysis, it was found that activation energy of chain process is 14.5 kcal/mole (whereas it is equal to 20-25 kcal/mole for homogeneous radiation-thermal cracking). Thus, temperature of beginning of chain reaction (reversal point on curve of ln G - 1/T) lies ~150°C lower than in the homogeneous process. These facts are explained by reaction of disintegration of adsorbed radicals weakly bound with the surface. There is indicated the presence of two competing processes for weakly bound radicals formed in the elementary event of disintegration: reactions of disintegration and recombination with surface (formation of a strong bond). There is estimated lifetime of weakly bound radical at 150°C, value of which turned out to be equal to about 10^{-6} sec.

During investigation of model reaction of interaction of hydrogen with Al_2O_3 under action of γ-radiation, it was shown that experimental results can be explained only in the presence of dissociative chemosorption with subsequent formation of a strong bond, apparently of OH type.

It was shown that in elementary events of considered process there participate atoms of hydrogen and surface active centers, whose number for reaction $H + Al_2O_3 \rightarrow$ strong bond is $\sim 10^{12}$ cm^{-2}.

For determination of number of active centers there was applied a new kinetic method, which is based on the fact that in a static system, integral form of kinetic equation depends on value of difference A between total number of surface active centers and number of reacting particles. In particular, for the reaction

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[1] Radiolysis of hydrocarbons. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 158.

of hydrogen with Al_2O_3, integral forms of kinetic equations have the form:

$$\frac{1}{lV^{0.5}}\left(\frac{1}{n^{0.5}}-\frac{1}{n_0^{0.5}}\right)=k't, \qquad A=0;$$

$$\frac{2}{l\sqrt{AV}}\operatorname{arctg}\sqrt{\frac{n}{A}}\Big|_0^t=k't, \qquad A>0;$$

$$\frac{1}{l\sqrt{|A|V}}\ln\frac{1-\sqrt{n/|A|}}{1+\sqrt{n/|A|}}\Big|_0^t=k't, \qquad A<0.$$

Discussion

G. M. Zhabrova. What is the true radiation-chemical yield, for instance of hydrogen, in that region where there is no temperature dependence?

Yu. V. Pepelyayev. Yields of all radiolysis products were not determined. Yield of gaseous products C_1-C_5 is 3 times as great as in a homogeneous medium.

V. V. Voyevodskiy. During transition to chain mechanism, composition of products should change. Did you detect these changes?

Yu. V. Pepelyayev. It is known that during homogeneous radiolysis there are observed strong increases of yields of unsaturated compounds with transition to the chain process. In our experiments unsaturated hydrocarbons are absent both at room temperature (non-chain process) and during the chain process.

A. M. Kabakchi. To what energy corresponds radiation yield of products during radiolysis of heptane — energy absorbed by gas, by solid body or on the boundary?

Yu. V. Pepelyayev. In case of heptane we referred radiation-chemical yield to energy absorbed by liquid.

CONCERNING THE QUESTION OF DIFFUSION OF EXCITONS IN MOLECULAR CRYSTALS

V. M. Agranovich

Earlier, in work [1], it was indicated that experimental study of temperature dependence of coefficient of diffusion of excitons in molecular crystals made it possible to clarify in what form energy of electron excitation migrates in these crystals and what mechanisms of scattering of excitons are the principle ones. Indeed, if transfer of energy of electron excitation is realized by excitons, motion of which is accompanied also by displacement of local deformation of lattice of crystal ("localized" excitons), then as it was shown in work [2], coefficient of diffusion of these excitons $D_{лок}$ increases with temperature rise so that at temperatures of crystal higher than Debye temperature ($T \geq T_D$),

$$D_{лок} = D_0 \exp\left(-\frac{Q}{kT}\right).$$

Conversely, in the other limiting case, when appearance of exciton is not accompanied by local deformation of lattice ("free excitons"), coefficient of diffusion of excitons at temperatures $T \geq T_D$ decreases with temperature rise, where law of this drop is essentially determined by that mechanism of scattering which leads to the diffusion character of displacement of exciton through the crystal. Thus, if the only mechanism of scattering of excitons is scattering on phonons, then (see [1])

$$D_{св} \sim \frac{1}{\sqrt{T}}; \qquad (1)$$

if, however, excitons are scattered mainly on lattice defects, then temperature dependence of coefficient of diffusion turns out to be essentially connected with temperature dependence of equilibrium concentration of thermal defects.

Indeed, noticing that in this case mean free path of exciton is equal to $1/\sigma C$, where C is concentration of thermal defects and σ is scattering cross section of exciton on thermal defect, we find that $D_{CB} \approx \frac{vl}{3} = \frac{v}{3} \cdot \frac{1}{C\sigma}$. Here v is average thermal velocity of exciton, determined from relationship $\frac{Mv^2}{2} = \frac{3}{2} kT$, where M is effective mass of exciton. This, as earlier in work [3], we use the fact that under the considered conditions (molecular crystals, not very low temperatures), time of thermalization of exciton $\tau_T \approx 10^{-12}$-10^{-13} sec (see [1]) is small as compared with its lifetime $\tau_0 \approx 10^{-8}$ sec.

Inasmuch as in molecular crystals intramolecular interaction considerably exceeds intermolecular interaction, it is natural to assume that under the influence of thermal motion, in crystal there can occur change of equilibrium orientation of molecule relative to the surrounding molecules. Equilibrium concentration of thermal "defects" is determined obviously from relationship $C = N_0 e^{-\frac{u}{kT}}$, where u is the least of activation energies of formation of thermal defects; N_0 is number of molecules per unit volume. On this assumption, coefficient of diffusion of "free" excitons

$$D_{CB} \sim \frac{\sqrt{T} e^{\frac{u}{kT}}}{\sigma(T)}; \qquad (2)$$

i.e., it practically exponentially drops with temperature rise, inasmuch as σ depends on T exponentially.

In the above considerations concerning diffusion of free excitons, it was implicitly assumed that as a result of scattering the exciton "remains" within limits of the same exciton zone. In reality, in molecular crystals, in the region of lowest excited states, there are usually several closely crowded exciton zones (energy distance of the order of 0.05 ev), which can be connected, for instance, either with Davydov splitting or with formation of electron-vibrational zones. This circumstance leads to the case in which only at very low temperatures does only the lowest exciton zone participate in the diffusion of excitons. At higher temperatures, "population" of other zones is also important. Thus, in the case of two zones (a case which is important for such crystals as anthracene, which have two molecules per unit cell), the realized coefficient of diffusion

$$\overline{D(T)} = \frac{D_1(T) + e^{-\frac{\Delta}{kT}} D_2(T)}{1 + e^{-\frac{\Delta}{kT}}}, \qquad (3)$$

where Δ is energy distance between zones; $D_1(T)$ and $D_2(T)$ are coefficients of diffusion of excitons in first and second zones.

From formula (3) it follows that at $D_2(T) \gg D_1(T)$ in a certain range of temperatures there can be observed with increase of temperature not decrease of coefficient of diffusion of free excitons, but, conversely, its growth. If, however, $D_1 > D_2$ in that same range of temperatures, there can be observed a sharper drop of $\overline{D(T)}$. If quantity Δ is small and has the order of kT, then at $D_2 \gg D_1$, in accordance with (3), $\overline{D(T)}$ at low T at first decreases with temperature rise, at $T = \Delta/k$ sharply increases, and at $T > \Delta/k$ again drops. From what has been said, it follows that in certain favorable cases study of temperature dependence of coefficient of diffusion of free excitons can make it possible to estimate distance between exciton zones.

As already was indicated in work [4], for study of temperature dependence $\overline{D(T)}$ there can be used investigation of energy transfer from basic substance to impurity at small concentrations of impurity, when distance between molecules of impurity is much larger than mean free path of exciton. Further experiments in this direction are very promising.

Literature

1. V. M. Agranovich and Yu. V. Konobeyev. Optics and spectroscopy, 6, 241 (1959).

2. M. Trlifai. J. Czeck. Phys., 6, 533 (1956).

3. V. M. Agranovich. Optics and spectroscopy, 3, 84 (1957); News of Academy of Sciences of USSR, physics series, 23, 40 (1959).

4. V. M. Agranovich and Yu. V. Konobeyev. Solid state physics, 5, 1373 (1963).

Discussion

A. S. Davydov. You assume that coefficients of diffusion in the two zones differ sufficiently sharply? It seems to me that there are no grounds to consider that these coefficients differ essentially from each other or that splitting can be noticeable.

V. M. Agranovich. From this point of view, the most interesting are sharply anisotropic crystals. Diffusion coefficient in the upper zone should be, it seems to me, less than the coefficient of diffusion in the lower zone because exciton in upper zone has more possibilities to be scattered. In order to note the considered effect, a difference in diffusion coefficients of 2-3 times is sufficient. If structure of zones is different, such a difference is not eliminated.

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POLARIZATION-LUMINESCENCE METHOD OF INVESTIGATION OF MIGRATION OF ENERGY IN MOLECULAR CRYSTALS

N. D. Zhevandrov

Luminescence methods of investigation of migration of energy in solid and liquid solutions are based on concentration effects or on differences between optical properties of solvent and impurity. It is obvious that these methods can be applied to the study of migration in single-component crystals and in mixed crystals — to the study of migration between molecules of impurity.

For study of migration of energy in these cases, we have used the polarization-luminescence method based on the independence of polarization of luminescence of molecular crystals from polarization of the exciting light. Essence of it is the following: From principle of dense packing it follows that in a crystal there are not one, but several types of orientation of molecules. Their oscillators of radiation with linearly polarized excitation will be excited with various probabilities. This difference depends on position of electrical vector of exciting light. It follows from this that the degree of polarization of luminescence should depend on polarization of exciting light. This dependence in turn should be determined by orientation of crystal. Without going into detail here, we will note that investigations have always been conducted with an orientation which should correspond to the sharpest dependence.

Calculations conducted for certain crystals show that dependence should be very strong; in individual cases, change of degree of polarization composes from -50 to +100%.

However, experiments conducted on single crystals of many substances have shown that polarization of luminescence in all cases absolutely does not depend on position of electrical vector of the exciting light. This result, paradoxical at first glance, can be explained if we assume that in the crystal there occurs migration of excitation energy, as a result of which during the time of existence of excited state initial anisotropy created at the moment of excitation by polarized light is lost.

However, for confidence in this result, it is necessary to remove or to take into account a series of crystal-optical factors which complicate this phenomenon – in the first place, birefringence of the exciting light. The fact is that splitting of the exciting beam into components polarized in definite ways, which propagate in the crystal with different velocities, can also lead to independence of polarization of luminescence from polarization of excitation.

In order to remove this difficulty, we used different methods. Among them the most effective is to carry out excitation along the optical axis or to work with very thin single crystals (thickness d of the order of tenths of a micron, so that there is satisfied the condition $d\Delta n \ll \lambda$). There were also thoroughly taken into account other factors: optical activity, dichroism, secondary luminescence and others.

Results of all these experiments permit us to consider that independence of polarization of luminescence from polarization of excitation is proof of migration of excitation energy in crystals and can serve for a method of its investigation.

The character of the proposed method, which works on the "molecular level", makes it a sensitive and fine tool for investigation. As an example of its application can serve investigation of migration of energy between molecules of impurity. There was investigated anthracene with impurity of naphthacene with concentration of 10^{-3}-10^{-5} gm/gm in the form of thin single crystals (thickness about 0.5 μ) excited by light with a wave length (436 mμ) which is absorbed only by naphthacene and is not absorbed by anthracene. For small thickness of crystals and low concentration of impurity, intensity of its luminescence is very weak. Thus even a small "impurity" of light exciting anthracene can seriously distort results of experiment. We developed a special method overcoming these difficulties, and with its help we showed that between molecules of impurity (naphthacene) there occurs migration of energy up to concentrations of $6 \cdot 10^{-5}$ gm/gm. This corresponds to average distance between molecules of 26 lattice constants or 208 Å, where migration in this case cannot be explained by either resonance or exciton mechanisms, but has a specific nature.

It was possible to apply the described method to investigation of migration of energy in pure and mixed molecular crystals not only at room temperature, but also at the temperature of liquid nitrogen, and also to crystals of other types (for instance ionic crystals). Thus, in single crystals of zinc sulfide activated by copper, an analogous effect is apparently explained by migration of holes in the crystal.

The question is discussed in greater detail in the articles: N. D. Zhevandrov, Reports of AS USSR, 88, 677 (1952); 100, 455 (1955); N. D. Zhevandrov. News of AS USSR, physics series, 26, 67 (1962); N. D. Zhevandrov, V. I. Gribkov and Sh. D. Khan-Magometov. Optics and spectroscopy, 11, 629 (1961); 13, 96 (1962).

Discussion

V. L. Tal'roze. What decay time of the excited state did you take in your consideration?

N. D. Zhevandrov. De-excitation time was obtained from fluorometric data and composes several nsec.

V. L. Tal'roze. What are the smallest lifetimes which it is possible to measure by this method?

N. D. Zhevandrov. About 10^{-9} sec.

V. V. Voyevodskiy. What proofs exist that molecules of impurity (naphthacene) are not introduced into anthracene in the form of dimers, trimers, etc.?

N. D. Zhevandrov. The absence of such combinations is indicated, apparently, by the high yield of luminescence of naphthacene in anthracene. It is known that pure crystalline naphthacene does not fluoresce. The low solubility of naphthacene in anthracene also indicates the introduction of molecules alone.

V. V. Voyevodskiy. The latter circumstance rather indicates the possibility of formation of an inhomogeneous medium, and not a solution.

Question: How were microimpurities introduced into crystals?

N. D. Zhevandrov. Impurities were introduced into the melt from which the batch was crystallized, after which single crystals were grown by sublimation. Concentration of impurities in single crystals was determined spectroscopically.

V. I. Lakhovitskiy. Do you exclude the possibility of distribution of impurities by an unoriented method?

N. D. Zhevandrov. Yes. It was shown that polarization of luminescence of the base (anthracene) and impurity (naphthacene) are close to one another in their characteristics. This indicates that during their introduction, molecules of naphthacene are oriented just as molecules of the basic substance.

GENERAL DISCUSSION

Kh. V. Protopopov. What elementary processes lead to deactivation of excited molecules? Apparently a certain contribution to deactivation of molecules is introduced by temperature quenching. However, the main role is played by exciton processes. At large distances, in the case of benzene and alkyl benzenes, octupoles are important. At small distances, decomposition of the interaction into multipoles is impossible, and it is necessary to consider these systems not as point systems. Radii of interaction have to be small only due to resonance. It is possible that in the condensed phase, where distances are small, an essential contribution is given by the mechanism proposed by Dexter, i.e., energy transfer during overlapping of electron shells of neighboring molecules.

What is the role of microstructure of liquids in migration of excitation energy? What are peculiarities of microstructure of liquid and solutions in neighborhood of excited molecules? If in the liquid there is sufficiently high short-range order, then generation of exciton and its scattering on the region of short-range order will be possible; however, an actual free exciton cannot appear here due to the large number of defects. In neighborhood of exciton, which is localized on several molecules in the liquid, due to resonance forces short-range order can be greatly increased, and thus there occurs protection of the exciton from extinguishing by thermal collisions. Thereby, the system resists exchange of energy on phonons. Namely such a case is specific for liquids. Is there possible, then, an exciton mechanism? Yes, this is possible.

In what cases is propagation of electron excitation in condensed organic systems not diffusion propagation, but directed propagation? A certain directivity at distances of up to 5 molecular diameters is possible in the case of the average bond; in the case of the weak bond there occurs diffusion of excitation.

What are the peculiarities of processes of kinetics of energy transfer in condensed organic systems realized by free and localized excitons? For fast quasi-free excitons, processes of transfer and quenching apparently have to be statistical, and to be determined by probabilities that near the excited molecule there is a molecule to which energy will be transferred. In the case of free excitons, directivity can introduce a certain contribution to kinetics, but this question is debatable.

In the report I talked about self-regulation and self-organization. These terms are used not in the cybernetic sense. In the neighborhood of an excited molecule, orientation of short-range order is increased, and the wave of ordering propagates in the substance together with the excitation. Ordering itself favors an orientation of molecules which facilitates energy transfer, and this bond in view of the existing potential well for excitation protects from thermal collisions. Thus the exciton always moves in a "coat" of ordered and molecules organized in a certain way.

A. S. Davydov. My first remark pertains to the report of Kh. V. Protopopov. In crystals, excited states are divided into two types: exciton and local. In the locally excited state, one molecule is excited and the lattice around this molecule is deformed. Furthermore, excitation can embrace a certain region and shift through the crystal. This is purely exciton excitation. However, there is possible an intermediate case when the lattice is deformed within a comparatively large volume, including tens of molecules, and excitation of distribution is over all these molecules. Then excitation energy will be a function of the configuration of these molecules, and the configuration in turn will depend on excitation energy. This is that feedback which was discussed here. Such excitations in three-dimensional lattices turn out to be disadvantageous, but in one-dimensional systems they are possible, with energy less than for the usual free exciton.

Deformations in a crystal which are caused by the excitation itself disturb the lattice, and for this there is required energy; it is possible that in a liquid deformation will lead to a certain "crystallization"; thus, energy connected with excitation and energy connected with formation of a certain order will "help" each other. Therefore, it is possible that these formations will appear more easily in a liquid than in crystals. Thus, deformation in crystals is connected with destruction of the lattice, and in liquids – with formation of one; i.e., work is accomplished only against the thermal motion. Thus, it is not necessary that molecules be aligned in parallel. Rather, their location will be like the orientation in a crystal, where molecules are not parallel, but are oriented in a definite way. But this can be more advantageous than the disordered state, when on these molecules there is distributed excitation, and this excitation can, while gradually rearranging the liquid, migrate through the liquid.

There appeared the question about boundary conditions. If the sample has sufficiently large dimensions, then boundary conditions do not have essential value; it is necessary only that there be included a sufficiently large number of lattice constants. Also important is homogeneity of the substance; then displacement of the exciton is possible. Apparently such formations in liquids are more natural than in crystals.

Now I will dwell on the question of transfer of excitation energy between two molecules. Time for transfer of excitation between identical molecules should be inversely proportional to the third, and not the sixth power of distance. In particular, this law will be observed for distances between molecules of the order of 1/4 λ, where λ is length of the wave connected with that energy whose transfer is occurring, i.e., for comparatively large distances. Therefore, it seems natural that in experiments of N. D. Zhevandrov transfer is realized to a distance of up to 26 lattice constants; in systems with uniform molecules, energy can be transferred to a distance of up to 50 lattice constants. If molecules are not identical, then there will be realized the $1/r^6$ law, and transfer of excitation will depend on overlapping of spectra.

R. F. Vasil'yev. There were noted two ways of creation of excited states – the influence of radiation and light. Excited states can also appear due to energy released during chemical reactions, i.e., due to chemiluminescence. This method of excitation was used in the gas phase in order to obtain excited states of such physically stable, but chemically unstable molecules as, for example, CN, CO, CH, C_2, etc. In the liquid phase this method was not applied, since those few reactions in liquid phase which are accompanied by bright chemiluminescence are very complicated and confused, and there still have not been identified carriers of the glow; i.e., there have not been identified excited states.

Several years ago, in the Institute of Chemical Physics of the Academy of Sciences of the USSR, there was revealed weak glow during liquid-phase reactions proceeding by a simple, well studied mechanism. Detailed investigations of chemiluminescence with such reactions (thermal disintegration, liquid-phase oxidation) showed that these are complicated processes having several stages. It was possible to analyze these complicated processes and to study every stage separately.

Thus, during oxidation of hydrocarbons, excitation of glow occurs in elementary events of recombination of peroxide radicals, where it was shown that there are formed carbonyl compound in triplet electron-excited states. With this process there competes the process of formation of these carbonyl compounds in the unexcited state, and chemiluminescence itself is a result of radiative transition from excited state to ground state. It is natural that with the process of radiation compete all those processes which usually compete with radiation during other methods of excitation, i.e., processes of nonradiative deactivation with transition to the ground level (in liquid phase this occurs with participation of the quenching agent). Furthermore, there can occur energy transfer to another substance, to an activator, with its excitation and subsequent emission of a quantum of light by this activator. These questions are discussed in detail in the report. Now I want to emphasize that this new region is being intensely developed, both along the line of study of pure chemiluminescence during chemical reactions, and along the line of study of weak chemiluminescence revealed in biological systems (biochemiluminescence). The number of works in this region is small, but fully sufficient for discussion on a wide scale.

M. D. Galanin. In the report of Kh. V. Protopopov, there was expressed a very interesting assumption with respect to the existence of excitons in liquids.

Apparently, we do not now have experimental data about transfer of energy in liquids — data for which there would be required a cardinal reconsideration of existing models, construction of a new theory and, in particular, introduction of a hypothesis about excitons in the radiolysis of liquid media.

In connection with this, I would like to make the following remark — first, with regard to octupole-octupole interaction between aromatic molecules. Apparently transitions for the considered aromatic molecules are dipole transitions, although these are forbidden. Therefore, in examining them, we have to consider not multipolarity of ground state, but the moment of the transition (dipole).

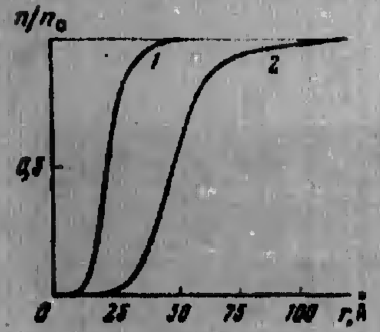
Secondly, it seems to me undesirable to interpret the magnitude of the experimental effect as a function of average distance between molecules. It is more correct to speak, thus, of concentration. Average distance between molecules in no way determines the probability of transfer, since this probability very sharply depends on distance.

Thirdly, as A. S. Davydov correctly emphasized, during interaction of identical molecules, there should be obeyed the $1/r^3$ law. However, when we deal with a excited molecule and with a molecule in the ground state, it is impossible to speak about identical molecules, since it is obvious that these molecules are in different electronic states.

Kh. S. Bagdasar'yan. I want to consider the case of energy transfer by the $1/r^6$ mechanism. There are many mechanisms of energy transfer, but this mechanism has been most fully developed theoretically. Therefore, in the first place it is desirable to clarify the boundaries of its applicability. For comparison of experimental data with theory, it is necessary to determine concentration dependence of some effect connected with energy transfer. Here is a simple case: diffusion of particles can be disregarded, for instance, when process of energy transfer occurs in a sufficiently viscous medium. Let us consider a stationary process, i.e., continuous excitation and spontaneous deactivation as well as deactivation under the influence of the energy acceptor (quenching agent). In this case it is possible to speak about a certain definite probability of detection of a certain excited particle at a certain definite distance r from the molecule of quenching agent. It is possible to say that there is a certain definite distribution function of excited particles around the molecule of quenching agent. This distribution function is obtained from the equation which N. N. Tunitskiy considered in his report:

$$\frac{\partial n}{\partial t}=\frac{D}{r}\frac{\partial^2 (nr)}{\partial r^2}-kn-\frac{\alpha n}{r^6}+\beta=0.$$

Here n is concentration of excited molecules; β is rate of generation of these molecules; α is energy transfer coefficient; k is constant of spontaneous deactivation in the absence of quenching agent.



Distribution function of excited molecules: r – distance between interacting molecules; 1) $\alpha = 10^{-32}$ cm^6 × × sec^{-1}; $k = 10^8$ sec^{-1}; 2) $\alpha = 10^{-30}$ cm^6·sec^{-1}; $k = 10^8$ sec^{-1}.

Let us consider the stationary case when $\partial n/\partial t = 0$ and also the case when it is possible to disregard diffusion $D = 0$. Then we immediately obtain distribution function $n = \dfrac{\beta/k}{1 + \alpha/kr^6}$ (see figure). Along the axis of abscissas there is plotted the distance between interacting molecules. At a sufficiently large distance, where action of quenching agent no longer appears, concentration of excited molecules is taken equal to unity. As can be seen, at sufficiently large α the stationary concentration drops practically to zero at a considerable distance from the molecule of quenching agent.

Around molecules of quenching agent are created very considerable concentration gradients of excited particles. When medium is mobile and diffusion is possible, we will have diffusion flux to molecules of extinguisher, which will to a greater or lesser degree distort the form of the distribution function, depending upon parameters α and k. If law of distribution is known, then fraction of excited molecules which will transmit their energy to molecules of quenching agent is determined by the quantity

$$\gamma = \frac{\int\limits_{R_0}^{R_\nu} 4\pi r^2 n \frac{\alpha}{r^6}\,dr}{\int\limits_{R_0}^{R_\nu} 4\pi r^2 \beta\,dr}.$$

where R_0 is sum of radii of reacting particles; R_ν is radius of sphere for one molecule of quenching agent:

$$\frac{1}{\nu} = \frac{4}{3}\pi R_\nu^3.$$

Carrying out integration, we will obtain dependence of effect of quenching on concentration of molecules of quenching agent ν:

$$\gamma = \frac{4}{3}\pi\nu\sqrt{\frac{\alpha}{k}}\,\mathrm{arctg}\left(\frac{3}{4\pi\nu}\sqrt{\frac{k}{\alpha}}\right).$$

Hence we may see that there is no simple relation between law of interaction and character of dependence on concentration ν. Therefore, direct transition from the law of interaction to certain average distances and the concentration dependence of the quenching effect seems to me to be groundless. This equation is of the type of the Stern-Volmer equation.

For small concentrations of quenching agent, there is obtained the formula

$$\gamma = \frac{2}{3}\pi^{2}\nu\sqrt{\frac{\alpha}{k}},$$

which permits us to compare the quantity $\frac{\alpha}{k}$ with experiment. Our formula differs somewhat from that which was derived by Förster and M. D. Galanin.

V. V. Voyevodskiy (concerning the report of N. N. Tunitskiy and Kh. S. Bagdasar'yan). Insofar as I understand formulation of the problem, the matter reduces to the following. Rate of interaction of B^* molecules with A in your case sharply drops with distance. From this it follows that molecules which are nearer react faster than those which are farther away. For this reason there can be observed a diffusion distribution, and it is diffusion which takes B^* into that zone where the reaction occurs. At the same time there is introduced the boundary condition $(\partial n/\partial r)_{R_0} = 0$; i.e., it is assumed that at the wall nothing occurs with the molecule (this follows from the fact that flux through the wall is equal to zero). It seems to me that there is a certain contradiction here. For its removal it is necessary to introduce a stricter condition. For example, we assume that there is a boundary layer of thickness Δr and that in the volume $4\pi r_0^2\Delta r$ there is a certain rate of interaction equal to α/r_0^6. Diffusion takes B^* into this layer with a rate proportional to $(\partial n/\partial r)_{r_0+\Delta r}$. Then

$$(4\pi r_0^2\Delta r)\, n_{r_0}\frac{\alpha}{r^6} = -\left(\frac{dn}{dr}\right)_{r=r_0} 4D\pi r_0^2$$

or

$$\frac{n_{r_0}\alpha}{r_0^6} = -\left(\frac{dn}{dr}\right)_{r_0} D$$

(band $\Delta r = r_0$). This will be absolutely strict and should lead, in the limit, to the same laws in the case considered by N. N. Tunitskiy and Kh. S. Bagdasar'yan. Indeed if α is so large that $n_{r_0} = 0$, then also $\left(\frac{dn}{dr}\right)_{r_0} = 0$, and it is possible to use any of these equalities as a boundary condition. If, conversely, $\alpha = 0$, then $\left(\frac{dn}{dr}\right)_{r_0} = 0$, but then $n_{r_0} \neq 0$, and finally, if α has an intermediate value, then it is necessary to look for solution in more complicated form.

I would like to make yet another general remark. In the greater part of the reports concerning mechanisms and models of transfer of energy and experimental proofs of these models, there was allotted much attention to theoretical considerations. I would like to turn attention to two experimental reports[1] in which, it seems to me, there is formulated some new model of energy interaction of particles in the irradiated system. This model leads us, on the basis of specific photochemical data (and not theoretical reasoning), to the fact that it is impossible to consider an excited aromatic molecule, in the solid phase, as well as in the liquid phase, apart from the medium surrounding it. We are obliged, thus, to take into account the existence of an "aggregate" of molecules. There appears the question of whether this concept can be applied to the problem about transfer of energy in the gas phase: maybe the interaction of hot atoms with molecules cannot be considered as their interaction with a separate C — H or C — C bond, but rather the hot atom + molecule system should be considered as a whole. I would like to turn the attention of theoreticians namely to such a possibility. In my opinion, it is possible to formulate some directed investigation of this question jointly with the experimenters.

L. S. Polak. Experimental data assumed at the basis of our theoretical consideration can be divided into three groups:

1) the composition of radiolysis products which we obtain in different ways does not change. Apparently excitation is taken from electron levels, so to say, up to the stage of chemical reaction;

2) inhibiting curves evidently have two segments. I do not consider the transition zone;

3) during radiolysis of cyclohexane in the presence of small impurities of benzene, benzene is not expended.

This set of experimental facts needs explanation. The most important of them to me is the concentration dependence, and any theory should explain this basic experimental fact first of all.

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[1] See reports of M. T. Kuz'min, L. V. Berezin, B. M. Uzhinov and B. N. Shelimov, N. V. Fok, V. V. Voyevodskiy in the present collection.

V. A. Krongauz. I want to say several words about mechanisms of energy transfer in liquids. First of all, it is necessary to clearly differentiate aliphatic and aromatic liquids. It seems to me that in the report of I. G. Kaplan there was not conducted a sufficiently clear delimitation. The absence of a delimitation is also noticeable during the derivation of certain relations which Yu. A. Kolbanovskiy, A. M. Brodskiy and their co-authors performed. In aromatic solvents, as follows from a series of experimental data, transfer of energy occurs essentially by a different mechanism than in aliphatic solvents. In particular, this is due both to the difference in lifetime of the excited state and with the difference between distances of transfer, i.e., to the mechanism of transfer. For instance, such a mechanism as jump of excitation from one molecule of aromatic solvent to another, let us say to benzene, is apparently not realized until it reaches an acceptor molecules. Weinreb [1] formulated direct experiments, which showed that if we dilute toluene with any inert solvent, for instance cyclohexane, then from this the efficiency of energy transfer from solvent does not decrease. If, however, there are ten molecules of cyclohexane for one molecule of toluene, then this eliminates transfer by means of jump of excitation from one molecule of toluene to another.

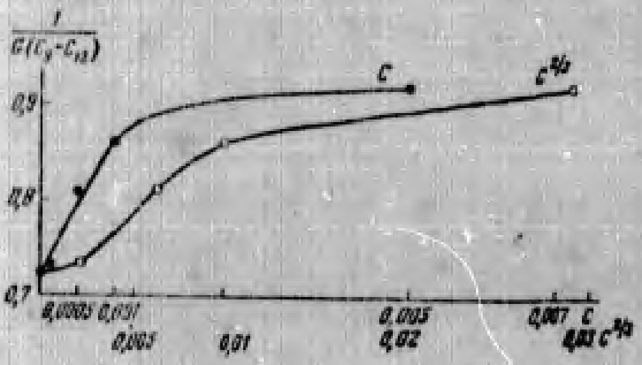

Fig. 1. Dependence of the reciprocal radiation yield of products C_9-C_{12} of radiolysis of n-hexane on concentration of benzene to the 2/3 and 3/3 powers (according to [4]).

In the case of aliphatic solvents, certain facts of inhibiting ascribed to energy transfer are a direct result of accepting of radicals. In any case it is necessary to consider that with addition of iodine or benzene to cyclohexane, lowering of yield of products is partially caused by accepting of radicals.

I would like to illustrate by experimental data the realization of the "2/3" and "3/3" laws which A. M. Brodskiy spoke of. In Figs. 1-3, according to data mentioned in works [illegible] and [4], there are constructed graphs of the dependence of effect of energy transfer on concentration of acceptor to the degree 2/3 and 3/3 powers. As can be seen, there are no grounds to consider that linear dependence for the 2/3 power is fulfilled better than for the 3/3 power.

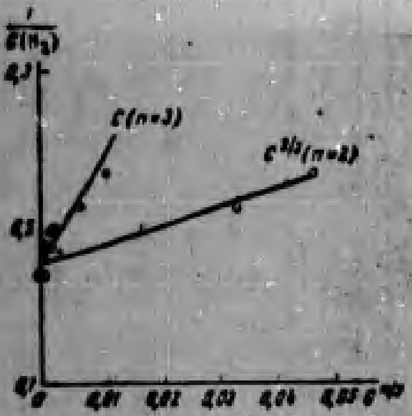

Fig. 2. Dependence of reciprocal of radiation yield of decomposition of benzoyl peroxide in benzene on concentration of anthracene (in relative units).

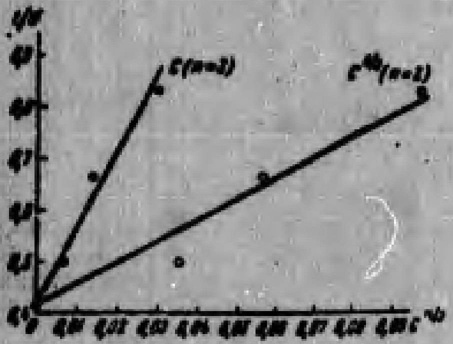

Fig. 3. Dependence of reciprocal of radiation yield of hydrogen during radiolysis of cyclohexane on concentration of I_2 (in relative units).

Finally I should say that character of concentration dependence cannot in any way serve as a basis for selection of one mechanism of reaction or another, since with all mechanisms at low concentrations there essentially occurs competition between deactivation and energy transfer, and yield will depend linearly on concentration. At high concentrations there is observed saturation, which is natural for any mechanism of energy transfer. I consider that the most important criterion during selection of a mechanism is composed of the absolute values of constants, which in the theory proposed by A. M. Brodskiy and Yu. A. Kolbanovskiy cannot be calculated, apparently, in view of the uncertainty of parameter A [3].

Literature

1. S. Cohen and A. Weinreb. Proc. Phys. Soc., B69, 593 (1956).

2. Yu. A. Kolbanovskiy and L. S. Polak. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 65.

3. A. M. Brodskiy and Yu. A. Kolbanovskiy. Reports of AS USSR, 139, 1081 (1961).

4. L. S. Polak and A. S. Shcherbakova. Petroleum chemistry, 2, 339 (1962).

I. G. Kaplan. I want to discuss on the theory of dependence of efficiency of transfer of energy on concentration which was presented in the report of A. M. Borodskiy. In the equation which is given in the report, there are contained three terms: The first reflects dependence from $1/R^2$, the second – $1/R^4$, and the third – on $1/R^6$. These terms are included in the following way:

$$W \sim \frac{1}{R^6}\left[1 + \left(\frac{\lambda}{2\pi R}\right)^2 + \left(\frac{\lambda}{2\pi R}\right)^4\right].$$

where W is probability of transfer. As has already been indicated in the report of A. M. Brodskiy, the first term ($1/R^2$) becomes determining only in the case when concentration of addition $C < 5 \cdot 10^{-5}$ mole/liter. However, not one experimental point was obtained in this region. Therefore, it is not understandable now the authors determined that in this region there is a sharp bend. Even if these terms were important, then with transition from a model system of interaction of two molecules to the problem in the medium, i.e., with transition to concentrations, averaging over the probabilities of finding molecules near each other is necessary. This is done in detail in works of Förster, Dexter and others. There is obtained quite a complicated exponential dependence, which with transition to low concentrations gives a dependence on concentration C to the first power. With transition to large C there occurs saturation, as should be expected. During taking into account terms $1/R^2$ and $1/R^4$, another dependence at small distances should not be obtained. The same calculations were performed for dipole-quadrupole interactions by Dexter, when probability of transition depends on distance as $1/R^8$. Even in this case, at small concentrations there is revealed dependence on C to the first power.

As was shown in preceding works of A. M. Brodskiy and co-authors, dependence on $C^{2/3}$ was obtained in the following way. Integral of probability of transfer W:

$$\int_{R_1}^{R_2} CW 4\pi R^2 \, dR, \quad \text{where } R \sim \frac{1}{\sqrt[3]{C}}, \quad R_2 \sim \frac{10}{\sqrt[3]{C}}.$$

was taken from the average distance to a certain large distance. Since the biggest contribution must be given by molecules which are at a distance closer than average, such disregard of the influence of neighboring molecules is incompetent. Disregard of influence of neighboring molecules and expression of limits of integration in terms of concentration led the authors to a dependence on concentration to the 2/3 power.

A. Ya. Temkin. Several remarks about diffusion equation in report of Kh. S. Bagdasar'yan: There are considered low concentrations (maximum concentration of excited molecules $\sim 10^{19}$ $1/cm^3$). Since lifetime of excited molecules is very small, they cannot arrive from somewhere from afar; they arrive only from a limited region of space near molecule of inhibitor. It is necessary to estimate dimensions of this zone around excited molecules. In practice, at low concentrations, number of excited molecules in this zone is small, and fluctuations of their number can be of the order of the average number of these molecules. Then the idea of concentration loses meaning.

The second remark: how would be possible to derive a criterion of applicability of the diffusion equation in integral form? Molecule B^* lives for a certain time τ (up to the transfer of excitation). During this time it can diffuse to a distance L. It is necessary to select a physically small volume in which there will be at least tens of molecules B^*. Magnitude of this volume is l^3. Condition of applicability of diffusion equation is that $l \ll L$. It is necessary to make such an estimate. If it is not satisfied, it is necessary to use integral or integro-differential kinetic equation.

N. N. Tunitskiy indicated that it is possible to use the conclusion of Smolukhovskiy, according to which corresponding diffusion coefficients are simply added. Meanwhile, the Smolukhovskiy proof pertains to motion of heavy particle in a medium of light molecules. At every collision the heavy particle receives a small impulse. This is the condition for transition from integral equation of theory of random walks to the Fokker-Planck differential equation. It is not satisfied when mass of particle is close to mass of molecules. Likewise, in theory of slowing-down neutrons, it is impossible to pass from kinetic equation to age equation in hydrogen-containing media. Therefore, we cannot take into account motion of inhibitor molecules by summing up diffusion coefficients.

The whole study was conducted for local region around molecules of inhibitor. In order to compare obtained results with experiment, it is necessary to produce summation over all these regions. Such summation leads to more "gently sloping" functions of dependence on distance than those which were given. Until such summation is made, it is impossible to relate results of calculation with experiment. This problem is analogous to the problem about tracks, where results of calculation for one track are averaged over the whole volume.

Yu. L. Khait. I want to discuss certain questions touched upon in the report of Yu. A. Kolbanovskiy and others. Let us consider briefly the question about transfer of energy absorbed by a solid body to molecules located on its surface.[1] We tried consecutively to consider the influence of temperature and ionizing radiations on

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[1] This question is considered in more detail in the monograph "radiolysis of hydrocarbons," Moscow, Publishing House of Academy of Sciences of USSR, 1962.

rate of activation processes. In the beginning, there were considered thermal activation processes in condensed bodies, taking into account the collective process of random localization of energy satisfying condition $E' \geq E \geq kT$ on separate bonds from a certain surrounding region, dimensions of which were calculated. Calculated rate of thermal activation process contains the pre-exponential factor

$$\nu_0 \sim e^{E/\varepsilon},$$

i.e., a factor which exponentially depends on activation energy E and does not depend on temperature. This permits us to approach the question of a compensating effect from a new point of view.

Further we tried to consider influence of ionizing radiations on rate of activation processes. Influences of heavy and light particles will be somewhat different. Let us consider electron with speed v and energy ε considerably exceeding excitation and ionization energies; motion of electron is considered classically. There is studied probability of excitation of molecule by the variable electric field created by the electron at distance v from its trajectory. For this purpose, there can be applied non-stationary perturbation theory. With its help it is possible to show that noticeable contribution to transitions with energy ΔE will be given by molecules located inside a cylinder of radius $r \approx hv/\Delta E$. Thus, there are considered relatively slow electrons ($\varepsilon \approx 10^2$ ev), for which a consistent theory of their interaction with molecules is absent. As a result, there are created local increases of density of excited states, which in our case can be described by means of introduction of local temperature, entropy, etc.

If on surface of solid body there is a monolayer of hydrocarbon or other substance, then it is possible to consider question about transfer to it of energy from solid body. For subsequent layers, such transfer is practically absent.

V. B. Kazanskiy. Will parameters of track depend on energy of particles?

Yu. L. Khait. Yes, they will, inasmuch as in formula of radius of track there is contained energy of particle $r \approx h\sqrt{2\varepsilon}/\Delta E\sqrt{m}$.

Theories of slowing-down of fast particles, due to Bethe, Bloch and others which are valid for particles with high energies, are practically invalid for the considered relatively slow particles, which forces us to use semiclassical methods. Thus, the motion of electron is considered to be classical, and transition probabilities in molecules under influence of field of electron are considered to be quantum-mechanical.

V. B. Kazanskiy. What is lower threshold of energy of electrons for which considered approximation is applicable?

Yu. L. Khait. Lower threshold of energy is determined by the fact that DeBroglie wavelength λ should be small as compared to dimensions of particles of medium and impact parameters.

V. L. Tal'roze. Are there direct experiments confirming the considerations presented by you?

Yu. L. Khait. For checking of ideas expressed in work of Yu. A. Kolbanovskiy and others, there are necessary direct, simple experiments. The proposed method represents a generalization of the method of consideration of thermal activation processes which has been checked with a wide group of substances, for instance during diffusion in solid bodies. Furthermore, earlier published data on heterogeneous radiolysis of alkanes and work reported here indicate qualitative coincidence of the considered physical concepts with experiment.

N. N. Tunitskiy. What physical theory and what temperature do you have in mind?

Yu. L. Khait. Some effective temperature, i.e., local temperature of a certain region of fixed dimensions describing concentration of electrons at corresponding levels which are created by an electron passing through. Real temperature of lattice can be lower. Question about interaction of slow particles with molecules of a medium with lowering of energy of particles has not finally been clarified. Interaction of electron and medium is considered with the help of perturbation theory.

Question. What is the radius of the track and how many particles are in it?

Yu. L. Khait. If energy of particle is of the order of one hundred electron volts, then radius of track is several tens of angströms. Hence it is possible to calculate the number of particles.

A. G. Kotov. I would like to present certain experimental facts, apparently having a relation to the question discussed here about mechanism of energy transfer from solid phase to molecules adsorbed on its surface. It is known that on the surface of preliminarily untreated silica gel or fused quartz (in this case they are equivalent, and experimental results, on the qualitative side, pertain to one as well as to the other) there is adsorbed water, and after γ-irradiation at the temperature of liquid nitrogen there is observed atomic hydrogen on the surface.

However, atomic hydrogen is observed not only after γ-irradiation of silica gel, but also after irradiation (with soft ultraviolet light from a mercury lamp of type [DRSh] (ДРШ) of silica gel preliminarily γ-irradiated and heated to room temperature. In dependence upon the time of irradiation, the intensity of one of the lines of the EPR spectrum of atomic hydrogen characterizing concentration changes along a curve which can be described by the yield and limiting concentration, where for a larger dose of preliminary γ-irradiation, limiting concentration and yield are greater. Under these conditions, dissociation of a molecule of water is possible only as a result of some mechanism of transfer of energy of a quantum absorbed by a color center of silica gel to a molecule of water adsorbed on the surface. This conclusion is confirmed by experimental results with thermo- and photodiscoloration. Depending upon heating temperature of γ-irradiated quartz, concentration of atomic hydrogen formed during a constant time of irradiation at 77°K decreases. Temperature range of this decrease coincides with data of source material on thermodiscoloration. During photodiscoloration, i.e., after prolonged irradiation at room temperature, concentrations of atomic hydrogen formed during a constant time of irradiation at 77°K also decrease along a curve close to exponential.

Concerning the mechanism of energy transfer, it is possible to say the following: since energy of affinity of a molecule of water (0.9 ev) and even of an OH radical (~2 ev) to an electron is insufficient for dissociation of the O – H bond in a molecule of water, as well as in an OH radical (5 ev), then participation of electrons located at the bottom of the conduction band without any additional effects seems doubtful. Besides, there still has not been revealed an influence of temperature on yield of atomic hydrogen which can be imagined by analogy with the temperature dependence of photoconductivity in the presence of F-centers. It is possible that in the given case there is some other mechanism of energy transfer without participation of electrons in the conduction band, for instance an exciton mechanism.

G. B. Pariyskiy (to A. G. Kotov). What characteristics of paramagnetic resonance spectra for the atom of hydrogen do you observe?

A. G. Kotov. Splitting – 500 gauss, line width – 0.8 gauss, g ≈ 2. The obtained EPR spectrum does not at all differ from the EPR spectrum found with γ-irradiation.

G. M. Zhabrova (concerning transfer of energy absorbed by a solid body). The question of transfer of energy of ionizing radiation in a solid body is very important for radiation catalysis. A radiation catalyst can only be a system which is able to transmit energy to molecules sorbed on its surface. There appears the question of whether the mechanism of energy transfer is connected with electronic properties of the solid material on which the ionizing radiation acts. I will discuss results of work conducted by colleagues of the catalysis laboratory, Institute of Chemical Physics of Academy of Science of USSR, V. I. Vladistrova, B. M. Kadenatsi and me, jointly with V. B. Kazanskiy and G. B. Pariyskiy.

There were investigated, by sorption, kinetic and EPR methods, a series of catalysts possessing various electronic properties (insulators, good semiconductors and semiconductors with low conductivity). Catalytical activity of compounds with respect to dehydrogenation of cyclohexane to benzene decreases in the following order:

$$NiO > ZnO > MgO > Al_2O_3 > SiO_2.$$

From the point of view of usual catalysis, the best catalysts are good semiconductors. In our case the best catalyst is NiO, and SiO_2 is practically not a catalyst in the reaction of dehydrogenation of cyclohexane to benzene. We tried to carry out this reaction by purely radiation means in range of temperatures from -196 to +20°C, where it is thermodynamically forbidden and consequently occurs only at the expense of radiation energy which can be transmitted through the solid body to molecules of cyclohexane. It was clarified what catalysts possessing good conductivity are inactive in this process. In the radiation process insulators work best of all.

The catalyst which is active in usual catalysis is inactive in radiation catalysis, and conversely. A radiation catalytical process sharply differs from homogeneous radiolysis. Homogeneous radiolysis of cyclohexane does not reach to benzene: here hydrogen is detached, and there are formed cyclohexane and dimerization products. In the radiation catalytical process there are carried out reactions of dehydrogenation, with formation of cyclohexene and benzene, isomerization, cracking and condensation. Consequently, here there is observed selectivity of the action -- acceleration of thermodynamically impossible reactions; i.e., there is revealed the specific character of transfer of energy absorbed by a solid body during irradiation to molecules of cyclohexane adsorbed on surface of the catalyst. By the EPR method it was clearly shown that on all catalysts which are the most active in this process there appears the radical C_6H_7 — an intermediate product of the radiation-catalytical process. At the same time, in homogeneous process of radiolysis of cyclohexane there are observed C_6H_{11} radicals.

Thus electronic properties of an irradiated solid body render a very significant invluence on process of energy transfer from solid body to reacting molecules. Mechanism of energy transfer is apparently electronic.

ADDITIONAL MATERIALS ON THE QUESTION OF TRANSFER OF ELECTRON EXCITATION ENERGY

A. S. Davydov

On the Question of Energy Migration

1. It seems to me that the most original theoretical proposition was made by Kh. V. Protopopov concerning the possibility of formation of excitations of the type of "orientons" in certain liquids. It has not been excluded that in a liquid the excitation can embrace a certain region which is fluctuatingly ordered both with respect to orientation and location of molecules, and then support this ordering. The excitation, together with a certain ordering, will be displaced in the liquid. Not the molecules will shift, but only their region of ordering. There is necessary theoretical development of this question. Finding experiments for confirmation of such formations is very important.

2. In the report of I. M. Barkalov, V. I. Gol'danskiy and others,[1] it was sufficiently convincingly shown that polymerization in solid phase is caused by short-lived states. It has not been excluded that such short-lived states are excitations propagating along the growing polymer chain. For clarification of the mechanism of polymerization in the solid phase, there are necessary theoretical and experimental investigations.

3. Migration of energy inside a molecule from one part of it to another and migration of energy from one molecule to another in gas, liquid and solid phases can occur in many competing ways. A considerable place at this symposium has been

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[1] See page [illegible] of this collection.

stricted to discussion of the nonradiative exciton mechanism of energy transfer. In examining of exciton excitations, it is not always considered that this excitation is concentrated not on one molecule, but embraces a certain region of the crystal. There is necessary theoretical investigation of the question of how this excitation becomes heat, radiation and energy of chemical reactions.

The contemporary theory of diffusion of excitons originates from the idea that excitation has a local character. There is necessary a theory which would explicitly take into account the distribution of excitation energy. This distribution of excitation over a certain region of a crystal covering hundreds of molecules ensures its relative stability and the small probability of its conversion to heat.

4. For clarification of role of migration of energy in process of polymerization there are necessary theoretical calculations of exciton states in polymer chains. Hardly justified is the simple transfer of ideas developed for crystals to one-dimensional objects containing hundreds of atoms. In my last work[1] it was shown that exciton states in thin crystal films containing hundreds of molecular layers possess a series of peculiarities.

If polymerization occurs in liquid or solid phase, then it is necessary to consider further the effect of the surrounding medium consisting of monomers. In certain cases, in the presence of a medium, there is possible formation of excitons of Van'ye-Mott type (electron and hole). Displacement of Van'ye-Mott excitons of large radius along the chain is equivalent to displacement of an ionic state.

There has absolutely not been studied the question of migration of energy along a saturated chain. In saturated hydrocarbons, in electron excitation there can participate only σ-electrons; therefore, excitation should be accompanied by large deformations of the molecules. There is also possible displacement of vibrational excitation along the chain.

5. One of the basic characteristics of the process of transfer of excitation from one molecule to another molecule located at a fixed distance from the first is duration of transfer of the excitation. During theoretical estimation of this quantity, we usually rely on works of Förster and Dexter, which were based on the use of the perturbation theory formula

$$\frac{2\pi}{\hbar}(\psi_f|V|\psi_i)|^2\rho(E_f)$$

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[1] A. S. Davydov. ZhETF (Journal of Experimental and Theoretical Physics), 45, 783 (1963).

for probability of transition per unit time from state ψ_1 to state ψ_f under the action of interaction operator V. This formula and all its results are valid only for intervals of time which are small as compared to the lifetime of state ψ_1. It is easy to show that this formula gives an incorrect value during calculation of time of excitation energy transfer between identical molecules. In this case the problem can be solved exactly (if we consider only two energy levels). There is necessary creation of a theory of transfer of excitation energy between molecules which would have a wider region of applicability.

6. At present there is practically absent a theory of transfer of excitations corresponding to triplet states. It is possible to expect that in the process of transfer of such excitations, of especially great importance will be the medium surrounding the molecule.

CONCERNING THE QUESTION OF MIGRATION OF ENERGY IN THE LIQUID PHASE

Kh. V. Protopopov

1. Resonance Energy Transfer in Aromatic Solutions

According to Weinreb [1], M. D. Galanin [2], T. P. Belikova and M. D. Galanin [3], in aromatic liquid solutions resonance energy transfer of electron excitation from solvent to solute supplemented by transfer of energy due to diffusion of molecules predominates. This point of view is not unique. Kallmann and colleagues [4, 5] consider that here fast migration of energy through molecules of solvent is important. Burton and colleagues [6, 7] and also Heller [8] develop the concept of domains. The author of this article accepts, with certain refinements, the theory of domains and supplements the latter with an orienton mechanism of migration of energy [9].

Undoubtedly, energy transfer from some excited state (in the simplest case – from an excited molecule) of the solvent to a molecule of solute represents a resonant process. It is necessary only to note that the Förster theory of resonance [10] in the form in which it is used in works [1-3] is unsuitable for usual aromatic solutions. Förster himself on this matter notes: "In any case I do not recommend the calculation of efficiency of energy transfer in liquid benzene by means of formulas published earlier, since these formulas correspond to a weak bond only with dipole-dipole interaction" [11]. Energy transfer with participation of higher multipoles, which is characteristic for aromatic solutions, can efficiently occur only to distances not exceeding molecular diameters [11].

On the other hand, Weinreb [12], investigating in detail the influence of Brownian movement on energy transfer in liquid scintillation systems, found that "consideration of Brownian movement does not fully explain, although it decreases the divergence between experimental values of efficiencies of transfer and values which should be expected according to Förster's theory." Furthermore, according to [6, 7], for such systems, rate constants of energy transfer to activator and quenching of solvent by oxygen are 4-5 times as great, and according to [4, 5] are approximately an order of magnitude greater than in the case of energy transfer by means of diffusion of molecules.

Thus, data on the character of resonant interaction, on the influence of diffusion of molecules and on values of rate constants of energy transfer and quenching processes will not agree with the theory of resonance with diffusion. Therefore, the theory of energy transfer in aromatic liquid solutions by means of resonance, taking into account diffusion, at least in that form in which it is presented in works [1-3] is erroneous.

2. Excited Domains in Liquids

Excited states in domains of liquids can be similar to those local non-stationary excited states which appear initially in molecular crystals and are nuclii of free excitons. Such states are described as the superposition of stationary states of the system with coefficients depending on time. This dependence describes increase of the region of initial localization of excitation (expansion of exciton wave packet) in time [13]. It is possible to expect that such local states appear initially in domains of liquids and then spread to all molecules of the domain [9]. The excitation wave, which corresponds to stationary state of the system, obviously cannot appear in the domain due to the limitedness of its dimensions, its short lifetime and imperfection of the structure as compared to crystal structure.

According to work [7], domains of benzene or toluene give the main contribution to energy transfer at concentrations of activators greater than 0.02 mole/liter not only in binary solutions, but also in ternary systems of the type of cyclohexane — benzene — terphenyl, at concentrations of diluents (paraffins) attaining 90%. This This apparently explains the high values of efficiencies of energy transfer in similar systems with diluents which were obtained in work [1].

3. Concerning Properties of Orientons

Formation of orientons in liquids is facilitated by the fact that resonance forces increase exactly that short-range order in the neighborhood of the excimer which is created by the usual Vander Waal's forces. Therefore, arrangement of molecules in an orienton should be similar to their stacking in corresponding crystals [14].

It is important that the orienton represents a self-consistent system appearing during interaction of a local exciton with its surrounding medium and creating conditions which promote preservation and motion of the local exciton. The "potential well" formed around the excimer during this interaction promotes localization of the exciton. Besides, the shell of bound molecules protects the exciton from external disturbances. It is interesting that to the orienton there corresponds not only a "potential well," but also a unique "entropy well," since the degree of ordering in it grows from the edges toward the center. Moreover, to the orienton there is inherent a definite structure. It consists of the following parts, which essentially differ with respect to the binding force between molecules: an excimer, which is the "nucleus" of the orienton; the inner shell, which is bound with the excimer by resonance forces; and the outer shell, which is of fluctuation origin. Rearrangement of excimer entails rearrangement of shells of the orienton.

It is very significant that motion of the orienton, which occurs without transfer of substance, can possess a certain directivity [9]. In works [15, 16] it is shown that on curves giving dependence of light yield of scintillation in aromatic solutions on average distances between molecules of activator, there are revealed the gently sloping sections which are expected during directed motion of orientons.

An important argument in favor of the orienton theory is experimental discovery of the effects of increase of quantum yields and de-excitation times, which are expected in this theory [15, 16], and also discovery of long-wave shift of luminescence spectra with increase of concentration of benzene and xylene [17], and also napthalene [18] and anisole [12] in the diluents. There are of course necessary experimental works on direct detection of orientons. In particular, orientons can be revealed by change of Rayleigh scattering of infrared spectra, indices of refraction, and also of dielectric and diamagnetic properties of aromatic liquids and solutions during intense, brief photoexcitation [15, 16]. Under these conditions, it would be interesting to investigate the possibility of Davydov splitting [19] in electronic spectra of liquids.

Also necessary are works on creation of the classical and quantum theories of orientons, and also investigation of cybernetic properties and the biological importance of orienton states.

Literature

1. S. G. Cohen and A. Weinreb. Proc. Phys. Soc., B69, 593 (1956).

2. M. D. Galanin. Transactions of Physics Institute of Academy of Sciences of USSR, 12, 3 (1960).

3. T. P. Belikova and M. D. Galanin. Optics and spectroscopy, 1, 163 (1956).

4. H. Kallmann and M. Furst. Liquid Scintillation Counting. New York – London. Pergamon Press, 1958, p. 3.

5. F. H. Brown, M. Furst and H. P. Kallmann. Organic and Inorganic Materials. New York – London, Wiley, 1962, p. 100.

6. S. Lipsky and M. Burton. J. Chem. Phys., 31, 1221 (1959).

7. J. M. Nosworthy, J. L. Magee and M. Burton. J. Chem. Phys., 34, 83 (1961).

8. A. Heller. Israel Atomic Energy Commis (Repts). 1961, No. 699.

9. Kh. V. Protopopov. Present collection, p. 127.

10. T. Förster. Ann. Phys., 2, 55 (1948).

11. T. Förster. In: Comparative Effects of Radiation. New York – London, Wiley, 1960, Disc., p. 320.

12. A. Weinreb. J. Chem. Phys., 34, 91 (1961).

13. R. M. Hochstrasser. Revs. Modern Phys., 34, 531 (1962).

14. A. S. Davydov. Present collection, p. 180.

15. Kh. V. Protopopov. Candidates dissertation, Leningrad, 1961.

16. V. O. Vyazemskiy, A. N. Pisarevskiy, Kh. V. Protopopov, and others. The scintillation method in radiometry. Moscow, Atomizdat, 1961.

17. T. V. Ivanova, T. A. Mokeyeva and B. Ya. Sveshnikov. Optics and spectroscopy, 12, 586 (1962).

18. A. Dammers de Klert. Molec. Phys., 1, 141 (1958).

19. A. S. Davydov. Theory of absorption of light in molecular crystals. Kiev, Publishing House of Academy of Sciences of Ukrainian SSR, 1951.

CONCERNING THE ELECTROMAGNETIC MECHANISM OF ELECTRON EXCITATION ENERGY TRANSFER DURING RADIOLYSIS OF DILUTE SOLUTIONS

I. G. Kaplan and M. D. Galanin

The electromagnetic mechanism of transfer of energy of electron excitation developed in works [1-5], to which the report of A. M. Brodskiy and others is dedicated, differs from the electrostatic mechanism of resonance dipole-dipole transfer developed by Förster [6] in that it takes into account lag. Such a lag during electromagnetic interactions must be considered at distances comparable with the interaction wavelength λ. Estimates show that the effect starts to show up at concentrations of impurity $C < 10^{-5}$ mole/liter. Probability of transfer at such large distances between molecules will be much less than the probability of spontaneous decay of the excited state. This signifies that mechanism of transfer of energy of electron excitation between molecules of solvent and impurity at distances $\sim\lambda$ reduces reabsorption, which has been studied thoroughly in optics. Direct nonradiative transfer does not occur to such distances.

Dependence of probability W of transfer on concentration of impurity, which is given in works [1-5] (at low concentrations $W \sim C^{2/3}$ and $W \sim C$ at $C > 10^{-5}$ mole/li[illegible] causes serious objections. With transition from the model problem of interaction of two molecules to interactions in a medium, it is considered that the basic contribution is given by molecules of impurity located at the average distance from the excited molecule of solvent. However, in connection with dependence of probability of energy transfer on distance $W \sim 1/R^n$, the contribution from near and distant molecules of impurity will greatly differ. Approximation by means of introduction of average distance is incorrect, and from the fact that probability of transfer decreases as $1/R^n$, it does not follow that it depends on concentration as $C^{n/3}$. The correct dependence on concentration of impurity for the resonance mechanism of transfer in those cases when diffusion is immaterial is given in works of Förster [6], Dexter [7] and M. D. Galanin [8]. At low concentrations of impurity, the probability of transfer is proportional to the first power of concentration.

Thus, consideration of lag of interaction for radiation chemistry is immaterial, and the concentration dependence advanced in works [1-5] is theoretically groundless.

Literature

1. A. M. Brodskiy and Yu. A. Kolbanovskiy. Reports of the AS USSR, 139, 108 (1961).

2. Yu. A. Kolbanovskiy and L. S. Polak. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 64.

3. A. M. Brodskiy, Yu. A. Kolbanovskiy and L. S. Polak. Petroleum-chemistry, 2, 54 (1962).

4. A. M. Brodskiy, Yu. A. Kolbanovsky and L. S. Polak. Intern. J. Appl. Radiation and Isotopes, 13, 148 (1962).

5. Radiolysis of hydrocarbons. Moscow, Publishing House of Academy of Sciences of USSR, 1962, Chapter V.

6. T. Förster. Fluoreszenz organischer Verbindungen. Göttingen, 1951.

7. D. L. Dexter. J. Chem. Phys., 23, 836 (1953).

8. M. D. Galanin, ZhETF (Journal of Experimental and Theoretical Physics), 28, 485 (1955).

ON MIGRATION (TRANSFER) OF ENERGY WITH PARTICIPATION OF TRIPLET STATES OF ORGANIC COMPOUNDS

V. L. Yermolayev

In radiation-chemical reactions, undoubtedly, an essential role is played by processes involving participation of triplet metastable molecules of organic compounds. Appearance and disappearance of triplet states frequently are the result of nonradiative transfer (migration) of energy of electron excitation. Transfer of energy from triplet molecules can occur by two mechanisms: exchange-resonance and inductive-resonance. Excitation of molecules in triplet state is effectively carried out only during exchange-resonance interactions.

1. Solid Solutions

a) By the exchange-resonance mechanism there is carried out transfer of energy from triplet organic molecules to unexcited singlet molecules, with transition of the latter to the triplet state. This form of transfer can induce optically forbidden transitions. For exchange-resonance transfer there is necessary at least slight overlapping of electron shells of interacting molecules; i.e., it occurs at distances of 10-15 Å. Triplet level of donor molecule should be located higher than triplet level of acceptor. Transfer of energy by this mechanism is permitted if the Wigner rule of conservation of total spin in the process of transfer is obeyed. Transfer has the form

$$^{3}\Gamma_{\text{Д}} + {}^{1}\Gamma_{A} \rightarrow {}^{1}\Gamma_{\text{Д}} + {}^{3}\Gamma_{A}.$$

A considerable part of triplet donor molecules transmit their energy to acceptor by the triplet-triplet mechanism at concentration of acceptor in the solid solution $5 \cdot 10^{-2}$ - $5 \cdot 10^{-1}$ moles/liter.

Literature

V. L. Yermolayev. Dissertation, Leningrad, 1958.

V. L. Yermolayev. Present collection, p. 133.

V. L. Yermolayev. UFN (Progress in Physical Sciences), 80, 3 (1963).

A. N. Terenin and V. L. Yermolayev. News of AS USSR, physics series, 26, 21 (1962).

b) In solid solutions there can take place processes of transfer of energy from triplet molecules of donor to acceptor, which has an intense absorption spectrum overlapping with phosphorescence spectrum of donor. Transfer occurs by inductive-resonance mechanism at distances of 25-60 Å. As a result of transfer, triplet molecule of donor is deactivated, and molecule of acceptor passes into excited singlet state, i.e.,

$$ {}^3\Gamma_{\text{Д}} + {}^1\Gamma_{\text{A}} \rightarrow {}^1\Gamma_{\text{Д}} + {}^1\Gamma_{\text{A}}^{*}. $$

Transfer does not obey the Wigner rule. In it there is realized competition of two intercombinationally forbidden transitions: radiation of phosphorescence in donor molecule and nonradiative transfer. Only optically allowed transitions are effectively induced.

Literature

Theory: M. D. Galanin. Transactions of Physics Institute of Academy of Sciences of USSR, 12, 3 (1960); T. Förster. Ann. Phys., 2, 55 (1948); Disc. Faraday Soc., 27, 7 (1959).

Experiment: V. L. Yermolayev and Ye. B. Sveshnikov. News of AS USSR, physics series, 26, 29 (1962); Reports of AS USSR, 149, 1295 (1963); V. L. Yermolayev. Present collection, p. 133.

2. Liquid Solutions

a) Triplet-triplet energy transfer occurring by exchange-resonance mechanism is especially effective in liquid de-oxygenated solutions and vapors. In liquid solutions, rate constant of triplet-triplet transfer process is close to the diffusion constant. Since time of existence of triplet aromatic molecules in absence of oxygen in most cases is very great, even in liquid solutions (10^{-6}-10^{-3} sec), then transfer occurs with high efficiency even at low concentrations of acceptor (benzene, 293°K, $[O_2] \approx 0$, $\tau_{TR} = 10^{-5}$ sec, concentration of acceptor $[A] \approx$ $\approx 10^{-6}$-10[illegible] mole/liter).

Literature

A. N. Terenin and V. L. Yermolayev. News of AS USSR, physics series, 1962, 26, 21 (and literature indicated in article).

b) With respect to the possibility of triplet-singlet transfer of energy in liquid solutions, the question is still vague. First observations in this direction have been made by R. F. Vasil'yev (see the present collection, p. 155).

3. Crystals

A number of works appearing in recent years indicate the possibility of effective migration of energy in crystals through triplet levels ("triplet exciton"). The mechanism is apparently exchange-resonance.

Literature

V. L. Yermolayev. UFN (Progress in Physical Sciences), 80, 3 (1963).

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2. FORMATION AND BEHAVIOR OF IONS AND ELECTRONS IN SOLID ORGANIC MEDIA

FORMATION OF ION-RADICALS DURING RADIOLYSIS OF FROZEN ORGANIC LIQUIDS AND POLYMERS CONTAINING DISSOLVED ADDITIONS

Kh. S. Bagdasar'yan

The present article presents a short survey of certain investigations [1-3] conducted in recent years in the laboratory of the author.

During action of γ-radiation on solutions of 0.005 mole/liter aromatic amines (diphenylamine, triphenylamine) in a mixture of methylcyclohexane and isopentane frozed at -196°C, there occurs formation of cation-radicals of amines, which can be identified by their absorption spectra in the visible region. Spectrophotometry should be carried out at the temperature of liquid nitrogen, since during heating of solution to room temperature there occurs irreversible disappearance of cation-radicals. Accumulation of cation-radicals is limited to a certain maximum concentration, which cannot be exceeded either by increase of concentration of amine or increase of dose; for cation-radicals of triphenylamine, the limiting concentration is equal to $\sim 10^{-5}$ mole/liter.

Analogous phenomena are observed during γ-radiolysis at -196°C of films of polymethyl methacrylate containing aromatic amines (to 0.2 mole/liter): diphenylamine, triphenylamine, β-naphthylamine, phenyl-β-naphthylamine, n-phenylene diamine, N, N-dimethyl-para-phenylenediamine, [DMPD] (ДМФД) and others. In these systems the limiting concentration of cation-radicals attains 10^{-3} mole/liter.

Initial radiation yield of formation of cation-radicals in hydrocarbon glass is equal to 0.16 (triphenylamine, 0.005 mole/liter) per 100 ev of energy absorbed by the entire system. In polymethyl methacrylate, yield is equal to ~3 (DMPD, 0.1 mole/liter). These data indicate a sensitization mechanism of formation of cation-radicals: energy absorbed by substrate causes ionization of amine.

During simultaneous presence of two amines in polymethyl methacrylate, there is observed "competition" in the formation of cation-radicals. Thus, at equal concentrations of β-naphthylamine and triphenylamine (0.06 mole/liter, dose $0.7 \cdot 10^{20}$ ev/gm), film is colored pink (cation-radical of β-naphthylamine). With a sixfold surplus of triphenylamine, the film is colored blue (cation-radical of triphenylamine). During simultaneous presence of n-phenylene diamine and DMPD (0.1 mole/liter each, dose $1.4 \cdot 10^{20}$ ev/gm), cation-radicals of both amines are formed in similar concentrations. Analogous experiment performed in hydrocarbon glass with mixture of diphenylamine and triphenylamine showed predominant formation of cation-radicals of diphenylamine. Experiments with the mixture of amines confirm sensitization mechanism of formation of cation-radicals and will agree with the assumption about the predominant ionization of amines with lower ionization potential.

Growth of electron-acceptor properties of medium increases yield and limiting concentration of cation-radicals. In polymethyl methacrylate, limiting concentration of cation-radicals is $\sim 10^2$ times as high as in hydrocarbon glass. In polyisobutylene there is not revealed formation of cation-radicals of DMPD and triphenylamine. Addition of carbon tetrachloride to hydrocarbon glass increases yield of formation of cation-radicals of diphenylamine. At concentration of CCl_4 equal to 0.05 mole/liter, concentration of cation-radicals is increased by ~3.5 times, and does not increase at higher concentrations of CCl_4.

Addition of small quantities (0.005 mole/liter) of dimethyl ether or diethylene glycol (electron donor) to hydrocarbon glass noticeably increases yield of anion-radicals of diphenyl (green color, $\lambda_{\text{макс}} = 650$ mμ), styrene (dark pink color, $\lambda_{\text{макс}} = 570$ mμ), carbon tetrachloride (dirty pink color, $\lambda_{\text{макс}} = 490$ mμ) and napthalene. These results agree with data of work [4]. Thus, yield of formation of both cation-radicals and anion-radicals is to a considerable degree determined by ability of medium to hold electrons, or accordingly positive holes, in traps sufficiently deep for the given temperature.

Under favorable conditions, every ionizing event of the substrate leads to formation of cation-radical (DMPD in polymethyl methacrylate) or anion-radical (diphenyl in tetrahydro-2-furan [4]). Yield of ion-radical in these systems is equal to ~5.

Formation cation-radicals apparently occurs as a result of migration of positive hole and approach of it to molecule of amine. Tunnel transition of electron from amine to hole completes the process. Probability of tunnel transition increases with decrease of ionization potential of amine. This permits us to understand the effect of competition.

In a polymer medium, transition of electron from amine to hole leads to protection of polymer from chemical transformations, since this way of neutralization of positive charge of the polymer molecule leads to release of comparatively little energy, which is equal to difference between ionizing energies of polymer molecule and amine (anti-rad effect). Introduction of aromatic amines and certain other electron-donor molecules into polymethyl methacrylate (β-naphthol, dithionyl disulfide) leads to decrease of yield of breaks of polymer chain by 1.5-3 times. It is possible that part of breaks occur as a result of electronic excitation of polymer chain and not its ionization. This part of breaks cannot be prevented by presence of amines.

It is necessary to emphasize that photochemical formation of cation-radicals of aromatic amines in frozen media [5] undoubtedly occurs by a completely different mechanism and is characterized by a low quantum yield, of the order of 10^{-3} [6].

Experiments described in this report open interesting possibilities for systematic investigations of electronic and ionic processes and processes of energy migration occurring in the condensed phase during action of ionizing radiation. At present these investigations are being conducted in our laboratory in different directions.

Literature

1. Kh. S. Bagdasar'yan, V. A. Krongauz and N. S. Kardash. Reports of AS USSR, 144, 101 (1962).

2. Kh. S. Bagdasar'yan and Z. A. Sinitsyna. Reports of AS USSR, 147, 1396 (1962).

3. R. I. Milyutinskaya and Kh. S. Bagdasar'yan. Journal of Physical Chemistry, 38, 770 (1964).

4. P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne and W. H. Hamill. J. Am. Chem. Soc., 84, 500 (1962); M. R. Ronayne, J. P. Guarino and W. H. Hamill. J. Am. Chem. Soc., 84, 4230 (1962).

5. G. Lewis and D. Lipkin. J. Am. Chem. Soc., 64, 2801 (1942).

6. W. C. Meyer and A. C. Albrecht. J. Phys. Chem., 66, 1167 (1962).

Discussion

A. T. Koritskiy. 1. Are there observed EPR signals in your systems?

2. Were negative ions observed by the optical method?

3. Was appearance of additional color observed upon the introduction of CCl_4?

Kh. S. Bagdasar'yan. 1. Works in this direction are being conducted. EPR signals are observed.

2. We did not observe optical absorption of negative ions in these systems. Possibly this is explained by the small coefficient of absorption of these ions.

3. No, this was not observed.

V. L. Tal'roze. Is it possible to indicate the chemical processes to which formation of ion-radicals leads?

Kh. S. Bagdasar'yan. The difficulty consists of small concentrations of products formed in our experiments. Investigation of decrease of molecular weight of polymers showed that additions play a protective role.

V. L. Tal'roze. Is it impossible to explain observed absorption spectra by complexes with charge transfer?

Kh. S. Bagdasar'yan. Such a possibility exists, since optical absorption spectra of separate ions and complexes with transfer of charge can be very similar.

A. T. Koritskiy. What is the mechanism of formation of ions?

Kh. S. Bagdasar'yan. Formation of ions can occur both as a result of charge transfer and as a result of excitation transfer.

A. T. Koritskiy. Were there conducted experiments on change of color of irradiated samples under action of light of various wavelengths?

Kh. S. Bagdasar'yan. Such experiments are being planned.

V. V. Voyevodskiy. 1. What are the considerations in favor of homogeneous distribution of addition throughout the medium?

2. What is the radiation yield in conversion to amine?

Kh. S. Bagdasar'yan. 1. Glasses and polymer films investigated by us were always optically transparent, which indicates homogenous distribution of additions (solution).

2. In conversion to amine, radiation yield is approximately 100-300.

INVESTIGATED BY OPTICAL METHODS OF ELECTRONS STABILIZED IN CERTAIN SATURATED HYDROCARBONS

V. G. Nikol'skiy, V. A. Tochin and N. Ya. Buben

It is known that during low-temperature radiolysis of organic substances, in them, in a considerable quantity, there are accumulated stabilized ions [1-3]. In order to obtain data about nature of traps in which electrons are localized during radiolysis of saturated hydrocarbons, in this work there were investigated color and photoluminescence of samples of hexane, nonane, 2.4-dimethyl undecane, tetradecane, cyclohexane, dicylcohexyl-4-decane, 1.2-dicyclohexyldodecane and high-pressure polyethylene irradiated with fast electrons at a temperature of 77°K. Dose of radiation varied from $5\cdot10^{4}$ to $2\cdot10^{8}$ rad.

All investigated hydrocarbons acquire during radiolysis a yellow-brown color, intensity of which increases with increase of dose. It has been revealed that after radiolysis samples of saturated hydrocarbons luminesce at 77°K under action of light. Spectrum of this glow (photoluminescence) constitutes a smeared-out band in the range of 4000-6000 Å.

Preliminary experiments have shown that coloring of investigated substances during radiolysis and their photoluminescence are not connected with formation of stable radiolysis products or with accumulation of stabilized alkyl radicals. This is indicated, in particular, by the disappearance of color during heating of an irradiated sample or during its illumination at a temperature of 77°K. In such thermally optically "bleached" samples, photoluminescence is not observed.[1]

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[1] With optical "bleaching" the concentration of stabilized alkyl radicals does not change.

These results have allowed us to conclude that coloring and photoluminescence of saturated hydrocarbons irradiated at 77°K basically are mainly determined by stabilized ions.

It has been shown that photoluminescence of irradiated hydrocarbons has a recombination character. This is witnessed, for instance, by the fact that in spectral composition this glow lies further into the shortwave region than the light exciting it.

In the work there were investigated: dependence of intensity of photoluminescence of irradiated sample on wavelength of exciting light (spectrum of excitation of photoluminescence) in the range of 4000-10,000 Å, change of excitation spectrum with dose, and also change of excitation spectrum of photoluminescence, which is observed during prolonged illumination of irradiated sample by monochromatic light. Besides this, for irradiated samples of polyethylene absorption spectrum at a temperature of 77°K and dependence of absorption coefficient on dose were investigated with the help of spectrophotometer [SF-2M] (СФ-2M).

Results obtained thus show that in the beginning of radiolysis of saturated hydrocarbons there occurs stabilization of electrons in traps of various types. However, even at doses ~0.1 Mrad the main part of captured electrons (70%) is localized in deep traps - from 2 to 3 ev. With increase of dose, concentration of electrons stabilized in shallow traps decreases; at doses of about 10 Mrad practically all electrons are captured in traps with depth greater than 2 ev. Redistribution of stabilized electrons in traps testifies to the fact that in the process of radiolysis, in the substance there are formed deep traps, the concentration of which increases with dose, at least up to several tens of Mrad.

Apparently these deep electron traps appearing in the process of radiolysis of saturated hydrocarbons consist of stabilized alkyl radicals. In particular, the following experimental data of this work agree well with the earlier expressed [4] assumption about stabilization of electrons on radicals:

predominant stabilization of electrons on deep traps (2-3 ev);

identical form of excitation spectra of photoluminescence for samples of all compounds irradiated at value of dose from 10-100 Mrad, independently of substance and its state of aggregation;

symbatic change of coefficient of absorption and concenctration of radicals with dose for samples of polyethylene irradiated with electrons at 77-100°K;

change of excitation spectrum of luminescence with increase of dose.

It is necessary to note that stabilization of electrons on deep traps revealed in this work testifies to the fact that recombination of ions during heating of an irradiated sample will be determined not by thermal releasing of the electron, but by thawing out of molecular mobility and migration of centers of capture. Indeed, it is easy to estimate that thermal ejection of electron from such traps (2-3 ev) will begin only at temperatures of 500-800°K, whereas all substances investigated by us pass into the liquid state at lower temperatures. In connection with this, conclusions about depths of electron traps which can be made during the analysis of form of curves of thermal de-excitation do not have physical meaning in this case.

Literature

1. J. H. Pannell and B. Manning. J. Chem. Phys., 23, 1368 (1955).

2. R. S. Alger, T. H. Anderson and L. A. Webb. J. Chem. Phys., 35, 49 (1961).

3. Ye. L. Frankevich and B. S. Yakovlev. News of AS USSR, OKhN (Department of Chemical Sciences), No. 9, 1699 (1962).

4. V. L. Tal'roze. News of AS USSR, OKhN, No. 2, 369 (1959).

Discussion

I. A. Myasnikov. 1. Does there exist a relation between the scheme proposed in your work and the scheme of luminescence proposed by V. A. Sokolov, F. F. Vol'kensteyn and A. N. Gorban'?[1] In the latter, an electron stabilized on a radical is detached during recombination of the radicals, and subsequent recombination of the electron leads to luminescence.

2. In what sense is the band model used?

V. G. Nikol'skiy. 1. A common feature of these models is stabilization of electrons on radicals.

2. The band model is used purely conditionally, only for clarity.

V. V. Voyevodskiy. For certain hydrocarbons and silica gel there is observed effect of increase of number of radicals when oxygen has access to samples irradiated in a vacuum. Is it impossible to explain this phenomenon by the fact that oxygen detaches electrons from radicals?

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[1] F. F. Vol'kensteyn, A. N. Gorban' and V. A. Sokolov. In the collection: "Surface properties of semiconductors." Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 179.

V. G. Nikol'skiy. In saturated hydrocarbons, within the limits of sensitivity of EPR method, there is not observed increase of concentration of free radicals during knocking of electrons out by light, and also at the moment of oxidation of alkyl radicals.

If in other systems concentration of ions composes a noticeable part of the concentration of radiclas, then in principle there can be observed the effect of which you speak.

V. V. Voyevodskiy. Is it impossible to consider the process of absorption of light by substance as a process leading to easing of mobility of lattice and thereby to recombination of charged particles, and consequently to the appearance of glow?

V. G. Nikol'skiy. In this case, during prolonged illumination of sample, it is possible to expect fall of concentration of radicals. This was not observed.

Question: How does concentration of radicals change under action of light?

V. G. Nikol'skiy. Under action of light, in EPR spectra of certain substances irradiated with small doses, there disappears the single line connected with charges captured by nonparamagnetic centers. At doses over 10 Mrad, concentration of radicals does not change during illumination.

Yu. N. Molin. What doses are needed in order to fill traps already available in system with charges?

V. G. Nikol'skiy. According to our data, filling occurs at doses not exceeding 1 Mrad, so that accumulation of stabilized charges in the radiolysis process is determined mainly by accumulation of new traps, i.e., radicals.

Yu. S. Lazurkin. Is saturation of concentration of radicals under irradiation impossible to connect with stabilization of charges on radicals?

V. G. Nikol'skiy. This is impossible, directly, since according to our data concentration of radicals capturing charge does not exceed 10% for all investigated doses of radiation up to 100 Mrad.

A. G. Kotov. How is your work connected with work of V. L. Tal'roze and Ye. L. Frankevich with respect to the study of electrical conductivity in irradiated saturated organic compounds?

V. G. Nikol'skiy. Qualitatively these phenomena are related, which confirms their generality.

ON MIGRATION OF CHARGE ALONG A HYDROCARBON CHAIN

Ye. L. Frankevich and B. S. Yakovlev

There is investigated high-voltage polarization [HP] (ВП) discovered by the authors, which appears in samples of saturated hydrocarbons irradiated at a temperature of 77°K [1, 2]. HP appears in the fact that after inclusion of a voltage in a circuit in which there is an irradiated pellet containing electrodes, current in this circuit slowly drops to a certain magnitude. When voltage in circuit is turned off, there is observed a reverse current, slowly dropping to zero. Method of investigation was earlier described in detail [2].

In Fig. 1 are presented curves of dependence of reverse current on time, which were recorded at various temperatures on the same irradiated sample of hexane. It is possible to see that curves are not described by exponential functions; however, after long times they approach straight lines, the slopes of which are greater, the higher the temperature of measurements is.

In Fig. 2 there are shown analogous curves for various saturated hydrocarbons. A common regularity for these curves is increase of time constant (calculated according to slope of rectilinear part of curve at large times) with increase of length of molecules.

Investigation of distribution of potential in sample under voltage and measurement of HP on samples of various thickness and various crystallinity allowed us to establish that polarization is caused by displacement of charges in certain microregions [2].

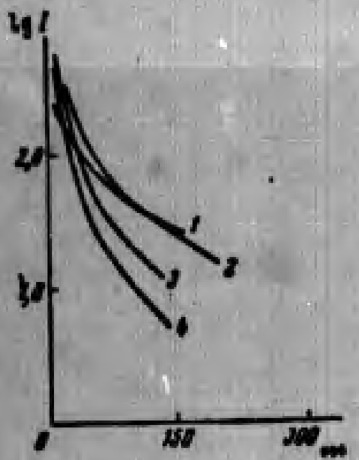


Fig. 1. Semilogarithmic anamorphoses of dependences of reverse current on time, taken for samples of hexane. Current I — in arbitrary units. 1) T = 126°K; 2) T = 130°K; 3) T = 137°K; 4) T = 143°K.

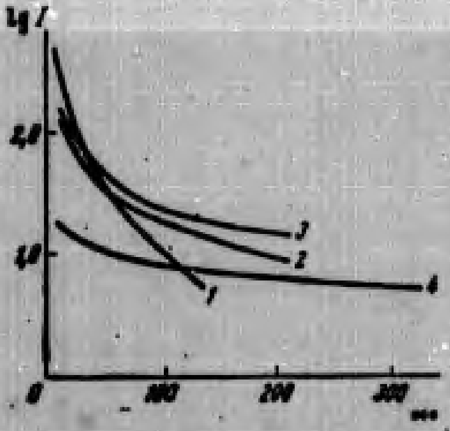


Fig. 2. Semilogarithmic anamorphoses of dependences of reverse current on time, taken for various saturated hydrocarbons. Current in arbitrary units. 1) hexane, $\tau m = 52$ sec; 2) heptane, $\tau m = 170$ sec; 3) decane, $t_m > 240$ sec; 4) tetradecane, $\tau_m > 550$ sec.

The proposed probable mechanism of high-voltage polarization consists of the following.

Electrons or hole formed under effect of radiation can be seized by radicals, which possess, as it is known, great affinity for electrons and lowered ionization potentials. From this it follows that in saturated hydrocarbons irradiated at low temperatures, there must be present ions of type $\ldots CH_2 - \overset{+}{C}H - CH_2\ldots$ and $\ldots CH_2 - \overset{-}{C}H - CH_2\ldots$. Motion of charge in such ions can be represented as transitions of proton or hydride ion H^- [3]. It is natural to assume that displacement of charge occurring thus is carried out more easily between neighboring atoms C belonging to one and the same molecule than between atoms C from different molecules. This assumption is sufficient for qualitative explanation of all peculiarities of HP in irradiated saturated hydrocarbons. Indeed, migration of charge along a bounded segment is equivalent to motion of charge in a system of potential wells, the number of which is equal to the number of atomic C in the molecule. Calculation of relaxation curves for such a system shows that for large times, drop of reverse current is characterized by one time constant τ, which is determined by height of barrier between wells and number of these wells.

According to curves of Fig. 1 there can be determined height of barrier: $U = 0.06 \pm 0.02$ ev. Steady-state electrical conductivity of sample is determined by transitions of charges (H^+ or H^-) from one molecule to another. These transitions are connected with overcoming of high potential barriers, and at low temperature occur comparatively rarely. Height of intermolecular barriers, according to results of investigation of electrical conductivity of paraffins after irradiation [4], composes ~0.6 ev.

According to the described model, relaxation time τ is proportional to square of number of shallow potential wells, i.e., to the square of number of atoms C in the molecule. In experiment, time τ sharply increases with increase of number of atoms C in molecule, and becomes immensurably large in the case of irradiated polyethylene. However, motion of charges occurring with low activation energy and caused by transitions of H^+ or H^- inside one molecule can also be observed in polyethylene. Indeed, such motion, due to the great length of molecules, looks like usual electrical conductivity: during heating of irradiated polyethylene, first of all motion of charges inside molecules is thawed; at higher temperature there are possible transitions between molecules. In Fig. 3 there is shown dependence of electrical conductivity of irradiated polyethylene on temperature, which was taken by us earlier [4]. Activation energy estimated according to initial rise of first peak is close to 0.1 ev, and corresponds within the framework of the described model to the first process. Recombination of charges "inside the molecule" possibly leads to appearance of the alkyl radicals observed during this time according to EPR spectra [4, 5].

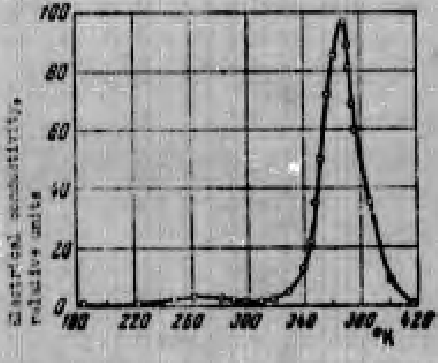


Fig. 3. Dependence of electrical conductivity of irradiated polyethylene on temperature.

Within the framework of the proposed HP model, there can be estimated concentration of ions accumulated in saturated hydrocarbons (dose of radiation 50 Mrad). Calculation by means of the Lorenz-Mosotti formula, on the basis of measured static dielectric constant of irradiated hexane ($\varepsilon_{CT} = 20$), gives concentration of ions ~10^{19} cm^{-3}.

The assumption that the radical is a trap for electron and hole permits us to estimate the expected concentration of stabilized charges. Indeed, in stationary conditions, under irradiation, the number of free electrons seized by radicals is equal to number of holes recombining with captured electrons: $k_1[R][e] = k_2[R^-][p]$.

If we consider that conditions for holes p and electrons e are identical, then $[e] = [p]$ and $[R^-] = [R] \cdot \frac{k_1}{k_2}$. Ratio of rate constants k_1 and k_2 is equal to ratio of cross sections of capture of charge by neutral particle (radical) and by a particle carrying the opposite charge. This ratio is apparently much less than unity, and consequently the concentration of stabilized charges is much less than concentration of stabilized radicals.

However, from the fact that theoretical and experimental estimates show that $[R^-] < [R]$, it does not follow that role of reactions with participation of ions in radiolysis processes is small, inasmuch as a noticeable part of chemical transformations can occur during radiolysis in processes of recombination of hole (or electron) captured by radical and free electron (or hole respectively).

Literature

1. Ye. L. Frankevich and B. S. Yakovlev. News of AS USSR, OKhN (Department of Chemical Sciences), No. 9, 1699 (1962).

2. Ye. L. Frankevich and B. S. Yakovlev. Journal of Physical Chemistry, 37, 1106 (1963).

3. V. L. Tal'roze and E. L. Frankevich. IV International Symposium on Stabilized Free Radicals. Washington, 1959, p. 22.

Ye. L. Frankevich and V. L. Tal'roze. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 651.

5. A. T. Koritskiy, Yu. N. Molin, V. N. Shamshev, N. Ya. Buben and V. V. Voyevodskiy. High-molecular compounds, 1, 1519 (1959).

Discussion

A. G. Kotov. Did you observe polarization in unirradiated samples of hydrocarbons?

Ye. L. Frankevich. There were no effects in unirradiated hydrocarbons comparable with those which were observed in irradiated systems.

V. K. Milinchuk. Does the mechanism proposed in your report assume simultaneous migration of charge and free valence?

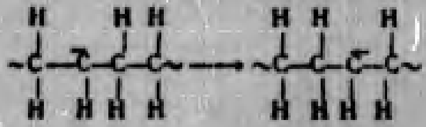
Ye. L. Frankevich. No, free valence can "stand" in place, or its migration can be connected with very high activation energy. A charge can migrate by itself. For this it is necessary only that a proton located in the neighborhood pass over to this charge.

V. K. Milinchuk. In your works there is shown the important role of ions in processes of radiolysis of molecules of saturated hydrocarbons. In the work of Charlesby and others[1] studying radiation cross-linking in polyethylene, conversely, it is shown that the observed effects are connected not with ions, but with radicals. How do these data agree with yours?

Ye. L. Frankevich. Conclusions of Charlesby and others were made on the basis of comparison of yield of radicals with yield of stable reaction products. Such comparisons are not very exact and do not have a quantitative character.

Kh. S. Bagdasar'yan. Please explain the character of migration of a proton with a diagram.

Ye. L. Frankevich. A diagram of migration can be drawn in the following way:



Kh. S. Bagdasar'yan. To what pertains the activation energy of 0.06 ev which was referred to in the report?

Ye. L. Frankevich. This is the activation energy of transfer of proton (or H^- ion) in a molecule of hydrocarbon to a neighboring carbon atom carrying a charge.

L. N. Ganyuk. Was there observed a dependence of relaxation time on dose?

Ye. L. Frankevich. In small intervals of change of dose this was not observed. In large intervals of change of dose, this effect is difficult to investigate.

V. K. Potapov. What is it possible to say about migration along a hydrocarbon chain not of a negative charge, but of a positive charge?

Ye. L. Frankevich. It is possible that a positive charge will migrate more slowly.

Yu. S. Lazurkin. Does concentration of ions depend on length of polymer chain?

Ye. L. Frankevich. With an accuracy up to an order of magnitude, it does not.

Yu. S. Lazurkin. How many ions were there per molecule of hydrocarbon, for instance hexane?

Ye. L. Frankevich. Many fewer than one (on the average).

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[1] Charlesby, Grace and Pilkington. Chemistry and technology of polymers, No. 2, 40 (1963).

Yu. S. Lazurkin. As far as I understand, for long molecules, for instance polyethylene there is a probability that in the same chain there will be ions of different sign. Is it possible to observe qualitative distinctions for cases of long and short molecules?

Ye. L. Frankevich. Polyethylene is a system qualitatively different from the others. For it we, in general, did not observe relaxation, since it occurs with very low rate.

Yu. N. Molin. Is it possible to expect change of composition of radiolysis products if it is carried out in an electric field?

Ye. L. Frankevich. In principle this is possible; however, the effect should be very small, since perturbing action of electric field as compared to that of thermal vibrations is small. Chaotic thermal motion of ion along hydrocarbon chain will be disturbed by electrical field only to a very small degree.

A. Ye. Kiv. Is a domain mechanism of polarization possible?

Ye. L. Frankevich. Your question asks if migration of charge can occur not within limits of one molecule, but in some region including several molecules. Although in principle this is possible, our experiments have not confirmed it. I have in mind experiments in which we conducted recrystallization of samples. It turned out that relaxation time is thus not changed. It follows from this that if domains exist, then they do not depend on dimensions of microcrystals of substance. This possibility seems to us improbable.

A. Ye. Kiv. Is there a dependence of relaxation time on direction of electric field?

Ye. L. Frankevich. Such a dependence is absent, just as hysteresis phenomena are absent.

V. K. Milinchuk. Does the mechanism proposed by you assume charge transfer between molecules?

Ye. L. Frankevich. Yes, this is the process of electrical conduction during strong heating of samples. Activation energy of this process is 0.6 ev, i.e., an order greater than activation energy of process of migration of charge inside molecule. Possibly this is connected with the fact that protons of two different molecules are located at a larger distance than protons of two neighboring CH_2 groups in the same molecule.

V. K. Milinchuk. What were doses of radiation in your experiments? Was there considered the role of the double bonds which had to be formed in irradiated molecules at large doses?

Ye. L. Frankevich. Data given in the report were obtained for a dose of 50 Mrad. We did not consider the role of double bonds.

Question: How do your data about the fact that numbers of radicals and ions are comparable agree with experiments of V. G. Nikol'skiy, for which number of ions is an order less than number of radicals?

Ye. L. Frankevich. I spoke only about orders of magnitudes, and in order of magnitude our data converge.

GENERAL DISCUSSION

Yu. S. Lazurkin. I would like to say several words concerning reports of V. G. Nikol'skiy and Ye. L. Frankevich and B. S. Yakovlev. In these works there is more convincingly shown the accumulation of unique holes and electrons stabilized on radicals, and, which is still more important, there are obtained methods of quantitative estimation of concentration of these formations and their behavior in paraffin and polymer molecules. It seems to me that these works are extremely interesting and apparently promising in the sense of further clarification of the mechanism of these phenomena. In connection with this, I want to make a remark concerning one conclusion which ensues from the work of Ye. L. Frankevich and B. S. Yakovlev. In both works it is shown that concentrations of hole and electron formations on radicals do not exceed several percent of the concentration of radicals.

It is interesting to clarify the cause why in the subsequent course of radiolysis there is not increased the quantity of such formations. In the report of Ye. L. Frankevich there were given numerical estimates. Let us say that for substance with molecular weight of about 200 (this is the heaviest investigated paraffin) there is obtained a concentration of ions of about $2 \cdot 10^{19}$ 1/cm^3. At the same time the concentration of molecules is $(2-3) \cdot 10^{21}$ 1/cm^3. This signifies that there is one charge per 100 molecules. We can depict these 100 molecules, and on every hundredth molecule there will "sit" one charge. Apparently there will be both positive and negative charges.

Let us now go to polymers. Let us take a paraffin with molecular weight of 200,000. If we assume that there the formation of these ions occurs in the same way, then on a molecule of paraffin there will "sit" ten charges — on the average five positive and five negative. In this work it was shown that in an electrical field there occurs directed motion of these ions inside the molecule, where for the average molecule, relaxation time is of the order of 100 sec. If we assume that migration of the proton can also occur in polyethylene molecule, then inasmuch as there the length of the molecule is 100 times greater, then relaxation time will no longer be 100 sec, but 10^4 times greater – namely 10^6 sec, i.e., 10 days.

Migration of charge occurs not only in an electric field; diffusion jump of proton occurs independently of whether there is a field or not. Therefore, charge in polyethylene should migrate with relaxation time of the order of 10 days. This means that if in a molecule of polymer there are charges of different sign, then in a time of the order of 10 days they recombine, in distinction from a low-molecular substance. It is possible, apparently, to try to reveal this phenomenon experimentally. Such migration of charge can be one of the reasons that in polymers there are not stored large concentrations of charged particles. Besides, this is one of the ways for the mechanism of migration to occur which seems to be to me very probable and well founded.

V. L. Tal'roze. In reports of Kh. S. Bagdasar'yan, Ye. L. Frankevich and V. G. Nikol'skiy, there was discussed the investigation of ions formed in solid, organic substances under the action of radiation. These works represent a very important stage, but only the first stage, in the forthcoming investigation of ionic processes in solid phase, since for radiation chemistry most important of all is the question of influence of ions on radiation changes and how this influence appears.

In order to explain the importance of this question and to show to what these works finally have to lead, it will be necessary for me to repeat certain conclusions which Ye. L. Frankevich and I made in works reported at the Washington symposium [1], and in particular at the conference on radiation chemistry in 1960 [2].

During motion of a fast particle in a gas, liquid or solid medium, there occurs ionization of molecules. If during a time of 10^{-13} sec electrons and ions recombine, then the direction of chemical processes and composition of products will be determined basically by other processes. If, however, ions are some way separated in the system, then there appears the possibility of chemical transformations through ionic processes; however, this is only a possibility.

Let us consider possible processes occurring under irradiation in a solid system consisting of molecules AB (A and B can be any groups of atoms). In the field of ionizing radiation there can occur both detachment of an electron and dissociative ionization. In the latter case we already have a chemical reaction occurring by ionic means. It is necessary, however, to consider that in condensed systems it is difficult for large particles to separate, due to the cage effect, and therefore probability of dissociative ionization can be very small. By detachment of an electron, there will be formed the ion-radical AB^+. It can enter into different reactions. Let us consider the main ones:

1. Interaction with neighboring molecule, i.e., ion-molecule reaction:

$$AB^+ + AB \longrightarrow \text{products}$$

2. Recombination with electron

$$AB^+ + e \longrightarrow AB.$$

The first process leads either to formation of new ions, i.e., to chemical changes, or to transfer of charge to another molecule. Thus, the problem is reduced to the question: will there occur chemical changes in the system during recombination of positive ion with electron, or negative ion if electron is seized in some trap?

In the gas phase, such processes lead, as a rule, to dissociation. In liquid, and all the more so in solid phase, this can be not at all so. In the first place, we should consider ionization potentials, magnitudes of affinity to electron and dissociation energies (with all corrections for the influence of phase).

When we work with saturated hydrocarbons, where ionization potentials are high, and magnitudes of affinity of any formed particles to an electron are small, then there is cause to think that during recombination there will be released so much energy (about 10 ev) that dissociation will occur. However, when we work with amines, aromatic or chloride compounds, then we have a system with low ionization potentials and high electron affinity. The difference between them can be approximately 5 ev, which is very close to the magnitude of energy of breaking of bonds; i.e., dissociation in this case may not occur.

The conducted investigation is intended to show the possible role of ionic processes in chemical changes under the action of radiation. After there are obtained in a number of works, it seems to me, very clear and demonstrative conclusions about stabilization of ions in different systems, it is necessary to make the following step and to demonstrate the chemical importance of these experiments, i.e., to show that ions can be intermediate products leading to a specific chemical transformation.

There exists extensive experimental material which indicates that an irradiated dielectric is electrically conducting. Thus, it is known that electrical conductivity in liquids is ionic. Besides, it is known that if we calculate concentration of ions, based on reasonable values of mobility, that it will turn out that ion yield constitutes a fully noticeable magnitude. Sometimes there are found grounds to disregard role of ions in estimates of Magee [3], according to which the electron in a liquid "departs" from its "parent" ion only for a very short time. It is true that now Hardwick has published a work [4] in which he has found agreement between energy transfer and ionization potentials, but, in trying to coordinate his data with conclusions of Magee, he describes transfer constants so that they correspond to a time of "free existence" of the electron of only 10^{-11}-10^{-12} sec.

I would like to turn attention to the fact that if we do not bypass the known physical fact of electrical conductivity of liquid dielectrics under irradiation, and, conversely, consider that a certain fraction of electrons "depart" from the ions, it is possible to explain certain experimental data which are known in the region of radiation shielding and sensitizations. Let us assume that an electron departs from an ion as a result of a primary elementary event, and then in the liquid there occurs diffusion of ions and electrons. Positive or negative charge can be captured by a molecule with high affinity to some form of charge, and after this, recombination of ions will occur with lower energy yield. Another possibility is that recombination will have time to occur until hole or electron is captured. The question in this formulation is reduced to estimation of what concentrations of acceptor are sufficient so that at reasonable dose rates, with which work usually is conducted, there was time for capture events to occur. We will estimate this with the help of the simplest kinetic equations, since I think that theoretical complications, with that real experimental information which we have, probably confuse the question rather than clarify it.

For the steady-state case (continuously irradiated system),

$$\frac{d(e)}{dt} = W_0 - k_1(e)(A) - k_2(e)^2 = 0,$$

where W_0 is rate of generation of ion pairs; (e) is concentration of "departed" electrons (or holes); (A) is concentration of charge acceptor; k_1 and k_2 are rate constants of corresponding processes.

Now it is necessary to select some reasonable values of k_1 and k_2. As it is known, in liquids it is frequently possible to use rate constants of bimolecular reactions which are close in order of magnitude to "gas-kinetic values", i.e., to 10^{-10}-10^{-9} cm^3/sec. Analysis of the equation given above permits us to write the condition for the electron or hole before recombination to be in a large number of cases accepted:

$$4k_2W_0 < k_1^2A^2.$$

If we take for k_1 and k_2 values of the order of 10^{-9} cm^3/sec, for W_0 values characteristic for the most frequently applied dose rate I($I \approx 10^2$ is rad/sec; $W_0 = 10^{14}$ 1/cm^3), then concentration of acceptor equal to 10^{12} 1/cm^3 turns out to be sufficient for accepting to be predominate. In liquids this corresponds to relative concentration of 10^{-7}-10^{-8} mole %, i.e., to a very small magnitude. I suspect that none of us has worked with solutions of such purity. I, in any case, have not. It is natural that to the extent that we err in magnitudes of k_1 and k_2, we err in this criterion.

Literature

1. V. L. Tal'roze and E. L. Frankevich. IV International Symposium on Stabilized Free Radicals. Washington, 1959, p. 22.

2. Ye. L. Frankevich and V. L. Tal'roze. Transactions of II-nd All-Union Conference on Radiation Chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 651.

3. A. N. Samuel and J. L. Magee. J. Chem. Phys., 21, 1085 (1953).

4. T. J. Hardwick. J. Phys. Chem., 66, 2132 (1962).

5. ACCUMULATION AND RECOMBINATION OF RADICALS IN SOLID MEDIA

ON THE THEORY OF ACCUMULATION OF FROZEN RADICALS IN SOLID BODIES[1]

G. K. Vasil'yev and V. L. Tal'roze

As is known [1, 2], during accumulation of radicals in solid bodies there are observed gradual deceleration of growth of their concentration and transition to limiting, or almost limiting, i.e., to very slowly increasing concentrations. In this work there are considered certain hypothetical mechanisms of processes leading to the phenomenon of "limiting concentration." Part of these mechanisms have been to various degrees considered by other authors; certain are considered in this work for the first time. First of all, we should note that inasmuch as in all cases concentrations of radicals are many orders higher than thermodynamically equilibrium concentrations, then the nature of the phenomenon is undoubtedly connected with kinetic processes occurring in the system, either during radiation influence or in a thermodynamically nonequilibrium system in the absence of a field of radiation.

Of the processes of the first type, in this work there are considered the following.

1. *Formation, along with frozen radicals, of radicals conserving mobility even at low temperatures (for instance atoms of hydrogen in hydrogen-containing substances).* Calculation of the corresponding kinetic scheme leads to the following asymptotic law of accumulation of radicals in the system:

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[1] Kinetics and catalysis, 4, 497 (1963).

$$R \simeq \sqrt[3]{\frac{3k_2 G j t}{k_3^2}}, \qquad (1)$$

where G is radiation yield of radicals; j is emissive power of radiation; k_2 is rate constant of process $R + H \rightleftarrows M$; k_3 is rate constant of process $H + H \rightarrow H_2$.

II. Processes of migration of charges to radicals. In this case it is assumed that radicals are formed as a result of recombination of charges, and with accumulation of radicals, in view of the fact that they possess positive affinity to holes, as well as to electrons [3], with greater and greater probability there occurs migration of charges to radicals, where they then recombine without formation of "new" radicals. In this case there is obtained an analogous asymptotic law of accumulation of radicals:

$$R \simeq \sqrt[3]{\frac{3k_2 \cdot 10^{-4} G^2 j^2 t}{(k_3 + k_4)^2}}, \qquad (2)$$

where G is number of ion pairs of formed per 100 ev of absorbed energies; k_2 is rate constant of process of recombination of charges with formation of radicals; k_3, k_4 are rate constants of processes of transfer of charges to radicals.

III. Migration of excitations. In this case it is assumed that radicals are formed as a result of decay of excitations, which with accumulation of radicals migrate to weakened bond located next to free valence, and then disintegrate without formation of "new" radicals. For accumulation of radicals there is obtained the following law:

$$R = \sqrt{\frac{2 \cdot 10^{-2} G j t}{\tau_2 k_3} + a^2} - a, \qquad (3)$$

where G is the number of excitations formed per 100 ev of absorbed energy; k_3 is rate constant of transfer of excitation to radical; τ_2 is characteristic lifetime of excitation with respect to dissociation; a is a constant not depending on emissive power of radiation.

IV. As processes of second type there is considered the thermal-chain model [4] without the assumption of existence of a critical temperature, where it is assumed that ejection of radical from potential well requires activation energy E. There is obtained an expression for limiting concentration:

$$\frac{n_{\text{кр}}}{M} \simeq 13{,}5\,\frac{\alpha\lambda}{W}\left(\frac{E}{R \ln \frac{1{,}08 \cdot \zeta^4 k_0 n_{\text{кр}}^{1/3}}{\lambda M}} - T_0\right). \qquad (4)$$

here k is Boltzmann's constant; W is heat of recombination of radicals; M is concentration of saturated molecules; k_0 is frequency of vibrations of particle in potential well; λ is coefficient of thermal diffusivity; α is a coefficient selected in such a manner that heat capacity written as $C = \alpha kM$, is equal to its value at temperature T_0; ζ is a quantity close to coordinate number of the lattice.

V. We consider the thermal-chain model during obtaining of radicals by radiation means. It is assumed that field of radiation creates in the material a field of "hot" points [5], which play the same role as places of recombination of radicals, with the difference their nature can be more varied (recombination of radicals and ions and decay of strong excitations). For critical concentration there is obtained the expression

$$\frac{n_{кр}}{M} \simeq 13{,}5\frac{\alpha k}{q}\left(\frac{E}{R\ln\frac{1{,}08\zeta k_0 n_{кр}^{1/3}}{10^{-2}Gq\lambda M}}-T_0\right), \qquad (5)$$

where q is energy released at the hot point; G is radiation yield of radicals.

Conducted comparison with experimental data shows that it is possible to satisfactorily explain the observed concentrations of free radicals (in particular nitrogen atoms) at the temperature of liquid helium with the help of the thermal-chain model. Actually observed concentrations of radicals at higher temperatures (in particular in organic compounds) are 1-2 orders lower than predicted by the obtained formulas. The conclusion is drawn that in certain real systems it is probably not possible to expect obtaining of concentrations of frozen radicals exceeding 0.01 (if we express them as a fraction of all bonds in the system).

Literature

1. G. I. Minkoff. Frozen Free Radicals. London, 1960.

2. Formation and Trapping of Free Radicals. Ed. A. M. Bass and H. P. Broida. New York, 1960.

3. V. L. Tal'roze. News of AS USSR, Department of Chemical Sciences, No. 2, 369 (1959).

4. J. L. Jackson. J. Chem. Phys., 31, 154 (1959).

5. M. A. Mokul'skiy. High-molecular compounds, 2, 119 (1960).

Discussion

V. K. Milinchuk. What is the excitation in your mechanism III?

G. K. Vasil'yev. We do not specify what the excitation consists of. For us it is important to estimate to what lifetimes of excitation this mechanism corresponds. In order to obtain limiting concentration of radicals by this mechanism, it is necessary to assume that rate constants of transfer have the order of 10^{-10}-10^{-12} cm^3/sec.

V. I. Lukhovitskiy. If a hole is displaced to a radical, then there is obtained an ion not having unpaired electrons. With what will it further recombine — with an electron? Then there again will be obtained an unpaired electron.

G. K. Vasil'yev. During recombination of ions, in this place there will be released energy. If this energy is sufficient for breaking the chemical bond, then it will do this. There are obtained three uncoupled bonds in this place. Two of them certainly are quickly coupled. There was one radical and there remained one radical, and radiation expended its energy.

V. S. Gurman. Can there be explained within the framework of mechanisms presented by you the experimental fact that in a frozen system during photolysis radicals are accumulated? There are no ionized states, and there is not observed emanation of hydrogen. Introduction of several percent of nonphotolyzable addition leads to increase of limiting concentration of radicals by one and a half to two times. Appearance of radicals of addition certainly does not explain such an increase.

G. K. Vasil'yev. I do not understand very well what system you are talking about, but if you are speaking about thermal-chain model, it is in general inapplicable for such organic systems.

V. L. Tal'roze. For complex systems the thermal-chain model is not applicable. In real systems there certainly acts the totality of all mechanisms. Regarding your system specifically, it is possible to assume, for instance, that the impurity is an exciton trap, and then model III will take place. It is natural to look for more rigorous approaches in the simplest systems, such as atomic nitrogen in frozen molecular nitrogen. In this case, with those approximations which were reported here, this theory gives a reasonable answer.

In our report we wanted to emphasize that the first three mechanisms do not lead to the appearance of limiting concentrations of radicals, whereas the thermal-chain theory does this. In the case of atoms N in lattice N_2, only this theory is applicable.

S. Z. Roginskiy. To what extent did you consider change of concentration of free radicals after cessation of irradiation?

V. L. Tal'roze. In certain cases it is possible to observe, according to source material, that concentration of radicals somewhat decreases after cessation of irradiation if limiting concentration is already attained. On the other hand, in certain systems, for example, carboxylic acids, limiting concentration is not changed after cessation of irradiation. Our computations pertain to a great extent to cases when limiting concentration is not changed after cessation of irradiation.

S. Z. Roginskiy. Is it possible, by changing method of generation of free radicals, to change limiting concentration of radicals?

V. L. Tal'roze. The most striking fact of all those known about limiting concentrations is that with different methods of generation of radicals, limiting concentrations are close to each other, if not equal. This fact corresponds in the very best manner to thermal-chain model. We will note that results on limiting concentrations obtained by various authors by [EPR] (ЭПР) methods can be compared with accuracy up to coefficient 2-3.

N. A. Bakh. Quite frequently limiting concentrations of radicals are attained at large doses, when very significant changes of the substance already occur. Did you consider this in your calculations?

V. L. Tal'roze. No, because there are many examples when limiting concentrations are attained at comparatively small doses.

N. A. Bakh. Are there any data on limiting concentrations of radicals formed by action of heavy particles, and what is it possible to expect here?

G. K. Vasil'yev. Such data are unknown to us. Undoubtedly track effect will strongly complicate picture.

I. G. Kaplan. Is thermal-chain model accurate during photolysis?

V. L. Tal'roze. Our assumptions are sufficiently general and pertain to various cases of destruction of radicals, independently of the method of their formation. It is natural, however, that when, for instance, there is no ionization, then there is no sense in talking about the possibility of the electron-hole mechanism.

I. G. Kaplan. If you started from the theory of "hot points" of Yu. S. Lazurkin and M. A. Mokul'skiy [1], then your conclusions should not pertain to the case of photolysis.

V. L. Tal'roze. In examining of thermal-chain mechanism, we started from the thermal wave theory of Jackson [2], who used theory of Semenov-Frank-Kamenetskiy. We applied the same approach but with an essential reservation. Jackson used critical temperature, which he selected as a parameter. A radical perishes if it turns out to be in the region with critical temperature. In our work, first there is considered kinetics of the process, since there is introduced a certain probability of destruction of the radical in this region. Secondly, we consider that hot points are formed not only in places of recombination of radicals, but also during recombination of ions, with local excitation. In such cases temperature of hot points photolysis can be 2-3 times less than, for instance, during radiolysis.

Now about the relationship between various mechanisms. Certainly it is possible to select their parameters so that they will satisfy obtained data. However, [illegible] case of such simple systems as atoms of nitrogen in lattice of molecular nitrogen, only application of thermal-chain model is possible.

A. G. Kotov. Do your models allow existence of different types of radicals (for instance ion-radicals)?

V. L. Tal'roze. Not one of the models specifies the type of active particles, with the exception of the model connected with motion of the charged particle. In general, consideration of ion-radicals should be made only during consideration of specific systems.

Question: Does magnitude of dose enter into your formulas?

G. K. Vasil'yev. In direct form, no. There are contained various exponential dose rates and times.

Literature

1. M. A. Mokul'skiy. High-molecular compounds, 2, 119 (1960).

2. J. L. Jackson. J. Chem. Phys., 31, 154 (1959).

CONCERNING THE QUESTION OF THE MECHANISM OF "STEP" RECOMBINATION OF FREE RADICALS IN IRRADIATED SOLID SUBSTANCES[1]

Ya. S. Lebedev, A. I. Mikhaylov,
and N. Ya. Buben

The step character of recombination of free radicals in irradiated inorganic systems for the first time was observed in works [1-3]. Lately there has been observed the same recombination in cyclohexane and n-octyl alcohol [4]. Recently it was shown that recombination of macroradicals in irradiated polyethylene [5] and polypropylene [6] at low temperatures also occurs in "steps", in distinction from recombination at temperatures higher than room temperature [7]. We studied processes of recombination of free radicals in various frozen organic substances – phenol, napthalene, glycine, malonic and palmitic acids, and others. In majority of studied cases, destruction has a step character, i.e., at a given temperature there disappears only a definite part of the accumulated radicals (Fig. 1). Analysis of results obtained here and in the literature permits us to make the following conclusions with respect to phenomenology of "step" recombination:

1) "steps" are observed in a very wide range of temperatures (phenol ~70°, malonic acid ~100°, glycine ~250°);

2) magnitude of concentration of free radicals remaining on a "step" (n_{CT}), is for a given sample a function only of temperature, this is confirmed by experiments on "splitting of steps" (Fig. 1).

3) dependence of n_{CT} on T in a number of cases satisfies the empirical

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[1] Kinetics and catalysis, 5, 1020 (1964).

relationship $\frac{n_{cT}}{n_0} = a - bT$ (Fig. 2);

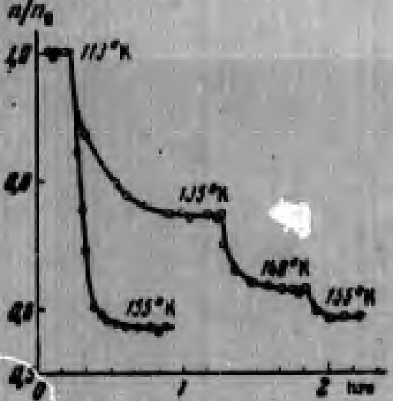

Fig. 1. Kinetics of recombination of free radicals in irradiated phenol (dose of radiation D = 50 Mrad, $n_0 = 7 \cdot 10^{18}$ cm^{-3})

4) construction of linear anamorphoses of kinetic curves shows that "step" recombination cannot be described by the usual kinetic equation of 1-st, 2-nd or 3-rd order.

The question about origin of recombination "by steps" as far as we know until recently practically was not discussed in the literature. In works [1, 3-5] there is expressed assumption about existence of "centers of different thermal stability," however, physical nature of such centers is absolutely unclear. It is obvious that effective recombination rate sharply drops with decrease of n. As preliminary hypothesis we assumed that elementary event of recombination is limited by collective excitation of a certain micro-region containing at least two active centers. In case of uniform distribution of radicals throughout the sample, this leads to the kinetic equation:

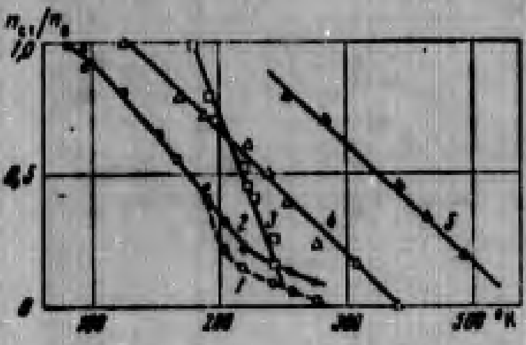

Fig. 2. Dependence of n_{cT} on temperature: 1, 2) glycine; 3) phenol; 4) malonic acid; 5) glass [1].

$$\frac{dn}{dt} = -kn^{\nu} \exp\left(-\frac{E_0}{n^{1/3} \Lambda RT}\right),$$

where E_0 is activation energy of first unit cell: Λ is its dimension. At $\nu = 2$, it is possible to obtain $\left(s = \frac{E}{n_0^{1/3} \Lambda RT}, \gamma = n_0/n\right)$:

$$skn_0 t \simeq 3\gamma^{2/3} \exp(s\gamma^{1/3}). \qquad (1)$$

If, however, radicals are localized, for instance in pairs, then, if we assume equal distribution of pairs with respect to energy $E_1 = \frac{r_1}{\Lambda} E_0$ in the interval (E_1, E_2), we will obtain $[k_1 = k^0 \exp(-E_1/RT)]$:

$$\frac{n}{n_0} = \frac{RT}{E_2 - E_1}[Ei(-k_1 t) - Ei(-k_2 t)]. \qquad (2)$$

Calculation shows that equations (1) and (2) well describe kinetics of "step" recombination and agree with conclusions 1, 2 and 4. From equation (2) there also follows conclusion 3, since upon appearance at a "step," usually

$$k_1t > 1,\ k_2t < 1,\ Ei(-k_1t) \approx 0,\ Ei(-k_2t) = C + \ln(k_2t),$$

whence $n/n_0 = a - bT$, where $a = E_2/(E_2 - E_1)$ $b \sim \ln t + \text{const}$. From Fig. 2 it is possible to estimate that $E_2/E_1 = 3$ (malonic acid), $E_2/E_1 = 1.7$ (glass), etc. In certain cases, however, dependence of n_{CT} on T is better described by relationship $n_{CT}T^3 \approx$ const, which ensues from (1).

Thus experimental results are satisfactorily described by the proposed model if we consider nonuniformity of the distribution of radicals throughout the sample. Such nonuniformity should become immaterial at very high concentrations and at the end of the thawing curve; this will qualitatively agree with experiment.

Authors are thankful to academician V. V. Voyevodskiy for his discussion of this work.

Literature

1. J. Roch. Ann. Phys., 5, 1401 (1960).

2. G. B. Sergeev, V. S. Gurman, V. J. Papisova, E. U. Yakovenko. V International Symposium on Free Radicals. Uppsala, 1961.

3. J. M. Flournoy, L. H. Baum, S. Siegel. J. Chem. Phys., 36, 2229 (1962).

4. V. K. Yermolayev, Yu. N. Molin, and N. Ya. Buben. Kinetics and catalysis, 3, 314 (1962).

5. F. Cracco, A. J. Arvia, M. Dole. J. Chem. Phys., 37, 2449 (1962).

6. V. K. Milinchuk and S. Ya. Pshezhetskiy. The present collection, p. 251.

7. Yu. D. Tsvetkov, Ya. S. Lebedev, and V. V. Voyevodskiy. High-molecular compounds, 3, 881 (1961).

Discussion

S. Z. Roginskiy. What is the nature of dependence of activation energy of recombination on distance between particles?

Ya. S. Lebedev. It is reasonable to consider that it is more difficult for radicals to perish, the deeper they are in the solid body. We consider that during recombination there occurs simultaneous excitation of cells separating the radicals. If probability of recombination of neighboring radicals is proportional to $e^{-E/RT}$, then for separated radicals this is $e^{-NE/RT}$, where N is the number of these cells, i.e., a quantity proportional to distance.

G. I. Likhtenshteyn and B. I. Sukhorukov[1] conducted calculation of a simple model of cooperative reaction based on application of Markov chain theory. This calculation shows that effective activation energy of process should increase with increase of distance between reacting centers. Thermal-model of recombination, as can be seen from calculations of V. L. Tal'roze and G. K. Vasil'yev,[2] also leads to dependence of effective activation energy on average distance between radicals.

L. N. Ganyuk. Do not you consider that there is something in common between process of step polymerization and step recombination?

Ya. S. Lebedev. I will be able to say nothing on this matter.

G. G. Kotov. Does it follow from your experiments that rate constant of destruction depends on limiting concentration of radicals?

Ya. S. Lebedev. We usually worked at concentrations less then limiting. For instance, we irradiated phenol with a dose from 5 to 100 Mrad, while limiting concentrations are attained at doses of the order of several hundred Mrad.

V. K. Milinchuk. Is it possible from your results to estimate within range activation energy changes?

G. B. Sergeyev. Is it possible to estimate magnitude of $\Delta E = E_2 - E_1$?

Ya. S. Lebedev. It is possible to estimate not ΔE, but the ratio E_2/E_1, which is 1.5 - 3.

A. G. Kotov. Is it possible to say anything about physical mechanism of diffusion proceeding from your model?

Ya. S. Lebedev. Diffusion mechanism in the classical understanding certainly will not lead to step recombination. If we talk about directed diffusion, then this can be and should be considered.

A. L. Karasev. Is this effect not connected with the history of the sample?

Ya. S. Lebedev. In our samples we, within defined limits, did not notice dependence of kinetics of recombination on rate of freezing and total dose of irradiation of samples. In cyclohexane, according to source material, such a dependency is observed, but there all "stepness" of recombination is developed in a very narrow edge of temperatures, and possibly is simply connected with the presence of inhomogeneous regions in the sample.

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[1] G. I. Likhtenshteyn and B. I. Sukhorukov. Journal of Physical Chemistry, 38, 747 (1964).

[2] V. L. Tal'roze and G. K. Vasil'yev. Present collection, p. 231.

FORMATION OF RADICALS DURING LOW-TEMPERATURE RADIOLYSIS OF AROMATIC COMPOUNDS

N. Ya. Buben, V. A. Tolkachev,
and I. I. Chkheidze

Investigation of radiolysis of aromatic compounds and their derivatives is of great interest due to their high radiation stability. In our work, by [EPR] (ЭПР) method, there was studied formation of radicals during low-temperature radiolysis of certain derivatives of benzene. In analysis of EPR spectra of the investigated irradiated substances, there were used spectra of simple radicals — phenyl [1] benzyl [2] cyclohexadienyl [3], phenoxyl [4], obtained in our laboratory and by other authors. Analysis of spectra of benzene and its mono- and dialkyl-substituted derivatives and also such derivatives of benzene as benzoic acid, analine and thiophenol (group I) showed that a characteristic peculiarity of radiolysis of these compounds is formation of secondary cyclohexadienyl radical as a result of attachment of a hydrogen atom to a phenyl ring. Spectrum of radicals of such type has been thoroughly studied in works [3, 5, 6]. It is the characteristic triplet with splitting of components $\Delta H = 45$-50 oe.

However, during radiolysis of such derivatives of benzene as C_6H_5OH, $C_6H_4(OH)_2$. $C_6H_5CH_2OH$ and $C_6H_4(OH)NH_2$ and $C_6H_5CH_2Cl$ (group II), radicals of cyclohexadienyl type are not formed (in certain cases, for instance C_6H_5OH, contribution of this radical is about 10%). EPR spectra of irradiated substances of this group constitute single lines with weakly resolved hyperfine structure, the total extent of which does not exceed 50 oe. On the basis of analysis of spectra of investigated substances and comparison of them with spectra of simple radicals, it is possible to establish, for instance, that in spectrum of irradiated benzyl chloride there are lines of radicals of two types – $C_6H_5\dot{C}H_2$ and $C_6H_5\dot{C}HCl$, and in the spectrum of irradiated phenol – lines of phenoxy radical. Mass spectrometric measurements carried out by G. K. Vasil'yev and V. L. Tal'roze that yield of hydrogen during radiolysis of phenol and benzyl chloride is very small and constitutes about 0.02 molecules/100 ev.

Thus, very low yield of hydrogen and absence of radicals of cyclohexadienyl type for compounds of group II indicate that formation of radicals during radiolysis occurs by an essentially different mechanism than in the case of group I. It is possible that secondary reactions of atoms of hydrogen for compounds of group II lead to formation of water during radiolysis of phenol, and HCl during radiolysis of benzyl chloride. Such directivity of secondary reactions is a peculiarity of radiolysis of these compounds, inasmuch as during reaction of phenol with hydrogen atoms, from the discharge there are formed radicals of cyclohexadienyl type [7]. This may be due to energy transfer to hydroxyl group, detachment of atom H from it and subsequent reaction of this atom with hydroxyl group of neighboring molecule. Selectivity of secondary reactions of H atoms is apparently caused by the fact that molecules of phenol are oriented in lattice thanks to presence of hydrogen bonds. Such an orientation, however, makes possible the molecular detachment of water from other molecules of phenol.

Peculiarities of radiolysis of benzyl chloride can also apparently be explained either by directivity of secondary reactions or a molecular process of detachment of HCl.

Literature

1. V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben. Journal of structural chemistry 6, 709 (1962).

2. V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben. Reports of the AS USSR, 147, 645 (1962).

3. V. A. Tolkachev, Yu. N. Molin, I. I. Chkheidze, N. Ya. Buben, and V. V. Voyevodskiy. Reports of the AS USSR, 141, 911 (1961).

4. T. J. Stone and W. A. Waters. Proc. Chem. Soc., 1962, 253.

5. H. Fischer. Kolloid Z., 180, 64 (1962).

6. S. Ohnischi, T. Tanei, and J. Nitta. J. Chem. Phys., 37, 2402 (1962).

7. N. Ya. Buben, V. A. Tolkachev, and I. I. Chkheidze. News of Academy of Sciences (AS) of USSR, Department of Chemical Sciences, No. 6, 1143 (1963).

Discussion

V. V. Voyevodskiy. In the group of compounds II, which are formed during radiolysis, H atoms are not attached to molecules of substance, but give HCl or H_2O.

I. I. Chkheidze. Mass spectrometric analysis does not reveal H_2O and HCl. This, however, still does not prove that H_2O and HCl are not formed in small quantities.

Yu. N. Molin. What is the fate of H atom formed from methyl group during radiolysis of toluene?

I. I. Chkheidze. It probably detaches hydrogen from phenyl or methyl group. We did not measure radiation yield of molecular hydrogen in toluene.

V. A. Sharpatyy. 1. What is the influence of functional groups on the place of detachment of H atoms in compounds investigated by you?

2. Were the given values of G (H_2) obtained during thawing of the sample after irradiation?

I. I. Chkheidze. Inasmuch as at low temperature the formed hydrogen can not emerge completely from the sample, the ampule with substance was thawed after irradiation.

Hyperfine structure of spectrum permits us to make conclusions about place of attachment of H. For instance, in the case of phenol, H is attached at the ortho- and para- positions with respect to the OH group. In thiophenol attachment of H occurs at the meta-position with respect to the SH group. In these systems, unfortunately, spectrum of radical of attachment turns out to be so wide that it can conceal the spectrum of the radical corresponding to detachment of H atom.

N. A. Bakh. How do you explain difference in H atoms formed from CH_3 group and from ring?

I. I. Chkheidze. Atoms of hydrogen detached from ring possess a smaller reserve of kinetic energy, and are chiefly attached to the ring with formation of C_6H_6R radicals. Hydrogen detached from CH_3-group is "hotter" and is capable of detachment reactions [1]. By the way, experiments conducted in the laboratory of L. I. Avramenko [2] indicate strongly in favor of the fact that capability of H atom for detachment reaction strongly depends on energy which this atom carries. Fischer [3] conducted reaction between H atoms and benzene at a temperature of about -80°C. He almost obtained an absolutely pure spectrum of C_6H_7. L. I. Avramenko and others conducted this reaction at temperatures of 20° and 220°C and established that the fraction of radical C_6H_5 increases with temperature. An analogous picture is obtained for phenol.

Literature

1. N. Ya. Buben, V. A. Tolkachev, and I. I. Chkheidze. Kinetics and catalysis, 4, 683 (1963).

2. L. I. Avramenko, N. Ya. Buben, R. V. Kolesnikov, V. A. Tolkachev, and I. I. Chkheidze. News of AS USSR, Department of Chemical Sciences, 1962, 2079.

3. H. Fischer. Z. Naturforsch., 17a, 693 (1962).

RECOMBINATION OF RADICALS IN CYCLOHEXANE IRRADIATED IN GAS CRYSTALINE STATE

N. Ya. Buben, A. P. Pristupa,
and V. N. Shamshev

Recombination of free radicals constitutes one of the simplest reactions in the solid phase. However, mechanism of recombination has till now been insufficiently studied. It is obvious that meeting of two radicals can occur either as a result of their diffusion, or during transfer of free valence through the substance without displacement of molecules. It is possible to expect that mechanisms of second type are especially essential in case of high-molecular compounds. Nonetheless, it seems to us that even for polymers it is impossible to exclude completely recombination of radicals caused by thawing of motion of separate sections of the macromolecule. Estimation of magnitude of diffusion coefficient of the entire polymer molecule as a whole, as this is done in the work of S. Ye. Bresler and colleagues [1], certainly does not solve the problem.

During radiolysis of frozen organic substances with small molecular weight, it was earlier established [2] that process of recombination is mainly connected with self-diffusion, since in most cases recombination occurs with great speed near temperature of melting or devitrification of substance. But in certain connections (for instance in cyclopentane, cyclohexane, neopentane, and others) radicals recombine at considerably lower temperatures, near the point of polymorphous transition (T), this is connected with the process of rearrangement of the crystal lattice [3, 4]. However, irradiation of such substances at $T > T_{п}$ does not make it possible to accumulate radicals in them in measurable concentrations; this indicates fast recombination of formed radicals at any temperatures higher than $T_{\text{п}}$, and not only during change of the lattice. Analysis shows that in all cases when indicated peculiarities in behavior of radicals are observed at $T_{\text{п}}$ there occurs transition of substance into the gas crystalline state, in which this occurs intense rotation of molecules in lattice [5, 6].

We have studied with help of [EPR] (ЭПР) method kinetics of recombination of radicals in irradiated cyclohexane near $T_{\text{п}} = 186^{\circ}K$ and at higher temperatures. It turned out that transition into gas crystalline state is accompanied by sharp change of rate constant and activation energy of process of recombination. Thus, at $T \cong 180^{\circ}K$ $k = 10^{-22}$ cm^3/sec, in accordance with results of other works [7]. Activation energy of recombination of radicals in interval 160-175°K is equal to 20 kcal/mole [7]. At $T = 188^{\circ}K$, it is possible to observe radicals in cyclohexane only during irradiation with fast electrons ("under the beam"), where stationary concentration of radicals composes $\sim 10^{16}$ cm^{-3} and changes with dose rate j proportionally to $j^{1/2}$. After cessation of irradiation, recombination is completed in several seconds. More exact information about kinetics of recombination of radicals in gas crystalline state was obtained from time dependence of amplitude of EPR signal in the absence of unfolding of magnetic field after cutoff of electron beam. In range of temperatures 188-236°K, rate constant changes according to the law $k = 3 \quad 10^{-8} e^{\frac{-8000}{RT}}$ cm^3/sec. Thus, during transition through $T_{\text{п}}$, change of temperature altogether by 8° leads to increase of k by approximately 10^5 times. At the same time, activation energy sharply decreases from 20 to 8 kcal/mole.

Analysis of results of X-ray-structural investigations of lattice of cyclohexane and data on nuclear magnetic resonance permits us to conclude that change of kinetics of recombination is connected with small decrease of density of packing of molecules during transition to the gas crystalline state. Assuming that molecules diffuse throughout the crystal of cyclohexane by means of jump into vacancies, and using values of frequencies of jump obtained from measurements of second moment of line of proton magnetic resonance [8], we estimated time necessary for recombination of the formed radicals. It will agree well in order of magnitude with the measured value.

Therefore, we should consider that low-temperature recombination of free radicals near point of transition into gas crystalline state also occurs mainly by a diffusion mechanism.

Inasmuch as in frozen cyclohexane at a temperature of about 200°K intermolecular jump of hydrogen atoms practically does not occur, it is doubtful whether it is possible to expect it at low temperatures and for longer hydrocarbon molecules. Apparently migration of valence by such a mechanism is associated with considerable difficulties. This is confirmed by low recombination rate of radicals in majority of irradiated polymers at temperatures of 300°K. Therefore, the role of migration of valence during recombination of radicals in low-molecular organic substances seems to us to be secondary.

Literature

1. S. Ye. Bresler, E. N. Kazbekov, V. N. Fomichev, F. Sech, and P. Smeytek. Solid state physics, 5, 675 (1963).

2. V. K. Yermolayev, Yu. N. Molin, and N. Ya. Buben. Kinetics and catalysis, 3, 58 (1962).

3. N. N. Semenov. Pure and Appl. Chem., 5, 353 (1962).

4. A. B. Robins. Nature, 191, 1150 (1961).

5. A. I. Kitaygorodskiy. Reports of AS USSR, 124, 861 (1959).

6. Symposium on plastic crystals and rotation in the solid state. Oxford, 5-6 April 1960 – Phys. and Chem. of Solids, 18 (1961).

7. H. Szwarc and R. Marx. J. chim. phys., 57, 680 (1960).

8. E. R. Andrew and R. G. Eades. Proc. Roy. Soc., A216, 398 (1963).

Discussion

Kh. S. Bagdasar'yan. What is mechanism of recombination below temperature of polymorphous transition?

N. Ya. Buben. I think that in this region there occurs disintegration of crystal lattice, just as near the melting and vitrification points.

A. M. Brodskiy. From what data does it follow that reaction occurs according to second order?

N. Ya. Buben. This follows from two facts:

1) steady state concentration of radicals is proportional to dose rate (or flux of electrons) to the 1/2 power (accuracy of measurements ~10%);

2) law of the second order is satisfied by kinetics of decrease of concentration of radicals after cessation of irradiation.

P. I. Dolin. Do you indeed have preexponential factor larger than number of collisions?

N. Ya. Buben. During recombination of radicals in solid polymers, there are observed values of pre-exponential factor exceeding gas-kinetic values by 10 orders and more. In our case this difference is not so considerable. For explanation of this there were utilized concepts concerning compensational effect. However, full clarity in this question is still lacking.

V. K. Bykhovskiy. Characteristics of lattices of polyethylene and teflon are in general close. At the same time, efficiencies of recombination of radicals strongly differ. If we hold strictly to consideration of a diffusion mechanism, this is incomprehensible.

N. Ya. Buben. I do not assert that mechanism of recombination of radicals in polymers is always a diffusion mechanism. Recombination rates of radicals in teflon and in polyethylene at the same temperature indeed differ. It is possible that at high temperatures in polymers migration of valence can also play a role. However mobility of segments of polymer chains can strongly differ even for samples of one polymer with different degrees of crystallinity, and therefore recombination rates of radicals in different polymers can be different with the "diffusion" mechanism.

V. K. Milinchuk. You considered diffusion and said nothing about migration of valence. Meanwhile, in polymers, for explanation of recombination there is utilized namely migration of valence. Could you indicate a system where, in your opinion, migration of valence is the determining factor.

N. Ya. Buben. The idea of migration of valence by means of jump of H atom to free valence seems at first glance indeed very tempting, and I do not have grounds to reject this mechanism of recombination completely. In the beginning of my report, I wanted only to stress that estimation of recombination rate of radicals by diffusion mechanism which was made in work of S. Ye. Bresler and colleagues,[1] is based on the unnecessarily difficult assumption of diffusion of a macromolecule with molecular weight of 300,000 as a whole. In reality, for recombination, frequently intense motion of separate segments of macromolecule is sufficient. Regarding, however, boundaries of applicability of migratory mechanism of recombination, it is possible to say the following: According to available data for low-molecular organic molecules at temperatures, we will say, below 0-20°C, it is possible to consider that mechanism of recombination in basically a diffusion mechanism. In polymers,

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[1] S. Ye. Bresler, E. N. Kazbekov, V. N. Fomichev, F. Sech, and P. Smeytek. Solid state physics, 5, 675 (1963).

as a rule, fast recombination of radicals occurs at room temperature and higher. I know one exception — polypropylene. It is possible that at such temperatures migration of atoms of hydrogen between polymer chains already plays a role, but its absence in polymers at low temperatures shows that such a reaction by no means occurs easily. The conclusion from our work is that for small organic molecules, the basic mechanism of recombination of radicals is apparently the diffusion mechanism.

S. Z. Roginskiy. Are there any data of yours or in literature about coefficients of diffusion in organic substances below and above temperatures of phase transition? Such data on coefficients of self-diffusion or diffusion of small molecules could promote clarification of question about correctness of ideas developed by you.

N. Ya. Buben. I do not know such data. There are, however, data on measurements of temperature dependence of width of [NMR] (ЯМР) lines, which show that in region of phase transition there occurs sharp change of line width, which is due to thawing of motion of molecules — mainly rotation.

V. K. Milinchuk. It is known that radiation yield depends on method of thawing.

N. Ya. Buben. Indeed, as Szwarc and Marx[1] showed, radiation yield of radicals strongly depends on conditions of freezing. In order to standardize conditions of experiment, we had to hold cyclohexane for a certain time somewhat below the melting point, so that crystallization was completed, and after that it gave reproducible results. If, however, cyclohexane is rapidly frozen to low temperature, then first there is observed unreproducibility of recombination rate near T_n, and secondly there is step recombination at low temperatures

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[1] H. Szwarc and R. Marx. J. Chim. phys., 57, 680 (1960).

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CERTAIN DATA ON RECOMBINATION AND TRANSFORMATION OF FREE RADICALS IN γ-IRRADIATED POLYMERS

V. K. Milinchuk and S. Ya. Pshezhetskiy

Usually recombination of radicals in polymers is connected with mobility of molecules or parts of molecules, on which there are free valences. During the study of radiation-chemical processes in polyethylene, in a number of works [1-4] there was discussed possibility of recombination of radicals which is caused by migration of free valence through the substance, where there were allowed transfers of valence inside the molecule as well as between molecules. However, these works do not experimental data which would confirm this mechanism.

During investigation of process of recombination of radicals in certain polymers during heating and irradiation by light at 77°K, we obtained results which can be explained from the point of view of migration of free valence through a macromolecule.

During investigation of recombination of allyl radicals of type

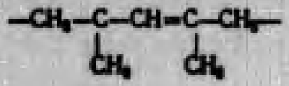
$$-CH_2-\underset{\displaystyle CH_2}{\overset{}{\underset{|}{C}}}-CH_2 \qquad (1)$$

initially formed in polypropylene, there was established the following:

a) concentration of radicals at given temperature in low-temperatures region (193-263°K) tends with time to a certain constant value of concentration of radicals, and not to zero value, i.e., recombination has a "step" character [5];

b) activation energy of recombination of radicals grows with increase of temperature from 5 kcal/mole at 193°K to 27 kcal/mole at 323°K [5];

c) there occurs transformation of radical (1) into allyl radical of the form



$$-CH_2-\underset{CH_3}{\underset{|}{C}}-CH=\underset{CH_3}{\underset{|}{C}}-CH_2- \qquad (2)$$

and polyene radical [6, 7]

$$-CH_2-\underset{CH_3}{\underset{|}{C}}-(CH=\underset{CH_3}{\underset{|}{C}})_n-CH_2- \qquad (3)$$

Transformation of radicals (1) into radicals (2) and (3) was registered according to change of hyperfine structure of [EPR] (ЭПР) spectrum. During heating of polypropylene (which had received a dose of ~25 Mrad), at a temperature higher than 263°K there was observed change of EPR spectrum in time (Fig. 1), which is connected with transformation of radical (1) into (2). Assuming that mechanism of formation of allyl and polyene radicals consists of migration of free valence of alkyl radical along polymer chain up to atom of carbon neighboring with double or conjugate bond, we carried out kinetic analysis of changes of hyperfine structure of EPR spectra. Proceeding from assumed mechanism of formation of allyl radicals, rate of this process should be equal to

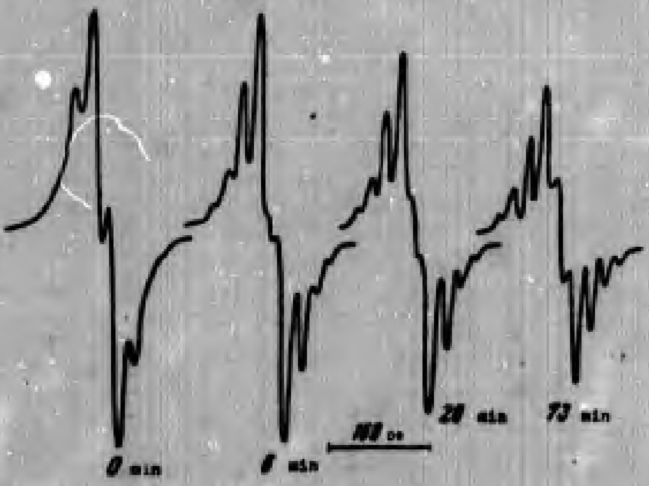


Fig. 1. Change of EPR spectrum of crystalline polypropylene depending upon time of heating at room temperature. Temperature of measurement 77°K. Dose ~25 Mrad.

$$\frac{d[R_2]}{dt} = k[R_1][C=C].$$

where $[R_2]$ is concentration of allyl radicals; $[R_1]$ is concentration of alkyl radicals; [C = C] is concentration of double bonds; k is rate constant of transformation of radicals.

Solution of this equation under definite assumptions gives for concentration of allyl radicals $\frac{[R_a]}{[R_0]} \simeq \frac{kt}{\lambda/[R_0] + kt}$, where $[R_0]$ is initial concentration of alkyl radicals.

Agreement between experimental data (plotted by points) and theoretically calculated curve (solid lines) is satisfactory (Fig. 2).

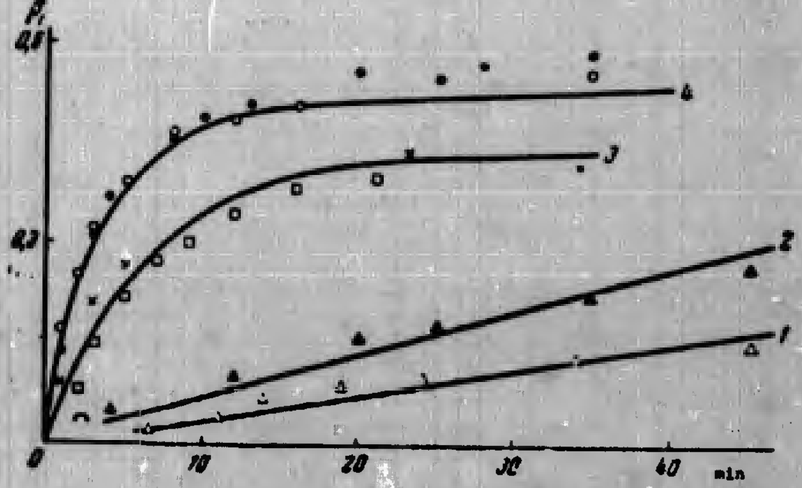


Fig. 2. Dependence of parameter β_1 on time heating at different temperatures (β_1 is ratio of concentrations of radicals (2) and (1)): 1 – 273°K; 2 – 290°K; 3 – 308°K; 4 – 323°K

Transformation of radical (1) into radical (3) was observed in polypropylene, which preliminarily was irradiated with doses of 500, 1000 and 1500 Mrad. As can be seen in Fig. 3 and 4, with increase of temperature, intensity of singlet line, which belongs to polyene radical, increases. Activation energy of transformation of alkyl radicals into allyl radicals is 6 ± 1 kcal/mole, and into polyene 4 ± 1 kcal/mole. As we see, activation energy of transformation of alkyl radicals into allyl and polyene radicals is close to activation energy of recombination of radicals at low temperatures. This witnesses in favor of the fact that mechanism of migration is common to processes of recombination and transformation of radicals in polypropylene.

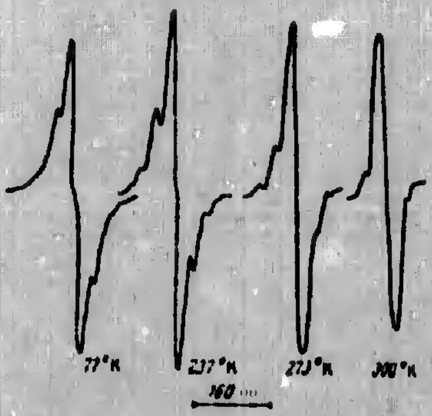


Fig. 3. Change of EPR spectrum of polypropylene depending upon temperature. Dose of preliminary radiation was 1000 Mrad. Temperature of measurement was 77°K. Dose ~20 Mrad.

Comparison of dependences of recombination of radicals on temperature for two groups of polymers of various structure, namely, polypropylene and polybutadiene with polyisobutylene and polyisoprene, confirms such a mechanism of recombination. For the first two polymers, jump of H atoms can occur between neighboring carbon atoms, whereas in polyisobutylene and polyisoprene such a possibility is absent. In Fig. 5 we may see that recombination of radicals in polypropylene and polyisobutylene occurs at considerably lower temperatures than in polyisobutylene and polyisoprene. This difference in recombination of radicals in these two groups of polymers can be explained by the fact that in polypropylene and polybutadiene recombination of radicals by the migratory mechanism is possible, and in polyisoprene and polyisobutylene it is lacking.

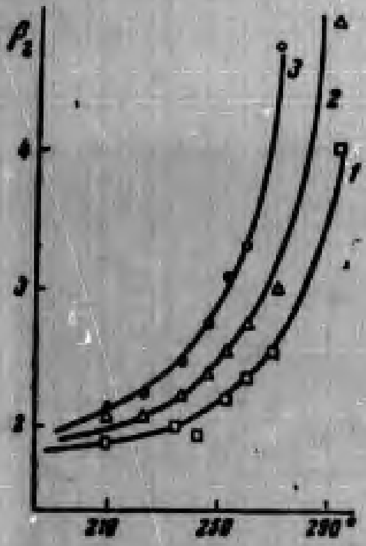


Fig. 4. Dependence of parameter β_2 on temperature of heating. Time of heating 5 minutes. (β_2 is ratio of concentrations of radicals (3) and (1)): 1 – 500 Mrad; 2 – 1000 Mrad; 3 – 1500 Mrad.

In favor of migratory mechanism of recombination of radicals witness data concerning the fact that preliminary irradiation does not affect recombination of radicals in polypropylene.

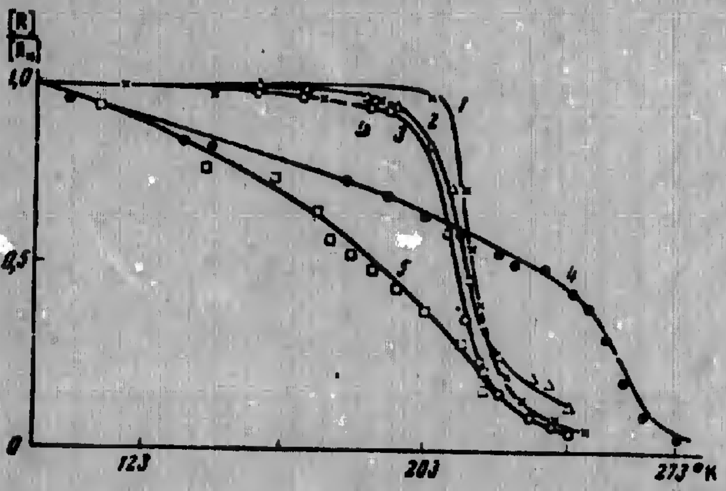


Fig. 5. Dependence of relative concentration of radicals on temperature. Time of heating 5 minutes. Dose ~15 Mrad: 1 – polyisobutylene; 2, 3 – polyisoprene (SKI NK and natural rubber); 4 – amorphous polypropylene; 5 – polybutadiene.

It is possible to conclude that recombination of radicals in polypropylene in the region of low temperatures occurs basically by the migratory mechanism. With increase of temperature, recombination due to displacement of sections of macromolecules or phase transitions also enters the picture. Increase of activation energy with increase of temperature to 27 kcal/mole and recombination of radicals at the vitrification point in amorphous polypropylenes [5, 8] agree with this.

During migration these can occur intramolecular recombination of radicals, as a result of which these are formed double and conjugate double bonds. Thanks to migration of free valence along chain of polymer there is also possible intermolecular recombination of radicals, with formation of "cross-links" between polymeric chains.

As we established earlier [6, 9], in polymers of various structure preliminarily γ-irradiated at 77°K (polyvinyl acetate, polystyrene, polymethyl methacrylate, polyvinyl alcohol, polybutadiene, natural rubber, and others), under the action of visible and ultraviolet light at 77°K there occurs destruction of radicals and also change of EPR spectra. Destruction of radicals in this case occurs at a temperature at which mobility of sections of macromolecules is practically excluded. Now it is possible to say that these effects are observed very clearly (after short exposures to irradiation) in polymers which contain absorbing groups before irradiation. Destruction of radicals after irradiation at 77°K was not observed in polydimethyl siloxane, which does not contain chromophore groups, and in which under the effect of radiation there are not formed groups which absorb in the region of visible and ultraviolet light. However, this does not permit us to conclude that radicals do not absorb, and that absorption is connected only with chromophore groups. As a rule, spectral region of absorption of polymer matrix is very wide (it can include both visible and ultraviolet parts of spectrum). This prevents us from experimental dividing regions of absorption of light by radical and matrix with help of filters.

At present, it is possible to assume that under action of light there can also occur migration of free valence along chain of polymer. Light absorbed by radical transmitted to radical along the chain from the chromophore group to a C — H bond neighboring with radicals facilitates jump of H atom. There is also possible another mechanism of destruction of radicals, which consists of the fact that C — H bond neighboring with radical dissociates, which leads to their destruction, with formation of a double bond.

In polyethylene, which, as it is known is transparent to visible and ultraviolet light, destruction of radical also occurs. However, it is known that in polyethylene there are formed double bonds in the process of irradiation.

Recombination of radicals in polymers under the action of light at 77°K gives an indication that one of the causes concentration of radicals "passing beyond the limits" during irradiation of polymers can be excitation of macromolecules by radiation.

Thus, the assumed mechanism of recombination of radicals permits us to explain the basic radiation-chemical effects during action of radiation on polymers — formation of double and conjugate double bonds and also "cross-links" and destruction of polymer chains without resorting to the reaction of disproportionation.

It is clear that this does not mean that other mechanisms of recombination of radicals do not act especially under the action of light. Tasks of further investigation will be more precise study of action of light on radicals and clarification of the mechanism of this action.

Literature

1. M. Dole and C. D. Keeling. J. Am. Chem. Soc., 75, 6082 (1953).

2. R. W. Pearson. J. Polymer Sci., 25, 189 (1957).

3. A. T. Koritskiy, Yu. N. Molin, V. N. Shamshev, N. Ya. Buben, and V. V. Voyevodskiy. High-molecular compounds, 1, 1182 (1959).

4. S. Ohnishi. Bull. Chem. Soc. Japan, 35, 254 (1962).

5. V. K. Milinchuk and S. Ya. Pshezhetskiy. High-molecular compounds — in the collection: Chemical properties and modification of polymers. Moscow, "Science" Publishing House, 1964, p. 70.

6. V. K. Milinchuk and S. Ya. Pshezhetskiy. High-molecular compounds in the collection: Chemical properties and modification of polymers. Moscow, "Science" Publishing House, 1964, p. 222.

7. V. K. Milinchuk and S. Ya. Pshezhetskiy. High-molecular compounds, 6, 666 (1964).

8. V. K. Milinchuk, S. Ya. Pshezhetskiy, A. G. Kotov, V. I. Tupikov, and V. I. Tsivenko. High-molecular compounds, 5, 71 (1963).

9. V. K. Milinchuk and S. Ya. Pshezhetskiy. High-molecular compounds, 5, 946 (1963).

Discussion

V. V. Voyevodskiy. What is the basic characteristic of the new mechanism proposed by you?

V. K. Milinchuk. The mechanism was proposed by Dole and Keeling [1], and the possibility of such mechanism was discussed in work [2]. But the experimental data which confirm it were absent. In particular, in the case of polyethylene, its preliminary irradiation did not affect recombination rate of radicals [2].

V. V. Voyevodskiy. No, for polyethylene, this irradiation apparently did influence it. Really, is transfer in paraffin chains not considered to be the same as in polyethylene? In our work [3] there is considered transfer of energy in long chains of paraffins, and not in polymers.

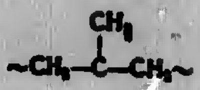
V. K. Milinchuk. In work [3] there was considered transfer of energy. Here there is considered migration of free valence.

V. V. Voyevodskiy. You consider that there is transfered free valence?

V. K. Milinchuk. Yes we consider that there is transfer of free valence which is accompanied by transition of hydrogen atom.

A. T. Koritskiy. How do you determine increase of concentration of allyl radicals during warming up of samples using the EPR method when you have a large quantity of alkyl radicals and only a small quantity of allyl radicals? How could you distinguish spectra of allyl radical and determine growth of its concentration under such conditions when the total concentration falls?

V. K. Milinchuk. First of all, during irradiation at temperature of liquid nitrogen there are formed basically alkyl radicals of the following structure:



$$\sim CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2\sim$$

During heating of samples to temperature of 263°K there occurs recombination without change of character of spectrum. With further increase of temperature, there is observed change of hyperfine structure.

We characterized our spectra in the following way. In process of heating, the greatest changes were undergone by the central component, the height of which we designated by symbol h_1. We took the ratio h_1/h_2, where h_2 is height of second component, measuring from the center. We considered that during that interval of time in which we considered this transformation, recombination of radicals was absent. Change of this ratio characterizes degree of transformation of radicals from alkyl into allyl. For polyene radicals there is presented an analogous dependence. Here we took ratio of heights of central line and side line, h_1/h_3. With increase of concentration of polyene radicals, this ratio was increased.

A. T. Koritskiy. It is known that formation of conjugate systems of double bonds and allyl radicals can be observed by using method of infrared spectroscopy. Did you apply this method?

V. K. Milinchuk. This investigation was not conducted by us. N. A. Slovokhotova and others [4] observed double bond in polypropylene.

A. T. Koritskiy. Did she observe increase of their concentration during heating?

V. K. Milinchuk. This I do not know.

A. T. Koritskiy. There have been published four works concerning this question [5-8]. Did you become acquainted with works of Lauton and Boivit [9, 10] and with other works where it was shown that in polyethylene, formation of allyl radicals, double bonds and polyene chains occurs at the temperature of liquid nitrogen?

V. K. Milinchuk. Yes, I know of these works. However, they do not contradict our data, since analogous results for polypropylene in the literature are absent. Besides, the works cited by you do not contain indisputable data about the fact that 77°K in polyethylene there are formed allyl radicals directly in the process of irradiation.

N. Ya. Buben. I have three questions for you. 1. You assume a migratory mechanism along the chain, is jump of H atom between molecules excluded?

V. K. Milinchuk. We consider intramolecular migration of free valence.

N. Ya. Buben. 2. Could you give the numerical value of rate constant of recombination in some interval of temperatures?

V. K. Milinchuk. For instance, in the interval 193-208°K, k $\approx 10^{-22}$ cm^3/sec.

N. Ya. Buben. 3. Do you not consider that action of ultraviolet and visible light reduces to absorption by the radical itself?

V. K. Milinchuk. Certainly light can be absorbed by radicals, but it can also be absorbed by the polymer matrix.

V. V. Voyevodskiy. You spoke of polydimethyl siloxane. Does there occur destruction of radicals under action of light?

V. K. Milinchuk. In polydimethyl siloxane destruction of radicals during irradiation by light does not occur.

V. V. Voyevodskiy. What radicals do you have in mind?

V. K. Milinchuk. Radicals formed as a result of detachment of hydrogen from methyl group. These radicals are basically stabilized.

V. V. Voyevodskiy. These radicals do not recombine in darkness?

V. K. Milinchuk. Correct. These radicals at 77°K do not disappear either in darkness or during illumination.

V. V. Voyevodskiy. What is molecular weight of polydimethyl siloxane?

V. K. Milinchuk. I do not have exact data.

V. V. Voyevodskiy. I ask because in polydimethyl siloxanes, depending upon their molecular weight, radicals either have or do not have the possibility to recombine at the temperature of liquid nitrogen.

V. K. Milinchuk. Yes; for instance methyl radicals can interact with the polymer molecule.

V. V. Voyevodskiy. And then they disappear.

Yu. N. Molin. Did you have everywhere "step" recombination?

V. K. Milinchuk. We observed "step" recombination in polypropylene and also in the binary system, polyvinyl alcohol + hydrazine, and in pure polyvinyl alcohol.

Yu. N. Molin. You said, I think, that you measured activation energy of recombination of radicals. How was this done?

V. K. Milinchuk. Activation energy was calculated on the basis of kinetic curves of recombination of radicals at different temperatures by the formula

$$\varepsilon = R\frac{T_1T_2}{\Delta T}\ln\frac{t_1}{t_2},$$

where t_1 and t_2 are times in which there was attained the one and the same degree of recombination at temperatures T_1 and T_2.

V. V. Voyevodskiy. In other words, activation energy was variable?

V. K. Milinchuk. Yes, activation energy grows with increase of temperature. At low temperatures it changed insignificantly.

V. V. Voyevodskiy. And what value is obtained for preexponential go factor?

V. K. Milinchuk. This factor changed depending upon temperature from 10^{-13} to 10^{-2} cm^3/sec.

V. V. Voyevodskiy. Does this mean that there is observed a compensating effect.

V. K. Milinchuk. Yes, in irradiated polypropylene a compensating effect is observed.

Yu. N. Molin. If I correctly understood, then your method essentially reduces to superposition recombination curves by change of scale. So, if recombination is "step" recombination, they in principle do not coincide, i.e., "tails" of curves will always give divergent results.

V. K. Milinchuk. Activation energy was measured according to those sections of recombination curves where rate of destruction of radicals is different from zero. From such curves it is possible to estimate activation energy.

Ya. S. Lebedev. Yu. D. Tsvetkov and V. V. Voyevodskiy also studied free radicals in irradiated polypropylene and came to a conclusion concerning consecutive formation of alkyl, allyl and polyene radicals [11, 12]. In the beginning we assumed alternatively two possible structures of allyl radical [11], however, then results obtained by Fischer and Hellwege [13] and by us [12], showed the preferableness of the following structure of allyl radical:

$$\sim CH_2{-}CH \mathrel{\overset{\cdots}{-}} C(CH_3) \mathrel{\overset{\cdots}{-}} CH{-}CH_2\sim$$

This structure somewhat differs from that which is given in report of V. K. Milinchuk and S. Ya. Pshezhetskiy.

Further, I want to note that measurements of relationship between concentrations of allyl and alkyl radicals have been conducted insufficiently reliably. Our experience in calculation of complicated EPR spectra shows that in badly resolved, multicomponent spectra superimposed on another, relationships between visible intensities of components may not correspond to relationship between integral intensities. It is unclear even how it is necessary to measure intensity of components of spectrum of alkyl radical in this case.

Analogously, data on activation energies of process of recombination calculated without taking into account the "stepness" of kinetic curves are insufficiently reliable. Calculation of activation energy according to "steplike" kinetic curves, if we start with the usual kinetic equations, can lead to the most various values, which are not correct.

V. K. Milinchuk. At first I will answer the remarks of Ya. S. Lebedev.

1. With regard to structure of allyl radical, it was depicted by me in the form

$$\sim CH_2{-}C(CH_3) = CH{-}C(CH_3){-}CH_2\sim.$$

In work of Fischer and Hellwege [13], there is proposed another interpretation of the spectrum, in which there is assumed spin interaction with protons of the central group CH_3 and large (~40 oe) splitting on β-protons. Such splitting is not observed in polymers.

Structure proposed earlier by Yu. D. Tsvetkov and Ya. S. Lebedev describes spectrum of 17 lines well if $A_{CH_3} = 1/2\ A_{CH_2}$, and explains the dependence of form of spectrum on temperature.

2. The remark on measurement of relative concentrations of allyl and alkyl

radicals is essentially true, but we consider that rough estimates can be conducted in such a way, inasmuch as we judged the concentration of allyl radical according to the intensity of the distinct central line. All the more so it is possible to use such a method in case of polyene radicals, since their line is very sharp.

3. Regarding the method of measurement of activation energy utilized by us, it is applied very widely, for instance, during the study of annealing of different centers in metals, where recombination occurs by a complicated law, during the study of destruction of color centers of lattice defects, etc. This is described for instance in the book [14].

V. V. Voyevodskiy. I would like to say several words regarding the report of V. K. Milinchuk. Data obtained by Fischer [13] and us [12] during the study of oriented films of polypropylene forced us to choose from two alternative structures of allyl radical the structure which Ya. S. Lebedev talked about, and which is substantiated in detail in the work of Fischer [13].

V. K. Milinchuk. But this structure does not explain temperature dependence of spectrum.

V. V. Voyevodskiy. In an case, if there is doubt concerning such a treatment of the spectrum, it is necessary to present new experimental data. It is impossible to give a new treatment of EPR spectrum by referring to the same experimental results on the basis of which the former treatment was given.

Now, regarding measurements of concentrations according to spectra and of activation energies. When there is no other method, it is done this way.

However, it is necessary always to remember that this method is extraordinarily crude, and to not attribute too great significance to results obtained by such a method, all the more so if you have obtained variable activation energy. Reference to the fact that such methods are applied in physics of metals are indemonstrable, inasmuch as there the treatment of kinetic phenomena is sometimes improperly approached.

Literature

1. M. Dole, C. D. Keeling. J. Am. Chem. Soc., 75, 6082 (1953).

2. A. T. Koritskiy, Yu. N. Molin, V. N. Shamshev, N. Ya. Buben, and V. V. Voyevodskiy. High-molecular compounds, 1, 1182 (1959).

3. Yu. N. Molin, I. I. Chkheidze, A. A. Petrov, N. Ya. Buben, and V. V. Voyevodskiy. Reports of the AS USSR, 131, 125 (1960).

4. N. A. Slovokhotova, Z. F. Il'icheva, L. A. Vasil'yev, and V. A. Kargin. High-molecular compounds, 6, 608 (1964).

5. N. A. Slovokhotova, A. T. Koritskiy, and N. Ya. Buben. Reports of AS USSR, 129, 1347 (1959).

6. N. A. Slovokhotova, A. T. Koritskiy, N. Ya. Buben, V. V. Bibikov, and G. V. Rudnaya. Transactions of II-nd All-Union conference on radiation chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 531.

7. N. A. Slovokhotova, A. T. Koritskiy, V. A. Kargin, N. Ya. Buben, V. V. Bibikov, Z. F. Il'icheva, and G. V. Rudnaya. High-molecular compounds, 5, 563 (1963).

8. N. A. Slovokhotova, A. T. Koritskiy, V. A. Kargin, N. Ya. Buben, and Z. F. Il'icheva. High-molecular compounds, 5, 574 (1963).

9. E. J. Lawton, J. S. Balwit and K. S. Powell. J. Chem. Phys., 33, 395 (1960).

10. E. J. Lawton, J. S. Balwit and K. S. Powell. J. Chem. Phys., 33, 405 (1960).

11. Yu. D. Tsvetkov and Ya. S. Lebedev. Journal of Structural Chemistry, 2, 607 (1961).

12. Ya. S. Lebedev, Yu. D. Tsvetkov and V. V. Voyevodskiy. Conference on physical methods of investigation of structure of molecules of organic compounds and chemical processes (theses of reports). Frune, Publishing House of Academy of Sciences of Kirghiz SSR, 1962, p. 44.

13. H. Fischer and K. H. Hellwege. J. Polymer. Sci., 56, 33 (1962).

14. J. Deans and J. Vinyard. Radiation effects in solid bodies, Moscow, IL, 1960.

OXIDATION OF ALKYL RADICALS DURING γ-TRANSITION IN AMORPHOUS SUBSTANCES

V. G. Nikol'skiy, I. I. Chkheidze,
and N. Ya. Buben

Lately there have been obtained data about the fact that during low-temperature radiolysis of saturated hydrocarbons there occurs stabilization of ions on formed alkyl radicals [1, 2]. In particular, in work [2] it is shown that already in the very beginning of radiolysis (at doses of ~0.1 Mrad), electrons stabilized in samples of saturated hydrocarbons are basically localized on alkyl radicals. It would be possible to expect that during heating of such samples there will be observed luminescence connected with recombination of accumulated ions namely in those intervals of temperature where stabilized alkyl radicals recombine, for instance, for an irradiated amorphous sample, in the region of vitrification [3]. However, we noticed that during heating of irradiated amorphous samples of dicyclohexyl butane, dicyclohexyl-4-decane, natural rubber, rubbers [SKB] (СКБ), [SKI] (СКИ), polyethylene and other organic compounds, there are observed two flashes of light: the first 60-80° below T_{GT}, and the second in the vitrification region. It is characteristic that in those cases when dose of irradiation of sample is less than 0.1-0.3 Mrad, during heating up there is observed only one — the first flash, and in the region of vitrification luminescence is absent.

In order to clarify the cause of this phenomenon, in the work there are investigated [EPR] (ЭПР) spectra of samples of high-pressure polyethylene, commercial paraffin, natural rubber, dicyclohexyl-4-decone, and 1, 2-dicyclohexyldodecone, irradiated with fast electrons at 77°K. With increase

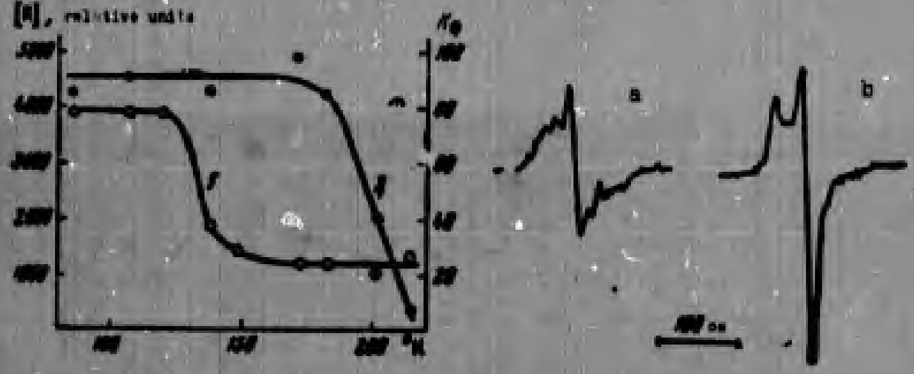


Fig. 1. Change of concentration of radicals (curve 2) and shape factor of line of EPR spectrum (curve 1) during heating of sample of dicyclohexyl-4-decone. Dose of irradiation ~0.2 Mrad; a) and b) EPR spectra at 100° and 150°K respectively.

of temperature of irradiated sample, there was observed formation of radicals of peroxide type due to the interaction of alkyl radicals with oxygen dissolved in the substance. In particular, for samples which before irradiation were vitrified in air, stabilized alkyl radicals were completely oxidized if their concentration did not exceed $2 \cdot 10^{17} - 1 \cdot 10^{18}$ gm^{-1}. In Fig. 1 are shown changes of concentration of radicals and shape factor of lines during heating of irradiated samples of dicyclohexyl-4-decone. As can be seen from the figure, total concentration of radicals in the sample during oxidation essentially does not change. It has been revealed that for all investigated compounds the rate of oxidation of alkyl radicals is sharply increased in the temperature interval located 50-80° lower than the vitrification point, i.e., where during heating up of irradiated sample there is observed the first flash of light. For instance, for samples of dicyclohexyl-4-decone (T_{CT} = 195°K) rate of oxidation of radicals increases by almost 1000 times with change of temperature from 120° to 140°K (Fig. 2).

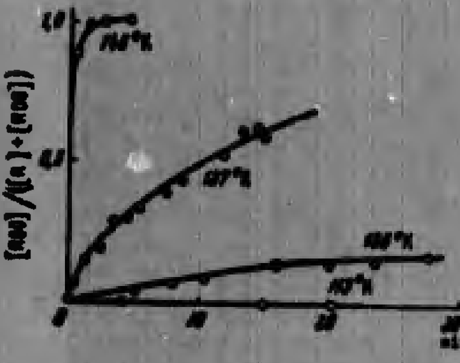


Fig. 2. Transformation of alkyl radicals into radicals of peroxide type in samples of dicyclohexyl-4-decone irradiated at various temperatures. Duration of irradiation 6 sec; dose ~0.2 Mrad.

It has been noticed that fast oxidation of alkyl radicals during heating of irradiated samples of polyethylene and commercial paraffin starts at the temperature of γ-transition, 150°-155°K. Apparently, also for other amorphous organic samples the temperature variation of rate of oxidation of radicals is determined first of all by releasing of mobility of segments ~CH_2~.

Thus, presence of two flashes of luminescence during heating up of an irradiated amorphous sample is connected with oxidation or recombination of stabilized alkyl radicals. This confirms conclusions made in work [2] about stabilization of ions on radicals.

Literature

1. Ye. L. Frankevich and B. S. Yakovlev. News of AS USSR, OKhN (Department of Chemical Services), No. 9, 1699 (1962).

2. V. G. Nikol'skiy, V. A. Tochin, and N. Ya. Buben. Present collection, p. 163.

3. V. K. Yermolayev, Yu. N. Molin, and N. Ya. Buben. Kinetics and catalysis, 3, 58 (1962).

Discussion

V. K. Milinchuk. In your work do you speak about recombination of radicals obtained in a vacuum or in air?

V. G. Nikol'skiy. Samples were irradiated in an atmosphere of nitrogen, but before irradiation they were vitrified either in a vacuum or in air, and in certain cases were thawed in a vacuum.

V. I. Lakhovitskiy. What are wave lengths of glows I and II?

V. G. Nikol'skiy. Glow occurs in interval of 4000-6000°A.

V. I. Lakhovitskiy. What is relationship between intensities of glows I and II for large doses of irradiation?

V. G. Nikol'skiy. In the presence of O_2 maximum of I with respect to temperature lies lower than the maximum of II. In the absence of oxygen, maximum of I is not observed, and maximum of II starts to increase linearly with increase of dose, starting at a dose of ~0.2 Mrad.

V. K. Milinchuk. To what radical is oxygen joined?

V. G. Nikol'skiy. To alkyl radical.

V. K. Pykhovskiy. Is irradiated high-pressure polyethylene in which electrons are stabilized colored?

V. G. Nikol'skiy. Yes.

V. K. Pykhovskiy. Is it catalytically active with respect to any hydrogen containing media, for instance water?

V. G. Nikol'skiy. I do not know.

V. K. Milinchuk. Apparently it is impossible to say that these are oxidized namely those radicals which are formed during irradiation in a vacuum. We observed that in polypropylene, peroxide radical at 77°K under action of ultraviolet light with energy of quanta accordingly about 90 kcal/mole becomes alkyl radical, EPR spectrum of which consists of four components and corresponds to the structure

$$\sim CH(CH_3)-CH-CH(CH_3)\sim$$

At the same time, during irradiation in vacuum there is observed the eight-component EPR spectrum of the radical

$$\sim CH_2-C(CH_3)-CH_2\sim$$

Thus, it is possible that there is observed not that radical which was in the vacuum, since there occurs displacement of valence (and corresponding transfer of atom of hydrogen) to neighboring atom of carbon.

PROCESSES OF FORMATION AND DESTRUCTION OF RADICALS IN PROTEINS AND POLYPEPTIDES IN CRYSTAL STATE

A. F. Usatyy and Yu. S. Lazurki.

As a result of investigation of free radicals in peptides and proteins by the [EPR] (ЭПР) method directly during their irradiation by electrons with energy of about 1 Mev, we showed [1], that kinetics of formation and destruction of radicals is described by equation

$$\frac{dN}{dt}=\alpha j-\gamma jN-\beta N, \qquad (1)$$

where N is number of radicals in unit mass of sample; j is intensity of irradiation; α is yield of radicals (per unit of absorbed energy); constants γ and β characterize rate of disappearance of radicals: γ — under action of the actual irradiation, β — due to interaction with other molecules.

During irradiation in vacuum (during continous evacuation) β = 0, and equation (1) is turned into

$$\frac{dN}{dt}=\alpha j-\gamma jN. \qquad (2)$$

Consequently, the essential fact is that radiation not only creates but also destroys radicals, thereby leading to phenomenon of saturation. Level of saturation in vacuum does not depend on intensity of irradiation in a wide range. The same level of saturation is observed during irradiation in air if intensity of irradiation is sufficiently great. Quantity of radicals with such full saturation is equal to

$$N_{\text{пн}}=\frac{\alpha}{\gamma}. \qquad (3)$$

There are possible different mechanisms, leading to disappearance of radicals from field of view of EPR by a reaction of the first order with respect to their concentration. This can be breaking away of side group from atom of carbon in the α- or β-position, which correspondingly leads to formation of a biradical or to nonsaturation. To another possibility V. L. Tal'roze [2] turned his attention, indicating that radicals in organic substances have to play the role of p- and n-traps (see also [3]). They can trap holes or electrons and be turned into ions, and also can themselves be subjected to ionization as a result of excitation formed in the molecule. For all possible mechanisms, the high probability of destruction of radicals by radiation observed in experiment requires participation of migration of excitation energy or charge from place of primary influence of radiation to the radical.

In the work there were investigated about 30 different amino acids, peptides and proteins of various molecular weights (degrees of polymerization) at room temperature. For polypeptides known to be linear and also proteins and ferments, whose tabulated molecular weight corresponds to one polypeptide chain (i.e., the molecule is not a complicated formation of subunits), there is obtained a correlation between degree of polymerization and constants $\alpha = 1/u_1$ (u_1 – energy, during absorption of which in substance there will be formed one radical), γ $N_{\text{ПН}}$ (all these magnitudes are measured independently of each other).

It was found that in the range of degrees of polymerization from 20-30 to 450, there is observed the approximate dependence

$$u_1 = (0{,}37 \pm 0{,}14) K, \tag{4}$$

where $K = M/\overline{M}_{3B}$ – degree of polymerization; M – molecular weight; $\overline{M}_{3B}$ – average molecular weight of peptide link (see figure, black points).

Equation (4), according to which energy expenditures on formation of one radical are increased with growth of length of chain, shows that in period between primary event of influence of irradiation and moment of formation of radical, in excited molecule there occur processes connected with partial dissipation of excitation energy. Thus, with increase of length of chain there occurs decrease of probability of breaking of chemical bonds in molecule. Inasmuch as in the whole indicated interval of molecular weights, magnitude u_1 linearly grows with length of chain, it is probable that these processes are connected with migration of excitation energy along the whole polymer chain.

Constant γ, efficiency of destruction of radicals by radiation, turned out to be independent of degree of polymerication and equal to

$$\gamma = (1{,}6 \pm 0{,}5) \cdot 10^{-21}\ \text{g/ev}. \qquad (5)$$

Experiment also gives value of full saturation

$$N_{\text{пн}} = (1{,}75 \pm 0{,}55) \cdot 10^{19} \frac{1}{M}\ \text{g}^{-1}. \qquad (6)$$

Comparison of (6) with calculated value (by means of formula (3))

$$N_{\text{пн}} = (1{,}7^{+\text{[illegible]}}_{-\text{[illegible]}}) \cdot 10^{19} \frac{1}{M}\ \text{g}^{-1}$$

confirms the initial kinetic equation.

The number of radicals per molecule at full saturation in the range of degrees of polymerization from 20-30 to 450 turned out to be equal to (see figure, small circles)

$$n_{\text{пн}} = 0{,}29 \pm 0{,}08. \qquad (7)$$

This number[1] shows that at full saturation, for every molecule containing a radical it is necessary on the average to have somewhat more than two molecules not containing a radical, although every molecule has already passed some number of times, depending upon dose, through the radical state. Consequently, destruction of radical occurs with higher probability than their formation.

If analogously to magnitude u_1 we introduce u_2, characterizing full energy expenditures on destruction of radical, then from formula (7) it follows that $u_2 < u_1$. Besides, if we assume that formation, as well as destruction of radical

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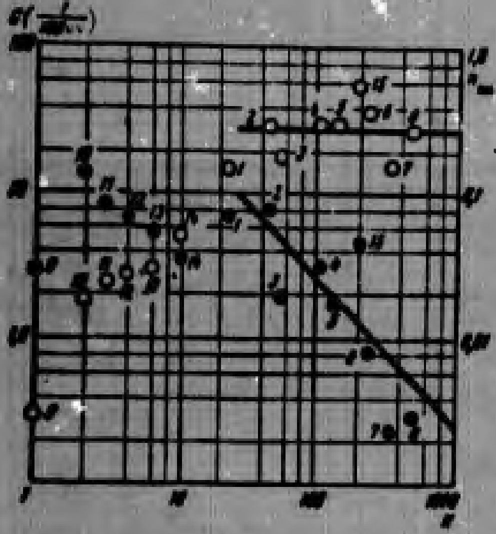
[1] In work [1] due to incorrectness of determination of concentration of radicals in standards, there were given oversized values of constants α, G, $N_{\text{пн}}$, $n_{\text{пн}}$. Below are given correct values.

Investigated polymer	$\alpha \cdot 10^{-\text{[illegible]}}$, 1/g·rad	G, 1/100 ev	$N_{\text{пн}} \cdot 10^{-\text{[illegible]}}$, 1/g	$n_{\text{пн}}$
Hemoglobin	0,046	0,77	0,9	0,04
Lysozyme	0,11	1,6	1,1	0,31
Salmin	0,13	1,9	1,3	0,18
Insulin	0,40	7,0	2,0	0,29
Tetraglycine . . .	0,45	7,3	5,7	0,08

Necessary corrections were also introduced and into the text of the present report during preparation of manuscript for press.



Dependence of radiation yield of radicals (G) (black points) and number of radicals per molecule at full saturation ($n_{ПН}$) (small circles) or degree of polymerization (K) ($G \sim 1/K$).
1) oxidized insulin; 2) insulin; 3) salmin; 4) ribonuclease; 5) lysozyme; 6) papain; 7) poly-L-glutamine acid; 8) polybenzyl glutamate; 9) glycine; 10) diglycine; 11) triglycine; 12) tetraglycine; 13) hexaglycine; 14) gramicidin; 15) trypsin.

is preceded by migration of energy through the whole molecule, then u_2 should also be proportional (see equation (4)) to degree of polymerization of molecule.

These considerations can be represented in following quantitative form. Let us assume that molecule with molecular weight M contains one or several radicals; then primary excitation appearing in it as a result of migration of energy can lead both to formation and destruction of the radical existing in it, where probability of destruction of one radical is proportional to number of radicals in molecule. Then, under conditions when it is possible to disregard all other processes of disappearance of radicals, for the rate of their accumulation in one gram of substance it is possible to write equation

$$\frac{dN}{dt}=\frac{1}{u_1}I-\frac{1}{u_2}I\frac{M}{N_A}\sum_{i=1}^{\infty} iN_i, \qquad (8)$$

where N_i – number of molecules in one gram, each of which contains i radicals. Since $\sum_{i=1}^{\infty} iN_i=N$, then from equation (8) it follows that

$$N_{ПН}=\frac{N_A}{M}\cdot\frac{u_2}{u_1} \text{ and } n_{ПН}=\frac{u_2}{u_1}. \qquad (9)$$

Here N_A is Avogadro's number; M is molecular weight.

Consequently, in order to satisfy experimental values $n_{ПН} = 0.29$, it is necessary to set

$$u_1 \cong 3{,}3u_2. \qquad (10)$$

Comparing equations (1), (4), (8) and (10), we also obtain at $\bar{M}_{ЗВ} = 115$.

$$\gamma=\frac{M}{N_A u_2}=\frac{K\bar{M}_{ЗВ}\cdot 3{,}3}{N_A\cdot 0{,}37K}=1{,}7\cdot 10^{-21}\ \text{g/ev}$$

in accordance with experiment (see equation (5)).

Thus, in crystalline protein and polypeptides with sufficiently long chains, formation and destruction of radicals during irradiation is connected with the preceding migration of energy to considerable distances, where and in both cases, apparently, this migration occurs along the polypeptide chain over its whole length.

For amino acids and short peptides there are observed somewhat different characteristics (see figure), which may be connected with amplification of role of intermolecular interaction in the crystal.

Literature

1. A. F. Usatyy and Yu. S. Lazurkin. Proc. Symposium on Biological Effects of Ionizing Radiation at the Molecular Level. Brno, 1962, p. 37-59.

2. V. L. Tal'roze. News of AS USSR, OKhN, No. 2, 369 (1959).

3. A. Charlesby. Nuclear radiations and polymers. Moscow, IL, 1962, p. 26.

Discussion

V. V. Voyevodskiy. Is form of spectrum identical both in presence of O_2 and in its absence? What is radiation yield of formation of radicals?

A. F. Ustayy. EPR spectra in presence and in absence of oxygen are different. Maximum yield of radicals is equal to 13 (glycylglycine).

Kh. S. Bagdasar'yan. According to your data, efficiency of radiation-chemical process depends on molecular weight of polymer. At the same time, for polymethyl methacrylate there are data according to which effectiveness of breaking of bond does not depend on molecular weight.

A. F. Usatyy. According to our concepts, dependence of yield on molecular weight appears in that case when region of propagation of the excitation leading to final chemical change spreads to all of the molecule. Otherwise, yield must not depend on molecular weight.

V. A. Sharpatyy. How form of EPR spectrum changed with increase of length of chain? It is known that yield of radicals strongly depends on presence of system of hydrogen bonds in polypeptide.[1]

A. F. Usatyy. Breaking of hydrogen bonds in native protein is usually connected with its denaturing. Certain of our measurements show that magnitudes of yields of radicals and limiting concentrations in denaturated and native protein

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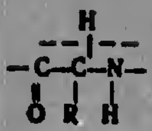
[1] L. A. Blyumenfel'd, V. V. Voyevodskiy and A. G. Semenov. Application of paramagnetic resonance in chemistry. Novosibirsk, Publishing House of Siberian Branch, Academy of Sciences of USSR, 1962, p. 188.

do not differ very strongly (by 2-3 times), but kinetics of disappearance of radicals after irradiation is different, which can be connected with different diffusion constants of gases.

Links of molecules of protein differ by the group R:



$$-\underset{O}{\underset{\|}{C}}-\overset{H}{\underset{R}{C}}-\underset{H}{N}-$$

Despite the fact that free valence can be localized for different R groups, form of EPR spectrum (overall) for different proteins little differs in width (15-17 gauss), although there exist certain badly resolved components in the center and wings of the spectrum.

A. A. Revina. How do you explain the fact that oxygen does not render an influence on yield of radicals and their limiting concentration?

A. F. Ustayy. Independence of presence of O_2 is observed in cases when either diffusion of oxygen into sample for some reasons is small, or at high intensities of irradiation, when rate of destruction of radicals by irradiation becomes predominant. If $N_{\Pi} = \alpha j/(\beta + \gamma j)$, then at $\gamma j > \beta$ $N_{\Pi H} = \alpha/\gamma$.

Yu. N. Molin. Is it correct that formula $u_1 = 0.37 \cdot K$ for efficiency of formation of radicals is valid only for large molecular weights of proteins? Since measurements of yields of radicals were conducted at room temperature, then recombination of radicals, which lowers their yield, is possible.

A. F. Ustayy. Yes, this formula is derived for polymers with long chains. Since recombination after irradiation is not discovered, then it apparently also does not noticeably occur during the irradiation, which is indicated by the first order of the kinetic equation with respect to concentration.

V. L. Tal'roze. You assume that decrease of yield with increase of molecular weight is connected with "resorption" of energy along the molecule. Thus do you have in mind some very strong "resorption," inasmuch as electron energy should become vibrational energy?

A. F. Ustayy. It is possible that there occurs migration of a bound, localized exciton, which gradually gives up energy to the lattice.

V. S. Gurman. What facts witness that radicals indeed perish under irradiation?

Yu. S. Lazurkin. From the form of kinetic equation, there naturally does not ensue simply a mechanism of destruction of radicals as a result of the effect of radiation. There can be expressed different assumptions concerning this mechanism, which need experimental verification. Nonetheless, we can talk about destruction of radicals by radiation, knowing that irradiation is a primary cause of the disappearance of radicals, and the rate of this process is proportional to intensity of irradiation.

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INVESTIGATION OF TRANSFORMATIONS AND REACTIONS OF RADICALS WITH MOLECULES IN CERTAIN SOLID MOLECULAR MATRICES AT LOW TEMPERATURES BY THE EPR METHOD

V. I. Tupikov, V. S. Pshezhetskiy,
and S. Ya. Pshezhetskiy

For radiation chemistry, knowledge of elementary chemical processes which will flow in field of radiation in condensed phases is essential. Purpose of present work is investigation of low-temperature transformations of radicals in solid molecular matrices in a field of radiation.

Under action of γ-radiation in solid ammonia, there are formed radicals NH_2, having [EPR] (ЭПР) spectrum of 9 lines. During prolonged irradiation (up to dose ~500 Mrad), EPR spectrum is changed: on the nine-line spectrum there is gradually superimposed a singlet line with width of ~40 oe. After disappearance of NH_2 radicals during heating, there remains only the singlet line. This indicates that in process of γ-irradiation there occurs transformation of NH_2 radicals into other radicals. It has been found that this singlet is identical with the singlet appearing during irradiation of solid hydrazine, which we earlier referred to the radical N_2H_3 [1]. Ratio of concentrations of radicals NH_2 and N_2H_3 decreases with increase of dose. It is possible to assume that there occurs two processes:

$$NH_2+NH_3 \longrightarrow N_2H_3+H_2; \qquad (1)$$
$$NH_2+NH_2 \longrightarrow N_2H_4. \qquad (2)$$

Since disappearance of NH_2 radicals during γ-irradiation occurs at the temperature of liquid nitrogen, it is obvious that their recombination is not connected with spatial displacement. It is possible to think that there occurs displacement of free valence (and correspondingly of a hydrogen atom) along chain of NH_3. There is also possible dissociation of radical NH_2:

$$NH_2 + h\nu \longrightarrow NH + H \qquad (3)$$

with subsequent reaction of radical NH:

$$NH + NH_3 \longrightarrow N_2H_4 \qquad (4)$$

During heating to 95-118°K, there will be formed hydrazine, the quantity of which corresponds to the quantity of NH_2 radicals [1]. This process probably is connected with certain reconstruction of lattice of solid ammonia at this temperature [2].

Processes of transformation of radicals in solid phase at 77°K occur also during action of ultraviolet light. Results of these experiments are presented in Fig. 1. At $\lambda \leq 3000$ A there occurs decrease of concentration of radicals without change of form of EPR spectrum. Disappearance of NH_2 radicals during action of ultraviolet light can be connected with processes (3) and (4), as well as with migration of valence facilitated by excitation of light. Since ammonia absorbs light with wavelength 1860-2200 A [3], which is practically absent in quartz ultraviolet, the action of ultraviolet light apparently consists of excitation of NH_2 radical its dissociation.

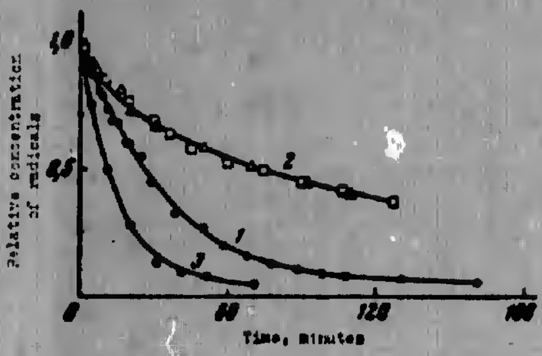


Fig. 1. Dependence of concentration of radicals on time of irradiation by ultraviolet light at 77°K. 1) change of concentration of NH_2 radicals in ammonia; 2) change of concentration of N_2H_3 radicals in crystalline N_2H_4; 3) the same in amorphous N_2H_4.

After irradiation of ammonia with ultraviolet light, preliminarily subjected to γ-irradiation, hydrazine is determined by the chemical method. Quantity of hydrazine is identical, independently of whether disappearance of NH_2 radicals occurred under action of light or as a result of heating.

Destruction of N_2H_3 radicals in γ-irradiated hydrazine under action of ultraviolet light occurs in region of $\lambda \leq 2800$ A. Hydrazine half absorbs in region of wavelengths 2800 A [4] and 2537 A [5]. In this case, it is difficult to give preference to either of the two above considered mechanisms of destruction of radicals.

Recombination of radicals by mechanism of migration of free valence obviously

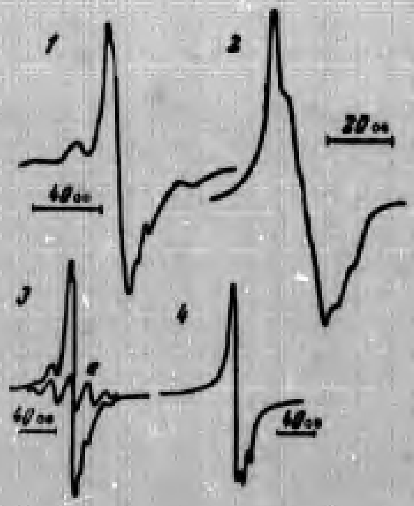


Fig. 2. EPR spectrum of γ-irradiated acetaldehyde (1); EPR spectrum of γ-irradiated acetaldehyde, recorded after irradiation by light (2); decomposition of spectrum 1 into spectrum a and spectrum 4 (3).

occurs during radical polymerization. Radical starts and closes the polymer chain. However, role of radicals in certain processes of polymerization in solid phase has not been firmly fixed. We have tried to clarify role of radicals during polymerization of acetaldehyde proceeding through the carbonyl bond at low temperatures, as was shown in works [6, 7]. EPR spectrum of radicals formed during γ-irradiation of solid acetaldehyde is shown in Fig. 2. It has 10 lines of hyperfine structure [HFS] (CTC) (a). During irradiation by ultraviolet light, this spectrum becomes a five-line spectrum (b). This gives us cause to consider that initial spectrum constitutes super position of spectra of not less than two radicals. We have decomposed the initial spectrum into two spectra: a five-line spectrum with binomial distribution of intensities 1:4:6:4:1 and splitting ~20 ev, and also a spectrum with five weakly resolved HFS lines. It is possible to assume that in the primary process there will be formed radical

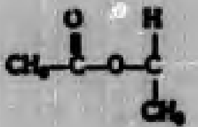
$$CH_3-C=O, \qquad (I)$$

which is then isomerized into the stabler radical

$$CH_2=CHO \qquad (I[illegible]$$

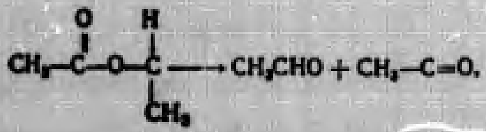
or reacts with a molecule of acetaldehyde.

Spectrum with five HFS lines and binomial distribution of intensities can be ascribed to the radical formed during reaction of radical (I) with mol[illegible] of acetaldehyde:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} \qquad (III)$$

Under action of ultraviolet light, there apparently occurs dissociation of radical (III):



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{H}{C}} \longrightarrow CH_3CHO + CH_3-C{=}O,$$

what leads to conversion of spectrum (a) into spectrum (b).

Radical (III) can lead a polymerization chain, consecutively joining molecules of acetaldehyde. In favor of the fact that radicals initiate process of polymerization are the following facts:

1) possibility of initiation of polymerization by ultraviolet light;

2) agreement between number of polymer chains and concentration of radicals (see table);

3) agreement of temperature ranges of destruction of radicals and polymerization.

If there occurs photodissociation of radicals (III), then ultraviolet irradiation of solid acetaldehyde in which there were formed radicals preliminarily by γ-irradiation should decelerate polymerization of acetaldehyde. Indeed if γ-irradiated acetaldehyde is irradiated by ultraviolet light, then there occurs decrease of degree of transformation, and also of average molecular weight of formed polyacetaldehyde (Fig. 3).

Thus irradiation by ultraviolet light interrupts the process of polymerization as a result of dissociation of radicals (III). Thus formed radicals (I) can initiate a new chain, but at the same time they can also break polymer chains.

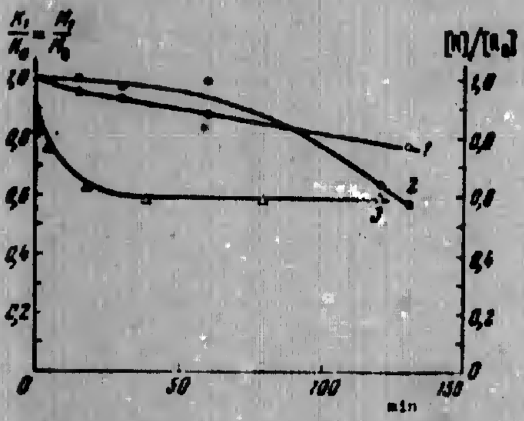


Fig. 3. Relative change of degree of conversion (1), average molecular weight of polymer (2), and quantity of radicals (3) in γ-irradiated acetaldehyde depending upon time of irradiation by ultraviolet light.

Concentration of Free Radicals and Polymer Chains in Irradiated Acetaldehyde

Dose of γ-radiation, Mrad	Number of radicals in 1 cm³ acetaldehyde	Number of polymer chains in 1 cm³ of acetaldehyde	Average molecular weight
0,1	$0{,}73\cdot10^{17}$	$1{,}62\cdot10^{17}$	$1{,}55\cdot10^{5}$
0,2	$0{,}94\cdot10^{17}$	$1{,}97\cdot10^{17}$	$1{,}49\cdot10^{5}$
0,5	$3{,}4\cdot10^{17}$	$4{,}8\cdot10^{17}$	$6{,}9\cdot10^{4}$
1	$5{,}7\cdot10^{17}$	$11\cdot10^{17}$	$3{,}2\cdot10^{4}$
3	$23\cdot10^{17}$	$26\cdot10^{17}$	$1{,}6\cdot10^{4}$
10	—	$56\cdot10^{17}$	$6{,}9\cdot10^{4}$

Literature

1. V. I. Tupikov, S. Ya. Pshezhetskiy, A. G. Kotov, K. V. Milinchuk, and V. I. Tsivenko. Journal of Physical Chemistry, 37, 138 (1963).

2. H. I. de Nordwall and L. A. K. Staveley. Trans. Faraday Soc., 52, 1207 (1956).

3. Landsberg and Predwoditeleff. Z. Phys., 31, 544 (1925).

4. F. O. Rice and F. Scherber. J. Am. Chem. Soc., 77, 291 (1955).

5. G. McDonald, A. Kahn and H. Gunning. J. Chem. Phys., 22, 908 (1954).

6. V. S. Pshezhetskiy, V. A. Kargin and N. A. Bakh. High-molecular compounds, 3, 925 (1961).

7. V. S. Pshezhetskiy, V. A. Kargin, and N. A. Bakh. High-molecular compounds, 4, 728 (1962).

Discussion

V. V. Voyevodskiy. Did you conduct estimate of diffusion rate?

V. I. Tupikov. It is known that for ammonia $T_D/T_{пл}$ = 0.54 (T_D is temperature at which diffusion starts to show up; $T_{пл}$ is melting point).

V. V. Voyevodskiy. But, after all, magnitude T_D is not a constant, and depends on concentration of radicals, rate of their formation, etc.

V. I. Tupikov. We did not carry out other estimates.

I. M. Barkalov. It is known that radiation polymerization of carbonyl compounds occurs by an ionic mechanism. Data about radical mechanism of polymerization of these compounds are absent in the literature. Do you completely exclude the possibility of an ionic mechanism of polymerization of acetaldehyde?

V. I. Tupikov. Conclusion concerning radical mechanism of polymerization of acetaldehyde, as I have already said, is made on the basis of the following experimental data: 1) initiation of polymerization by ultraviolet light; 2) coincidence of quantity of radicals with quantity of polymer chains; 3) coincidence of temperature ranges of polymerization and destruction of radicals.

I. M. Barkalov. In the work of Letort and Richard[1] it is shown that acetaldehyde is inclined to spontaneous polymerization near the fusion point. How did you take into account spontaneous polymerization? Disregard of contribution of spontaneous polymerization makes your conclusions concerning agreement between number of radicals and number of polymer chains doubtful. After all, it is necessary

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[1] M. Letort and A. J. Richard. J. Chim phys., 57, 752 (1960).

for you to melt the sample.

V. I. Tupikov. Contribution of spontaneous polymerization is very small. Therefore, it was not able to affect our results. Polymerization occurs at a temperature of -150°C; melting point of acetaldehyde is equal to -123.5°C. Thus polymerization occurs at a temperature lower than fusion point, which it is possible to observe visually according to change of optical density of samples.

V. K. Bykhovskiy. How is it possible to represent mechanism of recombination of NH_2, separated by molecules of NH_3?

V. I. Tupikov. Recombination occurs by means of transfer of atom of hydrogen from NH_3 molecules to NH_2 radical.

RADIATION CROSS-LINKING OF RUBBER POLYMERS

V. T. Kozlov

There were investigated the following rubbers: natural [NK] (НК), polyisoprene [SKI-3] (СКИ-3), chloroprene [KhK] (ХК), polybutadiene [SKD] (СКД), styrene butadiene [SKS-30 ARM] (СКС-30 АРМ), methylstyrene butadiene [SKMS-30 ARKM] (СКМС-30 АРКМ), and also saturated ethylene-propylene rubber [SKEP] (СКЭП).

In the table there are compared values of radiation-chemical yields of radicals G_R and cross-links G_c, formed during γ-radiolysis of solid (at -196°C) rubber polymers. Values of G_R and G^c were determined according to the initial linear segments of curves of accumulation of radicals, which were measured by the [EPR] (ЭПР) method at a temperature of -196°C, and cross-links measured in samples after heating up to room temperature according to the maximum of swelling in

Comparison of Yields of Radicals and Cross-Links Per 100 ev of Absorbed Energy During Radiolysis of Solid Rubber Polymers

Rubbers	$G_R/2$	G_c	$G_R/2G_c$
SKEP	0,275	0,50	0,55
NK	0,140	1,13	0,12
SKI-3	0,140	1,13	0,12
KhK	0,100	0,94	0,11
SKD	0,096	1,71	0,06
SKMS-30 ARKM	0,056	0,48	0,12
SKS-30 ARM	0,048	0,46	0,10

xylene.[1] As can be seen from the table, values of G_R are located in the following sequence: G_R (SKEP) > G_R (NK, SKI) > G_R (KhK) > G_R (SKD) > G_R (SKMS) > G_R (SKS), whereas the sequence of values of G_c has the opposite character: G_c (SKD) > G_c (NK, SKI) > G_c (KhK) > G_c (SKEP, SKS, SKMS). Only in rubbers with aromatic groups in molecules able, to a considerable degree, to disperse absorbed energy are there observed small yields of both radicals and cross-links. Character of sequence of values of G_R completely corresponds to the scheme of formation of radicals during radiolysis of solid hydrocarbons proposed by the group of investigators [2]. According to this scheme, for disintegration into radicals it is required that energy of first level of excitation E_1 be larger than, or at least equal to the energy of the broken bond: in this case $D_{CH} \approx 4$ ev; for saturated polymers (SKEP) $E_1 \approx 10$ to 7 ev; for unsaturated (rubbers) $E_1 \approx 6$ to 5 ev.

Proceeding from the indicated scheme of formation of radicals, the detached H atom can be hot or "thermal" depending upon magnitude of excess energy $E_1 - D_{CH}$. Degree of reactivity of H atoms can be estimated according to the consumption of "unsaturation" in rubbers under irradiation. This was done jointly with N. A. Klauzen by the method of infrared spectroscopy. As objects of investigation were selected the rubbers NK, SKD, and [SKBM] (CKLM), in which with irradiation there was determined the concentration of double bonds (irradiation was carried out in a vacuum at a pressure of up to 10^{-3} mm Hg or in a medium of inert gas).

As experiments showed (Fig. 1), in the absence of oxygen in polybutadienes or in systems protected by antioxidants, under irradiation at does of up to 60 Mr, consumption of double bonds was not revealed, at least within the limits of error of the method Infrared Spectroscopy [IRS] (ИКС) method (1.5 - 5%). This indicates the absence of reactions of attachment of H atoms and also of reactions of detachment by H atom of other hydrogen atoms, inasmuch as the latter reaction apparently occurs with a rate of 3-5 times lower than the first [3]. Absence of reaction of attachment of H atoms to double bonds in rubbers under irradiation can be explained, first, by the lower reactivity of H atoms as a result of their

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[1] Values of yields of the cross-linking process G_c were calculated without introduction of corrections for end effects, or the possibility of interlacing of chains. This apparently to a certain degree leads to lowering of values of G_c, which, however, should not be too large with increase of dose of irradiation and at room temperature of swelling (see [1]). Besides, introduction of correction factors probably will not change relative character of location of G_c in the series of investigated rubbers.

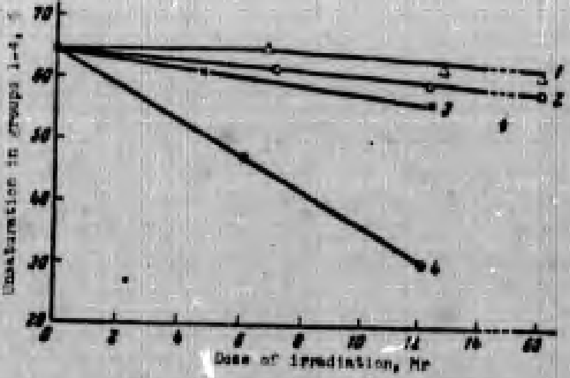

Fig. 1. Curves of change of "unsaturation" in groups 1-4 of polybutadiene rubber (SKBM) depending upon dose of irradiation on Co^{60} source under various conditions: 1) rubber containing 2% phenyl-β-naphthylamine irradiated in a vacuum (10^{-3} mm Hg); 2) purified rubber irradiated in vacuum (10^{-3} mm Hg); 3) rubber containing 2% phenyl-β-naphthylamine, irradiated in air; 4) purified rubber irradiated in air.

low available excess energy $E_1 - D_{CH}$ and, secondly, by the small quantity of atomic H, formed in unsaturated compounds as compared to saturated (estimate according to magnitudes of G_R). In turn, this can serve as an indication of the absence in the process of cross-linking of rubbers of a large contribution of reactions with participation of hot H atoms by the mechanism known from literature [4] for polyethylene.

Thus magnitudes of G_R are close to true values of yields of radicals, not considering, however, radicals closed by primary ions and electrons by the mechanism of V. L. Tal'roze and Ye. L. Frankevich [5]. During comparison of values of $G_R/2$ and G_c (considering that two radicals during recombination form one cross-link) one may see that for saturated SKEP approximately half of cross-links can be formed by radicals. The remaining half can appear as a result of interaction of secondary ions, i.e., ions closed by charges of radicals, inasmuch as, as follows from the data of Ye. L. Frankevich and B. S. Yakovlev [6], the concentration of such ions for solid hydrocarbons is comparable with concentrations of radicals, and composes for a dose of 50 Mrad $\sim 2 \cdot 10^{19}$ cm^{-3}, whereas for saturated SKEP for the same dose of irradiation, concentration of radicals composes $\sim 2.8 \cdot 10^{19}$ cm^{-3}. Altogether, radicals and secondary ions can form for a dose of 50 Mrad $\sim 2.4 \cdot 10^{19}$ cm^{-3} cross-links, which corresponds to the experimental concentration of cross-links obtained for this dose during radiolysis of solid SKEP.

As follows from the present work [5], processes of interaction of radicals and secondary ions occur in the same temperature-time interval during thawing out of motion in the system. Apparently there exists a complex of processes:

$$1)\ R + R \longrightarrow R{-}R; \qquad 2)\ R^{-} + R^{+} \longrightarrow R{-}R;$$

$$3)\ R + R^{-} \longrightarrow R{-}R + e; \qquad 4)\ R + R^{+} \longrightarrow R{-}R^{+}.$$

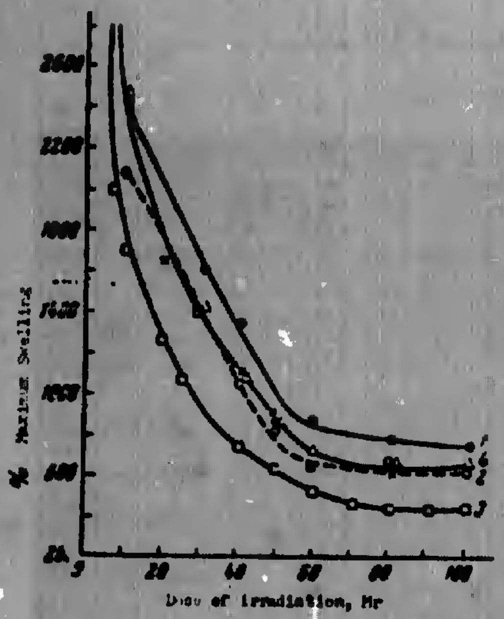

Fig. 2. Radiation cross-linking of NK and sol-fraction of NK (as percentage of maximum swelling in xylene) with the introduction of different quantities of DFPG and methyl styrene. 1) sol of NK; 2) sol of NK + 1.25 weight % DFPG; 3) NK; 4) NK + 10 weight % DFPG (Δ); 5) NK + 16 weight % methyl styrene (o).

The picture will be different in the case of unsaturated systems, which due to small value of E_1 (if above-indicated scheme of formation of radicals is true) have to be characterized by an "absolute" yield of radicals, including radicals closed by charges, which is less than for saturated hydrocarbons. And, at the same time, unsaturated systems possess sharply raised yields of cross-links as compared to saturated systems. In this case, the complex of processes 1-4 no longer will be decisive, and other processes of cross-linking, in particular ion-molecular processes, can obtain great importance:

$$RH^{+}+RH \longrightarrow R{-}R^{+} + H_2; \quad RH^{+} + \dot{R}H \longrightarrow R{-}R + H_3^{+}.$$

As a definite indication of the great significance of nonradical processes of cross-linking of rubbers can serve results concerning radiation cross-linking with participation of inhibitors of radical processes – radical acceptors such as diphenylpicrylhydrasil [DFPG] (ДФПГ) and salts of methods of variable valence [7] (Fig. 2).

As can be seen from Fig. 2, the presence in rubbers of 1.25 weight % DFPG accelerates radiation cross-linking. Regarding, however, salts, the latter definitely manifest a sensitizing action during cross-linking of rubbers, accelerating the process, as we showed earlier [8], by 1.5-1.7 times. If radiation cross-linking of rubbers were basically a radical process, then the presence of radical acceptors to a considerable extent would retard cross-linking.

Increase of content of DFPG to 10 weight % somewhat retards cross-linking. This can be explained by the increase of scattering of part of absorbed energy by phenyl rings with increase of their content in the system. It is obvious that with introduction into the system of 16 weight % methyl styrene, which is not a radical acceptor, in which the quantity of henyl rings approximately corresponds to the quantity of the latter in 10 weight % DFPG, radiation cross-linking is delayed to the same extent (see Fig. 2). The given results can serve as an argument in favor of the large contribution of the ion-molecular mechanism in process of radiation cross-linking of rubbers.

Literature

1. A. Charlesby. Nuclear radiations and polymers. Moscow, IL, 1962.

2. Yu. N. Molin, I. I. Chkheidze, Ye. P. Kaplan, N. Ya. Buben, and V. V. Voyevodskiy. Kinetics and Catalysis, 3, 674 (1962).

3. L. I. Avramenko, N. Ya. Buben, and R. V. Kolesnikova. News of Academy of Sciences of USSR, OKhN (Department of Chemical Sciences), No. 11, 2079 (1962).

4. A. N. Pravednikov and S. S. Medvedev. Transactions of I-st All-Union conference on radiation chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1958, p. 269.

5. Ye. L. Frankevich and V. L. Tal'roze. Transactions of II-nd All-Union conference on radiation chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 651.

6. Ye. L. Frankevich and B. S. Yakovlev. News of Academy of Sciences of USSR, OKhN, No. 9, 1699 (1962).

7. V. F. Yevdokimov, I. Ya. Poddubnyy, and I. A. Kuzin. DAN USSR, 141, 1097 (1961).

8. Z. N. Tarasova, M. Ya. Kaplunov and V. T. Kozlov. USSR Copyright No. 132795; Bulletin of inventions, No. 20 (1960).

Concerning the Question of Destruction of Radicals Under Irradiation

At present there are being discussed things which can cause phenomena of destruction of radicals under irradiation, in particular the following: Radiation itself creates microzones with temperature considerably higher than the average ambient temperature. In these microzones there are probably created for a short time conditions under which there occurs destruction of radicals located close to each other. Apparently such a process occurs in the case of linear polymers, for instance polyethylene, for which this mechanism was proposed by Yu. S. Lazurkin and M. A. Mokul'skiy [1].

We discovered a phenomenon which can be explained by processes of destruction of radicals under irradiation. This phenomenon consists in the following: curve of accumulation of radicals during radiolysis of solid (at -196°C) SKD (bonds 1-4 ~ 98%) has a nonlinear initial segment (up to dose of 150 Mr), curvature of which corresponds to increase of radiation yields of radicals G_R with increase of dose of irradiation, which is surprising. Usually curves of accumulation of radicals have an initial linear section and then there are observed deviations corresponding to concentrations of radicals "going beyond the limit." With increase of dose of irradiation, value of G_R constantly increases. For instance, at dose of 20 Mr, $G_R = 0.10$; at 40 Mr, $G_R = 0.13$; at 70 Mr, $G_R = 0.15$; at 115 Mr, $G_R = 0.17$; and in the interval of doses from 150 to 200 Mr, G_R attains maximum value of 0.19, where the dependence has a linear character. After this the curve of accumulation deviates in the direction of concentrations "going beyond the limit." Apparently in the beginning of the process of irradiation, in high-temperature microzones a certain number of radicals recombine.

As a result of these and possibly other processes, under irradiation there are formed transverse cross-links, which then hamper recombination of radicals. Transverse cross-links or side groups essentially affect character of destruction of radicals under irradiation. Thus, if in SKD by means of preliminary irradiation we create $5 \cdot 10^{19} - 1 \cdot 10^{20}$ gm^{-1} of transverse cross-links, then in this case the curve of accumulation of radicals will have the usual character, with an initial rectilinear section and constant values of G_R, equal to 0.19, which corresponds to the maximum value of yield of radicals obtained at large doses of irradiation (150-200 Mr) during radiolysis of initial SKD. Thus, formation of transverse cross-links promotes stabilization of radicals. At the same time, with a sufficient quantity of side groups in the initial polymer, for instance in NK, additional steric obstacles in the form of cross-links in the range of concentrations of radicals from 0 to $1.2 \cdot 10^{20}$ gm^{-1} do not affect the character of accumulation: initial segment of curve of accumulation of radicals is linear, with constant value of $G_R = 0.28$.

Furthermore, the action of light on radicals in the solid phase at -196°C (these data were obtained jointly with V. K. Milinchuk) causes their destruction, the rate of which for SKD exceeds the rate of destruction of radicals in NK by tens of times. The highest rate of the process of destruction of radicals in un-cross-linked SKD was recorded during irradiation by photons with energy corresponding to wave lengths $\lambda \leq 2500$ A. In the case, however, of preliminarily cross-linked SKD (concentration of cross-links up to $5 \cdot 10^{19} - 1 \cdot 10^{20}$ gm^{-1}) process of destruction of radicals under action of light is retarded, and its rate becomes close to the rate for the case of initial NK. Energy range of light quanta for which character of destruction of radicals is analogous to character of destruction

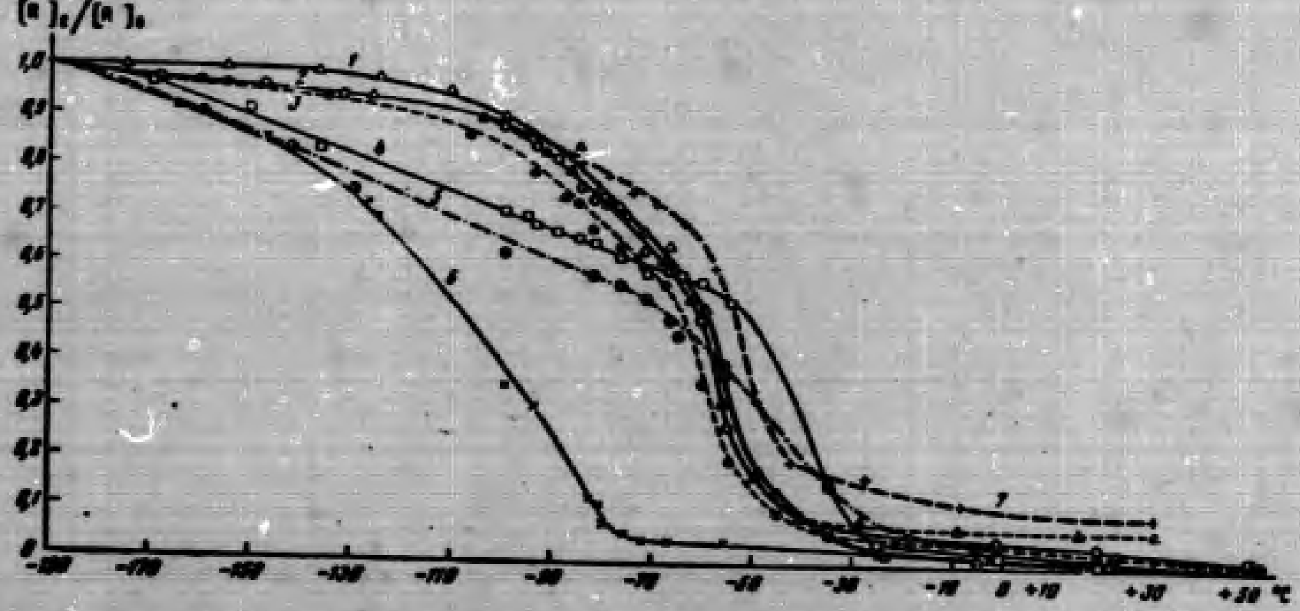

Fig. 3. Curves of destruction of radicals formed in frozen rubbers at -196°C under irradiation (15 Mr), with heating from -196° to +50°C; $[R]_t/[R]_0$ is relative concentration of radicals: 1) SKEP; 2) NK (o); 2) NK, cross-linked, density of cross-links $1.24 \cdot 10^{20}$ gm^{-1} (▲); 3) SKI-3: 4) chloroprene; 5) SKS-30 ARM; 6) SKD; 7) NK, cross-linked, density of cross-links $2.15 \cdot 10^{20}$ gm^{-1}.

of radicals under irradiation apparently corresponds to the long-wave part of the visible spectrum and the near infrared region. Energy release in high-temperature microzones in the form of high-frequency vibrations probably cannot overcome steric hindrances caused by cross-links or side groups, or give an impetus to destruction of radicals in such polymers.

The condition for destruction of radicals in polymers in which internal motions are sterically hindered is the beginning of thawing out of motion in the system and amplification of thermal vibrations of segments of chains. Thus destruction of radicals in high-temperature microzones under irradiation to a strong degree depends on structure of the polymer, just as in cases of destruction of radicals during thawing out or under the action of light. This process is noticed only for linear polymers not having steric hindrances, only on the initial stage of irradiation — before formation of a sufficient quantity of transverse cross-links.

Concerning the Question of Destruction of Radicals During Thawing Out

Character of curves of destruction of radicals formed by radiation in solid rubber polymers (Fig. 3) to a great degree depends on absence of steric hindrances created by side groups. Thus, curves of thawing out of ethylene-propylene rubber (SKEP), NK and SKI-3 coincide, although the first does not have double bonds in the monomer unit, but all three types of rubbers have a side methyl radical. Destruction of radicals occurs in region of temperatures of phase transition from solid into highly elastic state. For linear polybutadiene SKD, the curve has a smooth character, whereas for polybutadiene [SKB] (CKB), which has side branches, the curve reveals a step, as was shown by V. G. Nikol'sky and M. V. Alfimov [2]. Curve for copolymer of butadiene with styrene (SKS-30 [ARM] (APM)) also has a step character. A step can also appear for SKD if in it there are preliminarily formed steric obstacles in the form of cross-links.

Appearance of step on smooth destruction curves of radicals occurs apparently only during formation of steric hindrances, for instance in the form of cross-links, and only for polymers which in their initial state do not possess side radicals. If polymer has side radicals, then an additional number of steric obstacles in the form of cross-links no longer changes the picture. Thus, the destruction curve for NK preliminarily vulcanized to a state close to ebonite (between cross-links there are contained two-three monomer units)coincides with the curve for unvulcanized raw NK. During cross-linking of NK to the ebonite state (about one monomer unit between cross-links), the character of destruction of radicals is retained, but phase transition shifts somewhat toward higher temperatures. Data given in Fig. 3, pertaining to the case of destruction of radicals in stiffly cross-linked three-dimensional structures, in which displacements of segments of chains with radicals "sitting" on them are hampered, and the meeting of two radicals is practically excluded, force to look for some other form of destruction of radicals besides recombination of two radicals during collision. The overwhelming mass of radicals perish in the range of temperatures of phase transition, independently of the presence of considerable concentrations of cross-links; however, rigidity of the polymer system renders a certain influence on stabilization of the radicals which remain 1 minute after thawing (see Fig. 3).

Let us note that irradiation at room temperature after thawing of samples irradiated at the temperature of liquid nitrogen leads to the appearance of absolutely analogous spectra (widths and shapes of lines coincide). Curves of the dependence of rate of destruction of radicals on time of stay at room temperature are also similar. These radicals quite rapidly disappear during the first two hours, and after 10 hours there remain radicals which disappear extraordinarily slowly, and which still can be observed in concentrations of $(0.05\text{-}0.1)\cdot 10^{17}$ gm^{-1}, even after one and a half months following irradiation. In samples heated to +50°C, rate of disappearance of radicals increases by 10 times as compared to room temperature, where there the exponential law of drop of concentration of radicals as a function of holding time, which is also observed at room temperature, is approximately retained.

The presented data showing independence of rate of destruction of radicals on rigidity of system at the moment of thawing of motion of segments, and the comparatively intense interaction of the remaining radicals, in spite of the considerable distance between them, which is equal to hundreds and more angstroms, permit us to conclude that processes of destruction of radicals with increase of vibrational motion of monomer units of the system to a very small degree occur as a result of direct recombination of radicals due to the approach of radical containing segments to each other. Apparently increase of mobility of sections gives an initial impetus to processes of destruction of the nearest radicals. As a result of these processes, is energy released, which promotes the destruction of other radicals, supposedly as a result of a complex of reactions of "open" radicals and radicals "closed by a charge," as a result of phenomena discovered by V. L. Tal'roze, Ye. L. Frankevich and B. S. Yakovlev [3, 4].

Literature

1. M. A. Mokul'skiy. High-molecular compounds, 2, 119 (1960).

2. M. V. Alfimov and V. G. Nikol'skiy. High-molecular compounds, 5, 1388 (1963).

3. Ye. L. Frankevich and V. L. Tal'roze. Transactions of II-nd All-Union conference on radiation chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 651.

4. Ye. L. Frankevich and B. S. Yakovlev. News of Academy of Sciences of USSR, OKhN (Department of Chemical Sciences), No. 9, 1699 (1962).

INVESTIGATION BY EPR METHOD OF FORMATION AND TRANSFORMATION OF FREE RADICALS UNDER ACTION OF γ-RADIATION IN SALTS NH_4Cl, $N_2H_4 \cdot HCl$, $N_2H_4 \cdot H_2SO_4$ AND THEIR FROZEN WATER SOLUTIONS

A. G. Kotov and S. Ya. Pshezhetskiy

As it is known, character of radicals formed during irradiation of free molecules or condensed systems mainly depends on nature of dissociating particles. However, due to the "cage effect," which hampers spatial separation of fragments, formation of radicals in condensed phases occurs not so effectively as in the gas phase, and there predominate ways of dissociation which are less hindered by "cage effect" (for instance, detachment of hydrogen). At the same time, it is not obvious a priori that the role of matrix reduces only to the "cage effect." It is also not clear to what extent interaction with the matrix affects [EPR] (ЭПР) spectrum and nature of formed radicals. This question has still been little investigated. To it is dedicated the given report.

It was shown [1, 2], that during γ-irradiation of ammonium perchlorate there are formed ion-radicals NH^+. From the point of view of clarification of role of matrix, in the first place there should be determined whether ion-radicals are formed due to the fact that the initial particle is an ion whether this is determined by interaction with the ionic matrix. For this purpose there were investigated EPR spectra of γ-irradiated salts NH_4Cl, $N_2H_4 \cdot HCl$, $N_2H_4 \cdot H_2SO_4$ and their frozen water solutions. Obtained spectra are shown in Fig. 1. Analysis of spectra of γ-irradiated NH_4Cl showed what there are formed ion-radicals NH^+ (in solid ammonia there are also revealed NH_2 radicals). In salts of hydrazonium there are formed

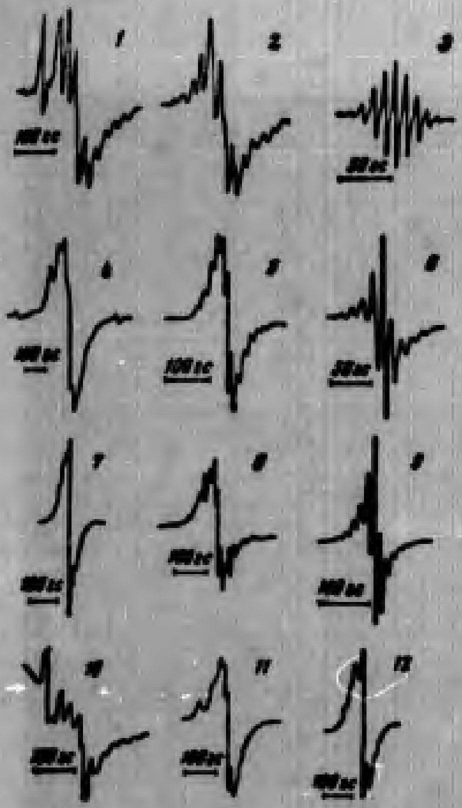

Fig. 1. EPR spectra of γ-irradiated salts NH_4Cl, $N_2H_4 \cdot HCl$, $N_2H_4 \cdot H_2SO_4$ and their frozen aqueous solutions: NH_4Cl: 1) directly after irradiation; 2) after heating at 150-200°K; 3) the same at 250-300°K. $N_2H_4 \cdot HCl$: 4) directly after irradiation; dose 100 Mr; 5) after heating at 250°K; 6) registration of spectrum at 250°K. $N_2H_4 \cdot H_2SO_4$: 7) directly after irradiation; dose 100 Mr; 8) directly after irradiation; dose 4 Mr; 9) registration of spectrum at 250°K. Water solutions: 10) NH_4Cl; 11) $N_2H_4 \cdot HCl$; 12) $N_2H_4 \cdot H_2SO_4$. [гс] = gauss

ion-radicals $N_2H_4^+$. Analogous form of spectra of water solutions of these salts (in case of hydrazonium salts spectra of solutions are analogous to spectra of salts irradiated by a large dose, 100-150 Mr) permits us to say that in molecular matrices of frozen water solutions there are formed the same ion-radicals. Thus, in matrices different in nature, there occurs formation of identical ion-radicals. Mechanism of formation of these particles consists of dissociation of the N — H bond, i.e., it is the same as during formation of radicals as a result of irradiation of solid ammonia and hydrazine [3].

However, form of EPR spectrum one of and the same ion-radical is not identical in different salts, and at first glance there is created the impression that from the same particle there appear different radicals. Study of temperature dependences of spectra has shown that while in frozen water solutions of hydrazonium salts, spectra do not differ from each other and are not changed with change of concentration and temperature, in solid salts spectra are different (at small doses of irradiation) and depend on temperature. This fact is explained by the different spin density on protons, which depends on interaction with surrounding ions. From crystallographic data it follows that the distance N ... Cl in hydrazonium chloride is equal to 3.31 A [4], and the distance N ... O in hydrazonium sulfate is 2.80 A [5]. It is natural to assume that due to large repulsion, spin density on protons referred to spin density on nitrogen nuclei will be larger in hydrazine sulfate. Indeed, the observed number of HFS components in spectrum of $N_2H_4 \cdot H_2SO_4$ and in spectrum of $N_2H_4 \cdot HCl$ (13) is obtained if we take $(\Delta H_H/\Delta H_N)_{SO_4} = 4$, and $(\Delta H_H/\Delta H_N)_{Cl} = 2$. With this assumption, temperature changes of these relationships explain temperature changes of EPR spectra.

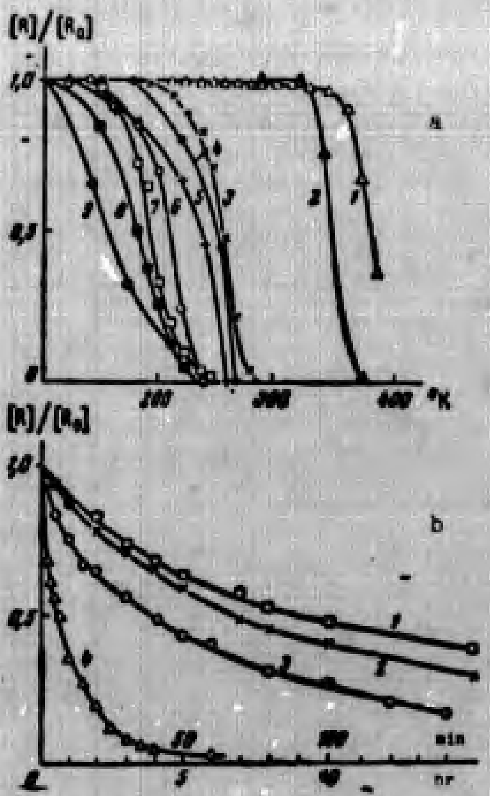

Fig. 2. Change of relative concentration of ion-radicals depending upon temperature of heating (a) and time of irradiation (b). a) 1) hydrazonium sulfate; 2) ammonium chloride after heating at 300°K; 3) hydrazonium chloride; 4) solution of $N_2H_4 \cdot H_2SO_4$; 5) solution of NH_4Cl; 6) solution of $N_2H_4 \cdot HCl$; 7) ammonium chloride; dose 25 Mr; 8) ammonium chloride; dose 150 Mr; 9) change of optical density of F-centers in NH_4Cl; b) Destruction of NH_3^+. 1) irradiation by visible light (λ = 360 mμ) at 90°K; 2) irradiation by visible light at 78°K (1 and 2 pertain to the lower time scale); 3) illumination by ultraviolet light at 78°K; 4) illumination by ultraviolet light at 90°K (3 and 4 – upper time scale).

During heating of frozen irradiated salts and solutions and during irradiation by light, ion-radicals perish. Change of their concentration is shown in Fig. 2. It is impossible to assume recombination of like-charged particles during their contact. Therefore, it is necessary to look for other mechanisms of destruction of ion-radicals. Obtained data show what one of probable mechanisms of destruction of ion-radicals consists of their recombination with electrons of F-centers. This follows from the agreement between temperature dependences of color [6] and rate of destruction of NH_3+ under action of ultraviolet light [7] (Fig. 2b). At the same time not all facts can be explained by this mechanism. For instance, there occurs change of concentration of NH_3+ in NH_4Cl under action of visible light absorbed by color centers ($\lambda_{макс}$ = 380 mμ). Since rate of destruction in this case does not depend on temperature, and color of sample is kept, then we should assume dissociation of NH_3+ to be the first step of destruction as a result of energy transfer by excitons.

Mechanism of destruction of ion-radicals in water solutions and in salts in which F-centers are absent remains unclarified. The main difficulty in explanation of destruction of ion-radicals is connected with their Coulomb repulsion, which forces us to assume mechanisms excluding direct interaction of these particles. By analogy with recombination with electrons liberated from F-centers of crystal, it is possible to assume their recombination with solvated electrons, although EPR spectra of frozen solutions do not reveal any signs of these particles.

Literature

1. T. Cole. J. Chem. Phys., 35, 1169 (1961).

2. J. S. Hyde and E. S. Freeman. J. Phys. Chem., 65, 1636 (1961).

3. V. I. Tupikov, V. I. Tsivenko, S. Ya. Pshezhetskiy, A. G. Kotov and V. K. Milinchuk. Journal of Physical Chemistry, 37, 138 (1963).

4. K. Sakurai and Y. Tomiie. Acta Cryst., 5, 293 (1952).

5. S. Nitta, K. Sakurai and Y. Tomiie. Acta Cryst., 4, 289 (1951).

6. H. Pick. Z. Elektrochem., B56, 753 (1962).

7. N. Mott and R. Gurney. Electronic processes in ionic crystals. Moscow, IL, 1950.

Discussion

N. Ya. Buben. From those curves which you gave in your report, it follows that F-centers perish at a temperature lower than NH_3^+. How then is it possible to use presence of color centers in the mechanism of destruction of NH_3^+?

A. G. Kotov. Here there were given heating curves for two doses; at large doses these destruction curves do not strongly differ. Besides, it is simple to see visually that color is changed.

P. I. Dolin. What is the role of water in formation of radicals, and what is their concentration?

A. G. Kotov. For NH_4Cl there is known the dependence of melting point on concentration of solutions. Concentrations were chosen in the region up to saturation, and role of water was reduced to role of an insulator of ions, but an insulator of different type than in the ionic crystal.

G. B. Manelis. Did you have solid solutions in water, or was there formed an eutectic? What is the order of destruction of NH_3^+, first or second?

A. G. Kotov. In this system there is observed step recombination, i.e., concentration of radicals does not drop to zero with increase of temperature. Therefore, there is obtained first or second order depending upon at what concentration measurement is started. Regarding the first question, consider that we were dealing with solid solutions in which at sufficiently large concentrations of salt there probably was also a eutectic.

V. A. Tochin. Did you observe change in EPR spectra under action of light?

A. G. Kotov. Yes we did. They are explained in the following way: Our initial spectrum consists of super position of spectra of three paramagnetic particles: a 9-line spectrum, 12 lines of NH_3^+ and an anisotropic line, apparently connected with Cl atoms. During irradiation by light, changes consisted of the following: at first anisotropic line disappeared, and whole spectrum changed from a 12-line to a 9-line spectrum.

V. A. Tochin. Was there seen EPR spectrum of F-centers?

A. G. Kotov. We did not find signs characteristic for spectra of F-centers.

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INVESTIGATION OF IRRADIATED AMMONIUM PERCHLORATE BY METHOD OF ELECTRON PARAMAGNETIC RESONANCE

Yu. M. Boyarchuk, N. Ya. Buben, A. V. Dubovitskiy,
and G. B. Manelis

Study of elementary processes in crystal lattice is of considerable interest for clarification of mechanism of thermal decomposition of solid bodies. In certain cases, it is assumed that processes of thermal decomposition occur with formation of intermediate active particles, atoms, or radicals, properties and behavior of which determine character of the decomposition.

The most convenient method of observation of radicals in solid phase is electron paramagnetic resonance. However, sensitivity of [EPR] (ЭПР) method usually does not permit the recording of metastable centers directly in the process of thermal decomposition. This is due to the very low steady-state concentration of such centers.

Certain useful information can be obtained by studying accumulation and recombination of metastable centers appearing as a result of action of ionizing radiation. Thus, it is possible to expect that certain paramagnetic centers obtained during irradiation are similar or identical to metastable particles formed during simple thermal decomposition.

We have studied the nature, accumulation and recombination of paramagnetic centers appearing under the action of ionizing radiation in pure ammonium perchlorate and in NH_4ClO_4 with additions of CaO, MnO_2 and $KMnO_4$. These additions are catalysts of thermal decomposition of ammonium perchlorate [1].

Measurements of kinetics of accumulation and recombination of paramagnetic centers were conducted in temperature interval of 100-400°K on an EPR spectrometer fixed directly under a beam of electrons with energy of 1.6 Mev [2].

Under the action of radiation in NH_4ClO_4, as analysis shows, [3], there arise three types of particles appearing in the EPR spectrum: ion-radicals NH_3^+, paramagnetic molecules ClO_3 and particles giving a wide singlet in the spectrum (width between points of maximum slope about 40 oe), probably F-centers.

From temperature dependence of anisotropy of hyperfine splitting of spectrum of NH_3^+, it was found that ion-radical NH_3^+ (and also ion NH_4^+ in NH_4ClO_4) has, along with rotation, also vibrational (translational) motion with potential barrier of 0.55 ± 0.05 kcal/mole. Thus vibrations have a predominant direction in the (100) plane of the crystal.

For fast estimation of stability of paramagnetic centers, there were recorded EPR spectra during "thawing" of a sample of NH_4ClO_4, irradiated at a temperature of 150°K, with rate of change of temperature of 1°K per minute. This experiment showed that upon achievement of temperature of 270°K, centers which give the wide singlet in the EPR spectrum completely disappear.

Study of kinetics of accumulation and recombination of radicals NH_3^+ and ClO_3 was conducted in the range of temperatures from 300 to 370°K. It was found that radiation yield of NH_3^+ increases with increase of temperature, with activation energy of 2.7 ± 0.5 kcal/mole.

Values of radiation yields of NH_3^+ and ClO_3 at a temperature of 295°K are equal to 0.4 1/100 ev and 10^{-2} 1/100 ev respectively.

Decrease of concentration (after cessation of irradiation) is described by second-order kinetic equation:

$$dc/dt = -kc^2.$$

Recombination rate constants are equal to:

$$k_{NH_3^+} = 10^{6.5} \exp(-8300/RT) \ \mathrm{sec}^{-1} \cdot \mathrm{mole}^{-1} \cdot \mathrm{cm}^3;$$

$$k_{ClO_3} \approx 10^{20} \exp(-20000/RT) \ \mathrm{sec}^{-1} \cdot \mathrm{mole}^{-1} \cdot \mathrm{cm}^3.$$

Additions of CaO, MnO_2 and $KMnO_4$ change recombination rate constant of NH_3^+. Formation of ClO_3 and NH_3^+ can be represented by a diagram:

$$ClO_4^- \rightsquigarrow ClO_4 + e \rightarrow ClO_3 + O;$$

$$NH_4^+ \rightsquigarrow NH_3^+ + H.$$

Recombination of ClO_3 molecules occurs according to the equation:

$$2ClO_3 \rightarrow Cl_2 + 6O$$

Oxygen can be seized in traps in the form O^{2-}; then recombination of NH_3^+, probably occurs on defects O^{2-}:

$$2NH_3^+ + O^{2-} \rightarrow \text{reaction products.}$$

Properties of ion-radicals NH_3^+ studied in this work, which are formed during radiolysis of NH_4ClO_4, permit us to obtain certain ideas concerning the behavior of active particles formed during thermal reactions in ionic crystals. Regarding radicals ClO_3, they are apparently also intermediate products during thermal decomposition of ammonium perchlorate.

Literature

1. Solid-state chemistry. Moscow, IL, 1961.

2. Yu. N. Molin, A. T. Koritskiy, A. G. Semenov, N. Ya. Buben, and V. N. Shamshev. Instruments and Expermental Techniques (PTE), Shamshev. No. 6, 73 (1960).

3. T. Cole. J. Chem. Phys., 35, 1169 (1960).

Discussion

V. I. Lukhovitskiy. You obtained oxygen in atomic form, and in the trap it turns out to be in the form of a negative ion. How does it acquire an electron?

A. V. Dubovitskiy. It is possible to assume that at a temperature of 270°K there occurs recombination of two F-centers. Such recombination, as it is known, occurs by a bimolecular law and can lead to formation of a so-called F_2-center, in which there are two extra electrons. On just such a center oxygen can be seized.

GENERAL DISCUSSION

Kh. S. Bagdasar'yan. I would like to express certain considerations concerning recombination of radicals in a frozen medium which occurs as a result of migration of valence. Such migration of valence can be considered as a diffusion process with a certain effective diffusion constant, and consequently recombination of radicals can be considered according to equations of diffusion kinetics, if we consider that during encounter of two valences there occurs their destruction. Then we obtain the following expression:

$$-\frac{dn}{dt} = 4\pi R D n^2,$$

where R is the sum of effective radii of these molecules or radicals; D is coefficient of effective diffusion, which can be estimated by the formula of Smolukhovskiy-Einstein, from the known relationship

$$x^2 = 6D\tau,$$

here x is a certain elementary displacement of the order of molecular dimensions; τ is time during which this elementary displacement is accomplished.

At the same time

$$\tau = 1/k,$$

where k is rate constant of monomolecular reaction, i.e.,

$$\tau = \frac{1}{k} = 10^{-13} e^{E/RT},$$

where E is activation energy of transition of atom of hydrogen from neighboring monomer unit.

Proceeding from these considerations, I made certain calculations. If we take $E = 8000$ cal/mole, then at 170°K we have $k = 1 \cdot 10^{18}$ cm^3/sec, which is very close to the magnitude obtained in the work of N. Ya. Buben and others. At 120°K this constant is obtained to be of the order of 10^{-22} cm^3/sec. These calculations give orders of magnitude close to that which is observed in experiment, and apparently, it is necessary to consider this mechanism.

Ya. S. Lebedev. I want to turn attention to the fact that the existence of a limiting concentration of radicals during irradiation of solid bodies formally ensues from the possibility of step recombination. If recombination does not go to the end, this means (independently of the mechanism of this phenomenon) that recombination rate W strongly depends on the total number of particles n, which is conditionally written as:

$$\partial W / \partial n \gg 0.$$

Then, independently of any concrete models, the equation

$$\frac{dn}{dt} = GI - W,$$

where the first term takes into account the formation of radicals, and the second takes into account their destruction, will give a limit which will not depend on dose rate, i.e., concentration will practically not change after turning off of the source of radiation. Thus, simultaneous existence of the phenomena of limiting concentration and step recombination is fully natural.

V. V. Voyevodskiy. I would like to express certain general considerations concerning accumulation and recombination of radicals. We have two different approaches to these processes. On the one hand, we study reactions of radicals after cessation of irradiation, i.e., the kinetics of their transformations into solid phase, and here it is clarified that these reactions are strongly influenced by thawing of internal motions, the possibility of transition from one regime of internal motions to another during transition through various "singular points," and also the regime of freezing. On the other hand, there is the question about behavior of radicals in the course of irradiation and achievement of limiting concentration. Models of these processes were offered in the report of G. K. Vasil'yev and V. L. Tal'roze, and also in the report of A. F. Usatyy and Yu. S. Lazurkin. In the case of reactions in the course of irradiation, in principle there are possible two approaches: 1) irradiation renders some influence on all of the crystal lattice as a whole. For instance, during irradiation energy is continuously dissipated and converted into energy of vibrational nonequilibrium motions. We know that various motions affect reactions differently. The "stationary concentration" of these motions is different from zero in the course of irradiation, and it will affect recombination reactions. Thus there have to be obtained effects of influence of dose rate, which were noted in the last report. However, we know that in certain experiments dose rate does not render an influence; 2) irradiation affects radicals and their further secondary reactions.

From this it follows that the questions of accumulation and recombination of radicals should not be detached from each other, inasmuch as their mechanisms can in some part be the same, although under irradiation there can be additional effects which it is necessary to take into account. It is necessary to overcome the disagreement in data which exists.

V. L. Tal'roze. I would like to note the exceptional interest which the report of A. F. Usatyy and Yu. S. Lazurkin causes. The conception of "resorption" of energy along all of the length of the molecule clashes with very serious difficulties.

There is no sence in talking about the hypothesis of "resorption of energy" within the framework of one molecule when the number of degrees of freedon is such that for every vibrational degree of freedom the energy is less than the energy of the vibrational level. Such "resorption" cannot occur without participation of neighboring molecules.

A remark with regard to the paper of Kh. S. Bagdasar'yan. Flow is it with those substances where destruction of radicals is observed at 90°K? In this case, rate constant of migration of valence should be no longer 10^{-22}, but 10^{-30} cm^3/sec. For this reason the externally attractive theory of migration of valence for the majority of objects, not for all certainly, was abandoned by us.

G. B. Sergeyev. Apparently in processes of accumulation and stabilization of radicals a large role is played by chemical reactions. In confirmation of this I want to present certain of our preliminary results on photochemical accumulation of radicals in cyclohexyl chloride and bromide, a mixture of chlorine and cyclohexene, and a mixture of HBr and cyclohexane at 77°K. There are not revealed radicals only during photolysis of cyclohexy bromide.

V. L. Tal'roze. One more remark with respect to the question: Can thermal hydrogen atoms conduct some reactions, can they for instance detach an atom of hydrogen, or can they not basically enter into recombination reactions? V. Ye. Skurat and I recently carried out the following investigation: On tungsten wire there are obtained H atoms (pressure of hydrogen in the system is several hundredths of a mm of mercury), which diffuse into a sample of completely deuterized polyethylene. The whole system is immersed in liquid nitrogen. In this installation there was recorded deuterium-hydrogen exchange, and there was investigated its kinetics. Consequently, it is possible to state that a thermal atom of hydrogen is able to detach atoms of hydrogen from molecules of polyethylene.

My last remark concerns the report of V. T. Kozlov. It is known that the number of cross-links is determined with low accuracy. Frequently there is met a divergence of 2-3 times or more. During determination of number of radicals, there is also possible an error of 2 times. Therefore, although V. T. Kozlov gives reasonable arguments in favor of ion-molecule reactions, it is necessary to regard them quite carefully.

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4. MECHANISMS OF CERTAIN PHOTOCHEMICAL AND RADIATION-CHEMICAL REACTIONS

CONCERNING THE QUESTION ABOUT MECHANISM OF PHOTOLYSIS OF AQUEOUS SOLUTIONS

V. S. Gurman and G. B. Sergeyev

It is known that during photolysis of frozen solutions of H_2O_2 in water at a temperature of 77°K in a wide range of concentrations, from 29 to 10^{-2} mole/liter, radical HO_2 is stabilized, and only during photolysis of solutions with concentration of 10^{-3} mole/liter is there recorded the spectrum attributed to OH [1, 2].

At present, it is accepted to consider that during photolysis of frozen H_2O_2 solution radicals appear according to the following mechanism:

$$H_2O_2 \xrightarrow{h\nu} 2OH;$$
$$OH + H_2O_2 \rightarrow HO_2 + H_2O.$$

Thus, in solution with concentration of 10^{-2} mole/liter (molecular ratio $H_2O:H_2O_2$ = 5500:1), in which radical HO_2 is stabilized, there should be realized a mechanism ensuring transfer of free valence to a distance of 15-17 molecular diameters of water.

For additional check of presence of such transfer, we conducted photolysis of fast frozen solutions of hydrogen peroxide and n-propyl alcohol in water. Photolysis was conducted by light from lamp [SVDSh-250](СВДШ-250) in a quartz Dewar at a temperature of 77°K.

From Fig. 1 one may see that at the molecular ratio $H_2O:H_2O_2:n\text{-}C_3H_7OH$ = 2100:1 of 1 on the spectrum of the radical recorded during photolysis of solution of H_2O_2 in water (2100:1), there is superimposed another spectrum. Figure 2 shows that this second spectrum belongs to alcohol radical formed obviously by the reaction

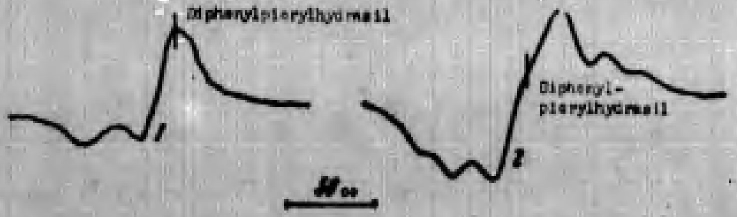


Fig. 1. EPR spectra of solutions of H_2O and H_2O_2 + n-propyl alcohol in water:
1) $H_2O:H_2O_2$ = 2000:1;
2) $H_2O:H_2O_2:C_3H_7OH$ = 2000:1:1.

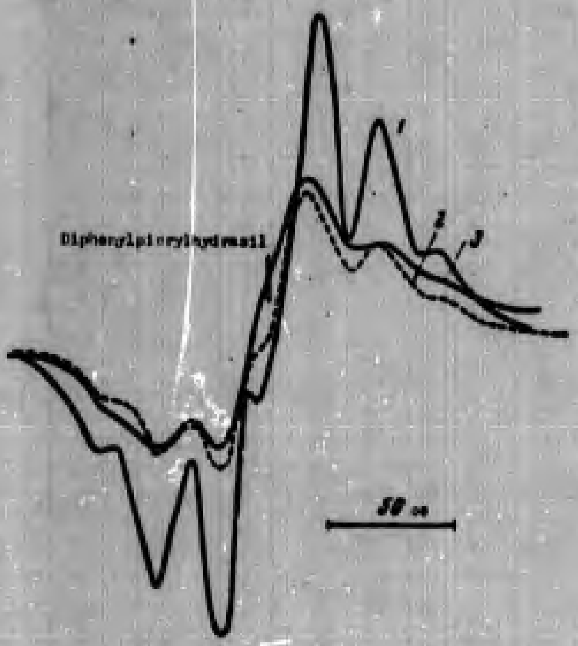


Fig. 2. EPR spectra of solutions H_2O_2 + n-propyl alcohol in water:
1) $H_2O:H_2O_2:C_3H_7OH$ = 2000:1:8;
2) $H_2O:H_2O_2:C_3H_7OH$ = 2000:1:3;
3) $H_2O:H_2O_2:C_3H_7OH$ = 2000:1:1.

OH + C_3H_7OH. Photolysis of frozen solutions of alcohol in water showed the absence of radicals recorded by the [EPR] (ЭПР) method.

Mechanism of transfer of valence explaining the above described processes can be, for instance, chain reaction of radical OH (possibly excited) with water: OH + H_2O = H_2O + OH, proceeding with participation of hydrogen bonds of ice.

Such a reaction was postulated in the mechanism of radiolysis of water by V. V. Voyevodskiy [3].

Literature

1. J. Kroh, B. C. Green and I. W. T. Spinks. J. Am. Chem. Soc., 83, 2201 (1961).

2. S. Ye. Kaytmazov and A. M. Prokhorov ZhETF (Journal of Experimental and Theoretical Physics), 36, 227 (1960).

3. V. V. Voyevodskiy. Transactions of II-nd All-Union conference on radiation chemistry. Moscow, Publishing House of Academy of Sciences of USSR, 1962, p. 102.

PHOTOSENSITIZED BIMOLECULAR REACTIONS

M. G. Kuz'min, I. V. Berezin,
B. M. Uzhinov, and Yu. A. Mikheyev

At present there are known numerous photosensitized monomolecular reactions. In these reactions, as a result of a collision of second kind, there occurs transfer of excitation energy from sensitizer the breaking bond of the reacting molecule. Usually there are then formed radicals or ions. However, in condensed systems, in principle there is possible another way of reaction (especially if excitation energy of sensitizer is less than binding energy). For closely relatively located molecules there exist collective energy levels, corresponding, for instance, to the four-center complex:

$$\begin{array}{ccc} A & \cdots & C \\ \vdots & & \vdots \\ B & \cdots & D \end{array}$$

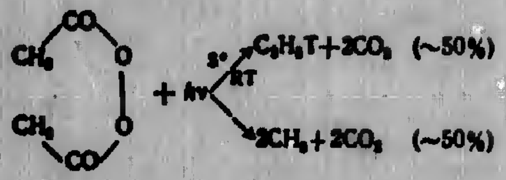
If energy of sensitizer is sufficient for formation of such a complex, then there can be observed a photosensitized bimolecular reaction:

$$S^{*} + AB + CD \longrightarrow S + AC + BD.$$

We have detected such photosensitized molecular reactions of isotope exchange in liquid and solid phases. During irradiation by ultraviolet light of a mixture of saturated hydrocarbons (for instance cyclohexane and pentatriacontane), one of which is tagged with deuterium or tritium, in the presence of sensitizers (benzene, anthracene, etc.), there is observed the exchange reaction of hydrogen

$$S^{*} + RH + R'T \longrightarrow S + RT + R'H.$$

It is obvious that then there also occur exchange reactions both by identical atoms of hydrogen and between homogeneous molecules. Apparently, such a analogous photosensitized reaction leads to formation of tagged ethane during photolysis of acetyl peroxide in tagged solvents:



It is found that in such exchange reactions there can participate only alkyl atoms of hydrogen. Hydroxyl atoms of hydrogen of alcohols and carboxylic acids are not exchanged. Also atoms of hydrogen of aromatic nucleus and in the α-position to it are not subject to exchange. It is shown that the reaction both in the case of hydrocarbons and in the case of disintegration of acetyl peroxide occurs by a molecular, and not by a radical or ion mechanism. Quantum yield is of the order of units (during consideration of all possible ways of reaction). Probability of exchange of a given atom of hydrogen partially depends on its radical reactivity. Isotope effect is small. Variation of sensitizers and wavelength of light permits us to estimate activation energy of bimolecular reaction for those cases when thermal reaction occurs by chain means (for hydrogen exchange in hydrocarbons ~70 kcal/mole).

Obviously by such a molecular mechanism there can occur a large number of different photochemical reactions. In particular, it explains the numerous cases of a difference in properties of "free radicals" obtained by thermal and photochemical methods. Such reactions can have special importance for solid and ordered media where there are a large number of collective levels.

Discussion

I. G. Kaplan. Energy level of excitation of anthracene lies lower than energy level of excitation of your reagents. What mechanism of energy transfer to reactants do you assume?

M. G. Kuz'min. I assume transfer of energy to the collective level corresponding to a four-center complex.

I. G. Kaplan. Thus, according to your hypothesis, a four-center complex strongly lowers energy relative to energy of one separate molecule. What is this lowering?

M. G. Kuz'min. It is possible to estimate energy of formation of such a four-center complex. It composes about 70 kcal/mole, which corresponds lowering of level by ~20%.

I. G. Kaplan. There should be conducted experiments which would show that there is indeed a new absorption band.

M. G. Kuz'min. There will not be an absorption band because for its appearance change of internuclear distance is necessary. Such a transition will contradict the Franck-Condon rule.

Yu. N. Molin. Do you think this four-center complex exists beforehand in the form of an intermediate product, or will it be formed only under the influence of excited molecule of sensitizer?

M. G. Kuz'min. This is an activated complex which will be formed as a result of transfer of energy from the sensitizer.

S. Z. Roginskiy. How do you estimate magnitude of quantum yield of these reactions?

M. G. Kuz'min. It is considered that probabilities of exchange of any two atoms of hydrogen are approximately of the same order of magnitude. Hence, according to the content of tritium in the final compound, and knowing the dose of irradiation by ultraviolet light, we can estimate the quantum yield. There is obtained a magnitude of order of units.

S. Z. Roginskiy. What is it possible to say about kinetic isotope effect in these reactions?

M. G. Kuz'min. During photodisintegration of acetyl peroxide, there is not revealed an essential difference between deuterium and tritium. It is necessary, however, to consider that with deuterium the accuracy of experiments is considerably lower than with tritium.

L. N. Ganyuk. Was there investigated action of inhibitors?

M. G. Kuz'min. Inhibitors, in the full sense of this word, were not applied. We used such radical acceptors as anthracene and iodine. If reaction passed through formation of a radical (H or R) then in the presence of radical acceptors we would have to detect the change of quantum yield of exchange simply due to the destruction of radicals as a result of change of the relationship between different parallel and successive reactions leading to exchange.

V. I. Gol'danskiy. Did you have a case when, after formation of such a complex, bonds regrouped somehow, let us say with formation of HT?

M. G. Kuz'min. We did not obtain hydrogen.

N. A. Bakh. What is the estimate of quantum yield of the reaction of decarboxylizing?

M. G. Kuz'min. 10%.

KINETICS OF PHOTOCHEMICAL DECOMPOSITION OF METHYL ALCOHOL AT LOW TEMPERATURES

B. N. Shelimov, N. V. Fok
and V. V. Voyevodskiy

We have shown [1] that alcohol radicals CH_3CHOH are very effectively decomposed by ultraviolet light, with formation of methyl radicals, which in turn enter into the reaction $CH_3 + C_2H_5OH \rightarrow CH_4 + C_2H_4OH$ with molecules of alcohol.

That fact that alcohol radicals are intensely decomposed under action of ultraviolet light was confirmed in works of Alger, Anderson and Webb [2], and also Johnson [3]. These authors revealed that decomposition of radical CH_2OH by light leads to formation of radical HCO [2] and also gaseous and liquid products [3].

For clarification of mechanism of photochemical transformations occurring with participation of alcohol radicals, we studied kinetics of accumulation of radicals and gaseous products during irradiation of dilute solutions of H_2O_2 and C_6H_6 in methyl alcohol.

Alcohol solutions sealed in quartz ampoules were irradiated with the [SVDSh-250] (СВДШ-250) lamp directly in the resonator of the [EPR-2] (ЭПР-2) instrument, which gave us the possibility to conduct recording of EPR spectra simultaneously with irradiation. After irradiation, ampoules were uncovered, and formed gases were analyzed by mass spectrometric method.

Analysis of obtained EPR spectra showed that during photolysis there are formed radicals CH_3, HCO and CH_2OH, time change of concentration of which in the course of irradiation, after turning off of the light and after turning it on again

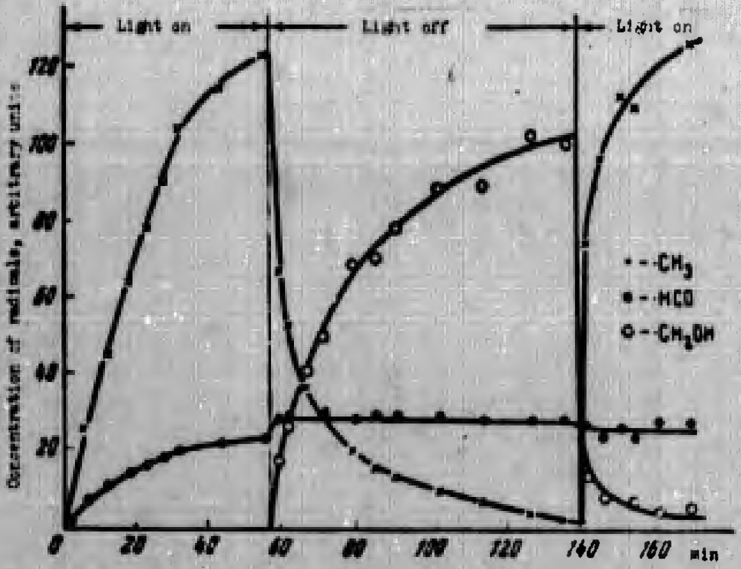


Fig. 1. Kinetics of accumulation and transformation of radicals in system $H_2O_2 + CH_3OH + h\nu$.

is represented in Fig. 1 for a solution of H_2O_2 in methyl alcohol. During photolysis of diluted solutions of C_6H_6 there was observed a kinetic picture similar to the one presented in Fig. 1.

Gas released during photolysis was a mixture consisting of 17% CH_4, 26% CO and 57% H_2. Composition of gas did not change with irradiation time, and their absolute quantities exceeded the quantities of radicals by a few times.

Measurement of concentration of H_2O_2 showed what in a certain time after the beginning of irradiation, hydrogen peroxide ceases to be consumed, whereas the quantity of gases continues to grow.

These facts indicate that under these conditions, in the solid phase there occurs an initiated reaction, which in a certain time after its beginning continues without participation of the initiator.

Initiation obviously is carried out in the following way:

$$H_2O_2 \xrightarrow{h\nu} 2OH, \ OH + CH_3OH \rightarrow H_2O + CH_2OH;$$
$$C_6H_6 \xrightarrow{h\nu} C_6H_5^{\bullet}, \ C_6H_5^{\bullet} + CH_3OH \rightarrow C_6H_6 + CH_2OH + H$$

Formed CH_2OH radicals are decomposed by light with formation of CH_3, which then enter into the reaction

$$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH.$$

We showed that during irradiation with the full light of a mercury lamp, there also occurs formation of radical HCO from CH_2OH and decomposition of HCO by the reaction.

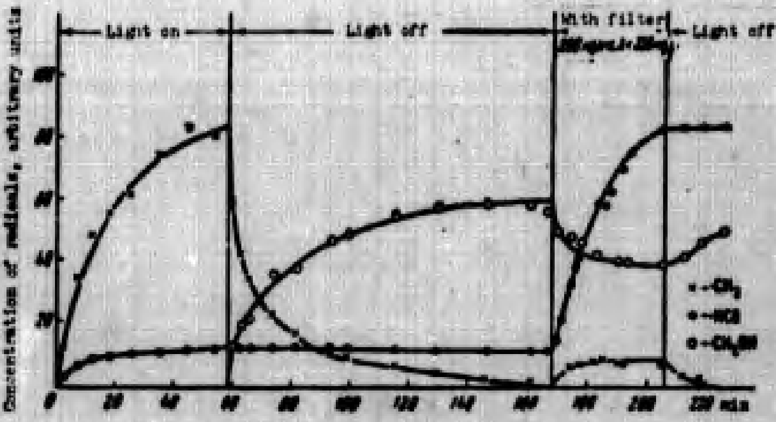


Fig. 2. Kinetics of accumulation and transformation of radicals in system $C_6H_6 + CH_3OH + h\nu$ (experiments with filtered light).

$$HCO \xrightarrow{h\nu} H + CO;\ H + CH_3OH \rightarrow H_2 + CH_2OH.$$

Indeed, during repeated irradiations by light with λ > 320 mμ decomposing HCO and not decomposing CH_2OH, concentration of HCO sharply drops and concentration of CH_2OH grows. If, however, conversely, we use light of 290 mμ < λ < 330 mμ, which decomposes CH_2OH and does not decompose HCO, then concentration of the latter grows in time, which one may see from Fig. 2 (as initiator in this case there was taken benzene, which does not absorb in this region of the spectrum).

Simultaneous formation of CH_3 and HCO, occurring as a result of absorption of light by radical CH_2OH, can be connected with the fact that this radical is joined by hydrogen bonds with one or several molecules of alcohol, and under the action of light this complicated radical R is decomposed by the scheme

$$R \rightarrow CH_3 + HCO + R'(CH_3,\ HCO,\ CH_2OH,\ H) + \text{products.}$$

This elementary reaction leads to increase of number of free valences, and therefore is a branching reaction, which follows from Fig. 2.

However, in spite of the existence of the branching reaction, there does not occur continuous growth of concentration of free valences; therefore, it is necessary to assume that under these conditions there also occurs a reaction of chain termination. This can be the reaction

$$CH_3 + H \rightarrow CH_4.$$

Thus, on the basis of data obtained in the work there can be made the conclusion that in this case there is realized a unique photochemical chain reaction. In distinction from the usual chain reactions initiated by light, under the action of light there occurs not only initiation, but also branching and certain processes of continuation of the chain.

Literature

1. B. N. Shelimov, N. N. Bubnov, V. V. Voyevodskiy, and N. V. Fok. In the collection: Paramagnetic resonance. Kazan', Publishing House of Kazan' University, 1960, p. 37.

2. R. S. Alger, T. H. Anderson, and Z. A. Webb. J. Chem. Phys., 30, 695, 1959.

3. R. H. Johnson. J. Phys. Chem., 65, 2144, 1961.

Discussion

L. N. Ganyuk. Why do you consider that hydrogen is detached from methyl group?

N. V. Fok. According to source material, in liquid as well as in frozen normal aliphatic alcohols, hydrogen is detached chiefly from the α-position. Furthermore, after turning off the light we observed formation of CH_2OH radicals by the reaction

$$CH_3+CH_3OH \rightarrow CH_4+CH_2OH.$$

S. Z. Roginskiy. What is the cause of high stability of HCO radical? Did you try to interrupt irradiation when there had not yet occurred saturation of concentration of these radicals, in order to see if this concentration changes?

N. V. Fok. HCO radicals are stable only in darkness; under the action of light they disintegrate by the reaction

$$HCO \xrightarrow{h\nu} H+CO.$$

We conducted experiments with cessation of irradiation at the moment of growth of concentration of HCO radicals and did not reveal any change of their concentration after turning off of the illumination.

N. A. Bakh. Did you not observe a reaction of release of hydrogen with formation of formaldehyde?

N. V. Fok. We did not succeed in detecting fomaldehyde in reaction products.

Yu. N. Molin. Are you sure that the quadruplet of the EPR spectrum observed by you is caused by methyl radicals, and not by some others, for instance CH_3O radicals?

N. V. Fok. Comparison of character of spectrum with the fact of release of methane in the process of irradiation permits us to conclude that the indicated spectrum can be ascribed namely to methyl radical.

Yu. N. Molin. Were yields of stable reaction products and radicals measured under comparable conditions?

N. V. Fok. Moreover, this was conducted in the same experiment.

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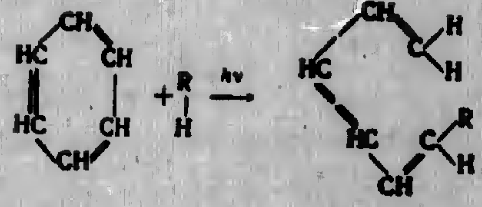
CONCERNING DISINTEGRATION OF HYDROCARBONS AT LOW TEMPERATURES PHOTOSENSITIZED BY BENZENE AND ITS DERIVATIVES

B. N. Shelimov, N. V. Fok,
and V. V. Voyevodskiy

During irradiation of benzene frozen at the temperature of liquid nitrogen (77°K) by ultraviolet light ($\lambda > 2000$ A) in hydrocarbon containers which are transparent for ultraviolet light, along with well-known radiative processes of fluorescence and phosphorescence, there also occurs decomposition of benzene, with breaking of the C — C bond of the benzene ring. As a result of a series of works [1-3], with the help of methods of ultraviolet spectroscopy and gas chromatography, it was established that a product of photochemical decomposition of benzene at 77°K is substituted hexatriene:



We will note that decomposition of benzene occurs only in dilute solutions, and only in the frozen state.

With the help of the [EPR] (ЭПР) method, we revealed [4, 5], that during irradiation of dilute solutions of benzene in methylcyclohexane and 3-methylpentane[1] at 77°K, along with hexatriene there are also formed alkyl radicals (respectively

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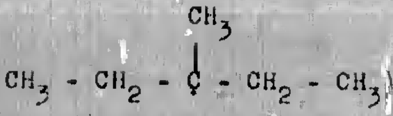
[1] These hydrocarbons vitrify well during freezing to 77°K.

methylcyclohexyl and  $CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3$). The same radicals also were recorded during irradiation of solutions of hexadeuterobenzene (C_6D_6). It also turned out that during irradiation of C_6H_6 in the above-indicated solutions, there will be formed hydrogen, and during irradiation of $C_6D_6 - H_2$, also small quantities (8-10%) of HD.

Formation of alkyl radicals and hydrogen during photolysis of benzene does not fit within the framework of schemes given in the literature which have been proposed for explanation of formation of substituted hexatriene; therefore, we should assume the presence some other processes which can explain these facts. The process leading to simultaneous formation of alkyl radicals and hydrogen can only be the reaction of disintegration of hydrocarbons which is photosensitized by benzene:

$$C_6H_6\,(C_6D_6) \xrightarrow{h\nu} C_6H_6^*\,(C_6D_6^*);$$
$$C_6H_6^*\,(C_6D_6^*) + RH \rightarrow C_6H_6\,(C_6D_6) + R + H.$$

Energy of a quantum of light absorbed by benzene (112 kilocalories/mole) is transmitted to molecule of hydrocarbon, which is incapable of absorbing ultraviolet light, and causes breaking of one of the C-H bonds (energy of breaking of the weakest of them is 86 kcal/mole [6]. Atoms of hydrogen formed in this process (probably hot) can enter into the following reactions:

$$H + RH \rightarrow H_2 + R;$$
$$H + C_6H_6\,(C_6D_6) \rightarrow H_2\,(HD) + C_6H_5\,(C_6D_5)$$

with the subsequent process

$$C_6H_5\,(C_6D_5) + RH \rightarrow C_6H_6\,(C_6D_5H) + R,$$

which probably occurs very rapidly in the solid phase.

In this work there was investigated dependence of initial rates of formation[1] of hexatriene $W_{\text{гекс}}$, radicals W_R and hydrogen W_{H_2} on concentration of C_6H_6 and C_6D_6 in 3-methylpentane at 77°K and the dependence of $W_{\text{гекс}}$ and W_{H_2} on temperature for C_6H_6 (C $2\cdot10^{-2}$ mole/l) in several solvents. It turned out that at 77°K,

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[1] Initial rate of formation is a magnitude proportional to quantum yield.

$\frac{W_{\text{гекс}}}{W_{H_2}}$ and $\frac{W_{\text{гекс}}}{W_{H_2}}\left(\frac{W_{\text{гекс}}}{W_{H_2+HD}}\right)$ depend on concentration of benzene for C_6H_6, as well as for C_6D_6. With increase of temperature, $W_{\text{гекс}}$ and W_{H_2} drop to zero in quite a narrow range of temperatures. However, this fall occurs according to various laws (nonsymbatic). These facts compose a weighty argument in favor of our assumption that processes of formation of hexatriene and photosensitization occur independently of each other.

Our measurements showed also that the ratio $W_{\text{гекс}}/W_{H_2}$ at the same temperature, the same concentration of benzene and in the same solution depends on structure of solvent (glasslike or fine-crystalline). Presence of crystal structure of solvent leads to decrease of $W_{\text{гекс}}$, and in a solution of C_6H_6 in cyclohexane $W_{\text{гекс}}$ turned out to be equal to zero at all temperatures. These phenomenon are possibly connected with the fact that for flow of the reaction with formation of hexatriene there is required a certain definite relative location of C_6H_6 and RH molecules. In a glasslike solution, where there can be realized with equal probability any relative location of C_6H_6 and RH molecules, probability of formation of hexatriene is greater than in a crystalline solution, where some one mutual location predominates which does not favor this reaction.

Let us now consider results obtained by us in experiments with certain derivatives of benzene. During irradiation of solutions of toluene in methylcyclohexane and 3-methylpentane with ultraviolet light at 77°K, there are formed alkyl radicals, and there is released molecular hydrogen.[1] During photolysis of deuterized toluene $C_6H_5CD_3$ synthesized by us in light 3-methylpentane there is released 94% H_2 and 6% HD, and during photolysis of o-D-toluene and n-D-toluene in the same solvent there is released almost exclusively light hydrogen. During photolysis of $C_6H_5CH_3$ in partially deuterized 3-methylpentane, there was discovered formation of H_2, HD, D_2.

These facts unambiguously show that also in the case of toluene there occurs photosensitized disintegration of hydrocarbons by the following scheme:

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[1] From the literature it is known [7], that during photolysis of toluene and other derivatives of benzene there also occurs formation of substituted hexatriene.

$$C_6H_5CH_3 + RH \xrightarrow{h\nu} \text{substituted hexatriene;}$$

$$C_6H_5CH_3^* + RH\,(RD) \rightarrow C_6H_5CH_2 + R + H\,(D);$$

$$H\,(D) + RH\,(RD) \rightarrow H_2\,(HD, D_2) + R;$$

$$H(D) + C_6H_5CH_3 \rightarrow H_2\,(HD) + C_6H_5CH_2.$$

The fact that we do not observe the EPR spectrum of $C_6H_5CH_2$ radical (formation of this radical during photolysis of toluene was shown [7] with the help of ultraviolet spectroscopy), can be understood if we consider that there will be formed, as can be seen from experiments in the system $C_6H_5CD_3$ + RH + hν, 10-12 times fewer of them than alkyl radicals.

It also turned out that photosensitized disintegration of hydrocarbons at 77°K also occurs in the case of ethyl benzene, cumene, o, m, n-xylenes, diphenyl and triphenyl methane, and other compounds.

Literature

1. G. E. Gibson, N. Blake, and M. Kain. J. Chem. Phys., 21, 1000 (1953).

2. E. J. Anderton, H. T. J. Chilton, and G. Porter. Proc. Chem. Soc., 1960, 352.

3. E. Migirdicyan and S. Leach. J. chim. phys., 58, 416 (1961).

4. N. N. Bubnov, V. V. Voyevodskiy, N. V. Fok, and B. N. Shelimov. Optics and spectroscopy, 11, 78 (1961).

5. B. N. Shelimov, N. V. Fok, and V. V. Voyevodskiy. Reports of the AS USSR, 144, 596 (1962).

6. N. N. Semenov. Concerning certain problems of chemical kinetics. Moscow, Publishing House of Academy of Sciences of USSR, 1958, p. 35.

7. I. Norman and G. Porter. Proc. Roy. Soc., A230, 399 (1955).

Discussion

A. N. Nesmeyanov. How does yield of products depend on concentration of hydrocarbon in benzene?

B. N. Shelimov. Dependence of yield of hexatriene on concentration of benzene is known from the source material.[1]

Yield of hexatriene passes through a maximum at concentration of benzene ~$2 \cdot 10^{-1}$ mole/l. Yield of alkyl radicals changes much more slowly than yield of hexatriene, and there is revealed only a small maximum.

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[1] S. Leach, E. M. Migirdisyan, L. Grajcar. J. chim. phys., 56, 749 (1959).

S. Z. Roginskiy. What is the quantum yield? Did you observe partial polymerization of hexatriene, and, in particular, is this connected with the maximum?

B. N. Shelimov. Maximum quantum yield of hexatriene is not known exactly, inasmuch as its coefficient of absorption is not exactly known. Approximately, the quantum yield is equal to 0.023. We did not determine the quantum yield of formation of radicals, but obviously it is of the same order.

Polymerization of hexatriene is indeed observed when after irradiation the solution is held in an atmosphere of oxygen or air for a long time. In evaporated solutions, polymerization is not observed, and the formed hexatriene is quite stable.

P. I. Dolin. What is the difference in behavior of amorphous and crystalline states, and how did you obtain amorphous and crystal states as desired?

B. N. Shelimov. During fast freezing there is obtained glass. If, however, sample is slowly cooled and sustained near melting point, then there is obtained a fine-crystalline opaque sample. Regarding the difference which is observed during measurement of initial rates of formation of hexatriene and hydrogen for glasslike and crystalline solutions, it turned out that, for instance, at a temperature of -196°C the ratio of initial rates of formation of hexatriene and hydrogen in the transparent solution is equal to 0.18, and in the crystalline solution — 0.04. At a temperature of -188°C, these magnitudes respectively are equal to 1.04 and 0.04.

A. T. Koritskiy. Did you compare photochemical yields of these reactions with different sensitizers with the height of the singlet level of the sensitizer? At what height of the first singlet level did you observe cessation of sensitization?

B. N. Shelimov. We investigated only substances for which singlet level is sufficiently high, and its energy exceeds energy of breaking of bond in a molecule of hydrocarbon.

We have other data which show that sensitization is possibly connected with the triplet state. We measured intensity and time of decay of phosphorescence for certain derivatives of benzene. It turned out for instance, that in the case of acids there is direct proportionality between product of initial intensity of phosphorescence by decay and rates of formation of hydrogen.

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CONCERNING THE QUESTION OF RELATIVE CONCENTRATION OF PRIMARY EXCITED STATES DURING THE ACTION OF IONIZING RADIATION ON SOLUTIONS

I. G. Kaplan

For clarification of the role of different secondary effects during radiolysis, including processes of energy transfer, it is very important to know stationary distribution of concentrations of primary excited states. In this report there will be presented certain considerations concerning this question.

Experimental determination of relative quantity of ions and excited molecules formed during irradiation of the solution is still not possible. Model calculations of Platzman [1] based on the example of the H_2 molecule give a ration of 1:1. For γ-radiation from Co^{60}, which is most frequently applied in chemistry, almost the whole effect reduces to the influence of fast Compton electrons on substance. If we do not consider the influence of slow electrons with $E < 100$ ev (the contribution from which is still difficult to estimate), then, as follows from the theory of Bethe [2], the probability of excitation of the k-th state of the atom (or molecule) with energy E_K is proportional to f_K/E_K, where f_K is oscillator strength of transition from ground state to k-th state. Inverse proportionality of E_K leads to the case in which chiefly valence elections will be excited, where there will occur excitation to high levels, since for molecules f_K can change by orders of magnitude with growth of k. For instance, for a solution of benzene in n-heptane $f_1 = 10^{-3}$ ($\lambda_1 = 2600$ A), $f_2 = 10^{-1}$ ($\lambda_2 = 2100$ A), $f_3 = 0.79$ ($\lambda_3 = 1900$ A) [3].

Thus the larger part of the excited molecules should be at high levels. The fraction of such highly excited molecules is further increased due to so-called "superexcited states" [4]. According to Platzman, the probability of ionization of molecule during absorption of energy greater than ionization energy remains less than units, even at (E - I) ~10 ev [5].

Since due to fast internal conversion (characteristic time 10^{-13} - 10^{-12} sec), the molecule from the highly excited state passes nonradiatively into the first singlet state, it would be possible to expect that among excited molecules there will mostly appear such molecules. However, data on γ-sensitized luminescence do not indicate in favor of such a conclusion. According to Sangster and Irvine [6], absolute efficiency of luminescence of a solution of 1.5 gm/l of anthracene in toluene at 30°C is 0.14% (from energy absorbed by the solution). Energy of a quantum of luminescence of anthracene is ~2.7 ev. Consequently, per 100 ev of energy absorbed by the solution, there is radiated 0.05 quantum. Quantum yield of luminescence of anthracene in benzene saturated with air is 0.2 [7], we will also take the same value of quantum yield in the case of toluene. Efficiency of energy transfer for a solution of 1.5 gm/l anthracene in toluene under the same conditions is 0.9 [8]. As a result, we obtain that in transfer of energy there participate 0.3 excited molecules of toluene for every 100 ev of absorbed energy. A magnitude of the same order should also be obtained for a solution in benzene. It follows from this that resonance transfer of energy along lower singlet levels cannot be responsible radiation-chemical yields of G > 0.5. Apparently there is quenching of excited molecules of the solvent caused by track or other effects.

Predissociation and transition into the triplet level compete with the process of internal conversion of molecules in highly excited singlet states. As follows from the data of work [9], the yield of fluorescence at room temperature for liquid benzene and certain of its substituents drops during excitation of the third transition to 20% of its value during excitation of the first electron transition. It is possible that one of the causes of this drop is an increase in the probability of singlet-triplet conversion with an increase in the excitation energy of the molecule (see also [10]). An increase in the number of triplet states is also promoted by the fact that in the processes of collision of molecules with slow electrons and also during recombination of ions, due to their large statistical weight the triplet states will most often form singlet states. However, the available experimental data do not allow us to estimate the relative quantities of triplet and singlet states that are formed during the action of ionizing radiation.

Literature

1. R. L. Platzman. Internat. J. Appl. Radiation and Isotopes, 10, 116 (1961).
2. H. Bethe. Ann. Phys., 5, 325 (1930).
3. J. R. Platt and H. B. Clevens. Chem. Revs., 41, 301 (1947).
4. R. L. Platzman. Radiation Res., 17, 419 (1962).
5. R. L. Platzman. J. phys. radium, 21, 853 (1960).
6. R. C. Sangster and J. W. Irvine, Jr. J. Chem. Phys., 24, 670 (9156).
7. P. Prinsgeym. Fluorescence and phosphorescence. M., IL, 1951, p. 285.
8. V. Bar and A. Weinreb. J. Chem. Phys., 29, 1412 (1958).
9. S. Kato, S. Lipsky and Ch. Brown. J. Chem. Phys., 37, 190 (1962).
10. R. M. Hochstrasser. Spectrochim. Acta, 16, 497 (1960).

Discussion

V. L. Tal'roze. You said that there are no data on ion yields during radiolysis. Why can't we use the old data of Taylor [1], V. I. Ivanov [2] and many others, which testify that the radiation ion yield is equal to unity in order of magnitude?

I. G. Kaplan. I spoke only of the ratio of ion yields and excited particles. This ratio is approximately equal to unity.

V. L. Tal'roze. What is the energy of higher excited state?

I. G. Kaplan. A magnitude that is smaller than the ionization energy. Incidentally, according to Platzman the excitation potential can be higher than the ionization potential and nonetheless an electron will not leave a molecule. Possibly this corresponds to two-electron excitations.

V. L. Tal'roze. How do you consider a process of the type

$$C_6H_6^{*} + C_6H_6 \rightarrow (C_6H_6)_2^{+} + e,$$

if it is thermodynamically possible? For the gaseous phase such reactions are usual; in the condensed phase they would open one of ways for energy "exchange," passing singlet state and by passing the hindrance factor.

I. G. Kaplan. If such process is possible, it probably would open one of the ways for dissipation of energy.

Kh. S. Bagdasar'yan. What is this magnitude of 0.14% you show?

I. G. Kaplan. The energy radiated by the solution is 0.14% of the absorbed energy.

Literature

1. F. L. Mohler, S. Lauriston, and L. S. Taylor. J. Research NBS, 13, 677 (1934).

2. V. I. Ivanov, News of the Higher Educational Institutes., Physics, No. 1, 115, 119 (1960); No. 2, 134 (1960); Atomic Energy, No. 7, 73 (1959).

EXPERIMENTAL CRITERIA OF DETERMINING THE NATURE OF THE PRIMARY PROCESSES DURING RADIOLYSIS

V. M. Byakov, B. V. Ershler, V. G. Firsov, and
M. A. Nezhevenko

There is now a widely-spread point of view according to which active particles that can react with solutes and with each other appear during radiolysis of aqueous solutions; during reactions of active particles among themselves molecular hydrogen and hydrogen peroxide are formed. However, there is also the opinion that these molecular products appear not through recombination of active particles.

To determine the nature of these primary processes we suggest using two experimental criteria: the I-regularities (I-dose rate) [1] and the dependence of the yield of H_2 and H_2O_2 upon the concentration of the acceptor of active particles.

1. Let us first consider the I-regularity criterion.

By very general and simple reasonings it is possible to show [1], that with equal distribution of active particles by volume, whatever their nature, the curve of dependence of yield of the products of "capture" of these particles by the acceptor upon the logarithm of the acceptor concentration during a change in the dose rate from I_1 to I_2 shifts by a magnitude of $1/2 \log (I_1/I_2)$. The form of the curve does not change.

Theoretical consideration of the process of radiolysis of aqueous solutions under the action of hard γ-rays and fast electrons [2, 3] explains the equal distribution of active particles and, consequently, of the I-regularity in a wide interval of the dose rate and concentration of acceptors. The existence of I-regularity is shown for acid solutions of trivalent titanium and bivalent iron

[4, 5], where shifts of curves of the oxidation yield of Ti (III) and Fe (II) exactly correspond to the magnitude of 1/2 log (I_1/I_2), expected on the basis of the theory of I-regularities. It has been shown experimentally that during radiolysis of an aqueous acid solution of H_2O_2, that is saturated with hydrogen exact fulfillment of the I-regularities is also observed.

The presence of I-regularities in an acid solution of H_2O_2 indicates achievement of an equal distribution of active particles in it. Apparently, the reducing (with respect to peroxide) particle here is the hydrogen atom or the molecular ion H_2^+. The same can be said about acid solutions of Ti (III) and Fe (II), where the active particle can also be a molecular hydrogen ion or hydride-ions of iron and titanium.

Experimental manifestation of I-regularities and theoretical prediction of them on the basis of the "radical model" of radiolysis are a convincing argument in favor of this model. The presentation about the essential role of excited molecules of water during radiolysis of aqueous solutions does not agree with the presence of I-regularities.

2. Let us consider the second experimental criterion.

At present there are two different points of view on the mechanism of the formation of primary molecular products. According to the first, a hydrogen molecule and hydrogen peroxide are formed by recombination of two active particles, for instance, $H + H \rightarrow H_2$; $OH + OH \rightarrow H_2O_2$.

According to the other presentation, molecules of hydrogen and peroxide appear as a result of the interaction of a water molecule with only one active particle (H^-, H_2O^*, H^*, OH^*).

It is easy to show what the last one model leads to a linear dependence between the yield of primary molecular products and the concentration of radical acceptors. However, this connection contradicts experimental data. The available experimental data simply show the existence of a linear dependence between yield and the cube root of the concentration of radical acceptors.

Our theoretical analysis shows that if we start from the first model, the dependence between the yield of primary molecular products and the concentration of radical acceptor corresponds to that obtained experimentally. This conformity is a convincing argument in favor of the presentation of the formation of primary molecular products of radiolysis basically through recombination of two active particles.

Literature

1. B. V. Ershler. DAN USSR, 129, 866 (1959).
2. B. V. Ershler and V. M. Byakov. Journal of Physical Chemistry, 36, 913 (1962).
3. V. M. Byakov and B. V. Ershler. Journal of Physical Chemistry, 36, 1579 (1962).
4. V. G. Firsov and B. V. Ershler. DAN USSR, 138, 884 (1961).
5. B. V. Ershler and V. G. Firsov. DAN USSR, 139, 662 (1961).

Discussion

I. A. Myasnikov. Do you have direct experimental data about the existence of hydrogen atoms and H_2^+ ions in the conditions of your experiments or are the conclusion concerning the existence of these particles based on indirect data and considerations?

V. M. Byakov. We have no direct experimental data. The conclusion concerning the existence of hydrogen atoms is based on the fact that in the conditions of our experiments this reaction occurs:

$$OH + H_2 \rightarrow H_2O + H.$$

V. V. Voyevodskiy. Are there direct experimental data on whose basis you reject the diagram that includes excited states, or was this done only because your experimental data are satisfactorily described on the basis of a mechanism with the participation of radicals? Did you try to describe your experimental data in the framework of the possibilities ensuing from a diagram that includes excited states?

V. M. Byakov. We consider that the dependence of the yield of molecular products of radiolysis upon the cube root of the concentration of the acceptor speaks against the mechanism of energy transfer with participation of the excited states. We did not conduct direct experiments that excluded the role of excited states.

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THE CELLULAR EFFECT DURING RADIOLYSIS OF HYDROCARBONS

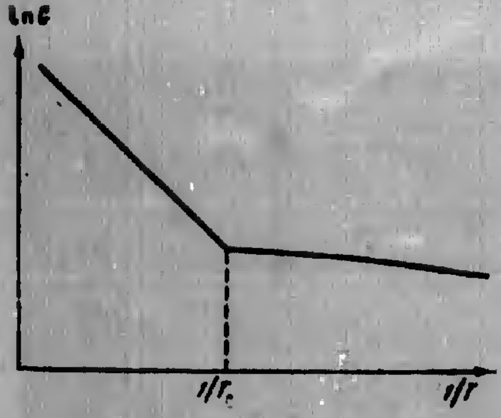
A. M. Brodskiy, V. B. Titov,
and K. P. Lavrovskiy

As was noted in a number of works, during recombination of thermal radicals formed as a result of a sequence of elementary acts during radiolysis of liquid hydrocarbons the cellular effect plays an essential role. In this report we will expound a method of appraising the cellular effect based on a study of temperature dependence of the rate of radiolysis. We previously noted [1], that the shown dependences have the general form represented on the figure for a specific example of the formation of H_2 during radiolysis of C_3H_8. The appearance of an activation energy different from zero, whose magnitude attains 3-5 kcal/mole, on the initial section up to a temperature corresponding to the break point (see the figure) is specific for radiolysis of liquids and does not have an analogy during radiolysis of gases, where the temperature shift on this section corresponds to an activation energy less than 1 kcal/mole. The presence of a characteristic break point T_c on the graph of the temperature dependence (see the figure) was connected [1] with the competition of the processes of recombination and disintegration of thermal radicals, the ratio of which changes with a change in temperature.

In particular, at point T_c the disintegration rate has an order of magnitude of the recombination rate:

$$v_{\text{расп}} \approx v_{\text{рекомб}}. \tag{1}$$

Substituting the comparatively small values of the recombination rate of radicals statistically distributed in the liquid [2] in expression (1) gives a decreased value of T_c. Actually, for liquids and gases T_c turns out to be approximately identical (~300°C), although in the gasious phase recombination occurs at a considerably higher rate. The assumption about the predominant flow of recombination of radicals in the "cell" permits removing this contradiction.



Typical dependence of the logarithm of the rate of radiolysis of liquid hydrocarbons on inverse temperature; G — radiation output.

As follows from simple computations, the average rate of destruction in this case will be proportional, with a coefficient approximately independent of temperature, to the magnitude described by a formula of this type

$$k_d\left(1+\frac{1}{k_d\tau_D}\right). \qquad (2)$$

where k_d is the radical destruction constant; τ_D is the characteristic time of escaping the cell due to diffusion. Formula (2) well describes the curve shown on figure, where the meaning of activation energy on the initial section makes sense — this activation energy of diffusion increases with an increase in the molecular weight of radicals. The break point T_c obviously corresponds to the temperature at which

$$k_d\tau_D \approx 1. \qquad (3)$$

Formula (3) permits making an interesting appraisal of the average "dimensions" of the cell on the basis of experimental data of the considered form. Thus, putting into formula (3), $\frac{1}{\tau_D} \simeq \frac{D}{d^2}$, where d is the effective dimension of the cell and D is the coefficient of diffusion, which for hydrocarbons is approximately equal to 10^{-5} cm²/sec. In using the experimentally determined activation energy of destruction and preexponential factor, which is considered equal to 10^{13} sec^{-1}, for the case of high-molecular hydrocarbons we obtain $d \approx 10^{-6}$ cm.

In conclusion we will note that the mechanism of the formation of radicals in a liquid cell can apparently be represented in the following way. At first there is disintegration of the molecule with the formation of a hot hydrogen atom (or another light radical) which then enters into the substitution reaction in direct proximity to the point of its formation, including with the initial molecule. This assumption is supported by the formation of ciclene during radiolysis of high-molecular hydrocarbons [3], proceeding obviously through biradical intermediate products.

Literature

1. A. M. Brodskiy, K. P. Lavrovskiy, and V. B. Titov. DAN USSR, 138, 1143 (1961).

2. N. N. Semenov. About certain problems of chemical kinetics of catalysis and reactivity. M., News of the Academy of Sciences of USSR, 1958.

3. A. M. Brodskiy, D. V. Makarov, and others. Oil-chemistry 2, 332 (1962).

Discussion

Yu. N. Molin. Does not the point T_c coincide with the melting point or the point of any phase transition?

A. M. Brodskiy. It does not.

Yu. N. Molin. Do all the results pertain to the liquid phase?

A. M. Brodskiy. Yes.

Yu. N. Molin. Now a second question. I can grasp why the yield of heptane, ethane, etc., increases with a temperature rise, but I cannot grasp why the polymer yield drops.

A. M. Brodskiy. The polymer yield drops for following reason. If the two radicals formed in the cell recombine basically below some temperature, then with an increase in temperature an alternative possibility of disintegration is opened, their concentration correspondingly decreases and there is, therefore, less yield of the polymer.

N. A. Bakh. Should the presence of some radical acceptors affect the temperature T_c and, correspondingly, the yields and concentrations of the products?

A. M. Brodskiy. Apparently, yes. We are now investigating this question. Such a fine effect has already been observed on a whole series of yields, within the limits of experimental error.

V. V. Sarayeva. How will this stagnation temperature T_c change for other compounds that have substituents?

A. M. Brodskiy. Those experiments I know about were conducted on hydrocarbons. For hydrocarbons T_c lies in a very narrow interval. For stable aromatic hydrocarbons the magnitude of T_c (the maximum of the magnitudes we know) is on the order of

400°C, i.e., the interval of temperatures T_c = 290-400°.

V. V. Voyevodskiy. You said that the temperature T_c is rather critical and that there are sharp breaks; from the other side, your cells are so great that there is no clear boundary between a particle in a "cell." Isn't this a contradiction?

A. M. Brodskiy. The idea of a cell is not a precise idea. In fact, this is simply one interpretation of accelerated recombination. The sharpness of the break is connected not with the cell, but with that rather sharp dependence of the disintegration rate of radicals upon temperature as compared to their recombination. The disintegration rate is determined by the sum of rate constants of two processes: one almost does not depend upon temperature and the temperature dependency of other is described by an Arrhenius equation with an activation energy of 20-25 kcal/mole. The large magnitude of the activation energy determines the sharpness of the break.

Yu. N. Molin. One more question. In your appraisal the cell dimensions have an order of 100 A?

A. M. Brodskiy. Yes, approximately.

Yu. N. Molin. This, of course, is a conditional boundary: 100-200 A. If we consider that two radicals are in such a region and if we consider chaotic diffusion, then they will have a greater probability of separating than recombining.

A. M. Brodskiy. We consider molecules with 20-30 carbon atoms rather long. If they turn out to be in the cell and are at a temperature lower than critical, basically they will recombine.

Yu. N. Molin. Such a conclusion is obtained without assuming that they have some directivity of diffusion?

A. M. Brodskiy. Yes.

Yu. N. Molin. And you did not calculate the probability of recombination as a result of chaotic diffusion?

A. M. Brodskiy. No, we did not.

V. V. Sarayeva. If we consider that the behavior of organic substances (in particular, hydrocarbons) is determined by the kinetic structure of the actual liquid, then it is possible to consider that this kinetic structure of the liquid should be determining not only during the processes of radiolysis, but also during other processes (in particular, during processes in the presence of free-radical acceptors).

On certain examples I want to illustrate that this is not so. We investigated the yield of products during radiation-chemical oxidation of hydrocarbons of a series of classes depending upon temperature (in the interval from -78 to +60°C and above). Changes of viscosity does not occur in this temperature interval. For radiation-chemical oxidation, just as for radiolysis (A. M. Brodskiy showed this) and, in general, for any processes, with different acceptors we always observe certain temperature breaks. But, in contrast to what is observed for radiolysis, this break (for instance for oxidation of hydrocarbons) occurs in quite another region of temperatures. Usually this region of temperatures is from +10° to +40°-60°C. If the cause of the break is in the cellular structure of the actual hydrocarbon, in my opinion such distinctions should be observed. This break depends on the structure of the compound and it characterizes the process of oxidation. On the other hand, if the break is connected with the cellular effect, its position should depend on the dose rate. However, a thorough investigations of processes of oxidation of isooctane show that, depending upon the dose rate, at different temperatures definite distinctions are observed. For instance, at temperatures below +10°C the dose rate does not affect the process of oxidation. At a temperature of +20°C at a dose rate of 10^{15}-10^{16} ev/ml·sec we observe independence of the yield of products from dose rate and at smaller dose rates the yield of products increases. At temperatures of +50° and 90°C we observe a dependence upon dose rate even at its large values. On the basis of these data we are inclined to consider that cellular effects do not appear in this case and the whole effect is connected with differences in the kinetics of the process, i.e., in one case purely radical processes occur (the region of low temperatures) and with an increase of temperature we pass into the region of radiation-thermal oxidation, where thermal process starts to play a noticeable role.

V. V. Voyevodskiy. Your data on oxidation does not coincide with the data on radiolysis?

V. V. Sarayeva. No.

V. V. Voyevodskiy. I feel that these data should not be compared.

V. V. Sarayeva. If we consider hydrocarbons, the phenomena connected with the yield capacity of a radical from a cell should not, in my opinion, depend upon the acceptor. Otherwise, it is possible to assume what oxygen (an acceptor) "pushes out" radicals from the cell and this is very difficult to understand.

V. V. Voyevodskiy. Let us consider two series of data: in one series (the data on radiolysis) the break point does not depend upon either the dose rate or the molecular structure. These are the data of A. M. Brodskiy, et al., and they explain them. You presented data on oxidation; here there is also a break, but it is located at another temperature; its position depends upon the dose rate and upon the molecular structure. Is it possible to compare these data?

V. V. Sarayeva. If consider hydrocarbons, it is possible to consider that cellular effect should be developed within limits of the same temperatures regardless of the form of the chemical reaction.

V. V. Voyevodskiy. In your experiments did you observe effects connected with small additions of peroxide?

V. V. Sarayeva. We conducted experiments on other objects with additions of peroxide and there indeed we observed the influence of these additions on the yield of products.

V. V. Voyevodskiy. What are the absolute values of radiation yields?

V. V. Sarayeva. They varied for different compounds. For isooctane, tens of molecules, and for esters, for instance, hundreds of molecules per 100 ev of absorbed energy.

A. M. Brodskiy. In her report V. V. Sarayeva expressed the assumption that the break temperature depends on cellular structure. In fact, T_c (the break temperature) is determined mainly by the activation energy of the considered reaction. If we pass from activation energy of 20-25 kcal/mole to one of 10 kcal/mole, the break temperature with the same effect on the cell should decrease by 2-3 times. In our experiments, $T_c = 600^\circ K$, but for processes with an activation energy of 12 kcal/mole, T_c should lie in the region of $300^\circ K$, which coincides with the data of V. V. Sarayeva. The proximity of T_c for all hydrocarbons results from the activation energy of the process of their disintegration being close for almost all hydrocarbon radicals. Moreover, if there is a surface that lowers the activation energy of disintegration of radicals, the break point is displaced up to $150^\circ C$ for the very same reason.

A second remark. In general, the break point during radiolysis can be caused by not only this. In particular, during oxidation it is necessary to consider the following. The activation energy on the initial section is 3-5 kcal/mole; this is the activation energy of diffusion. In principle, a "relay transfer" facilitating the yield of radicals from the cell is possible. During radiolysis of hydrocarbons this transfer does not exist and during oxidation it is possible. In this case we should also observe a break (incidentally, for relay transfer, the activation energy is 10-12 kcal/mole). Thus the data of V. V. Sarayeva does not contradict what was said in my report.

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INVESTIGATION OF THE EFFECT OF OXYGEN ON THE PRIMARY PROCESSES OF RADIOLYSIS OF ORGANIC COMPOUNDS

A. A. Revina, A. P. Podsoblyayev,
and N. A. Bakh

Application of the [EPR] (ЭПР) (electron paramagnetic resonance) method to investigate radiolysis and radiation-oxidation of certain organic compounds allows us not only to investigate the processes of formation and transformation of radicals, which are secondary processes, but also to reveal certain effects directly connected with the primary acts of the interaction of a substance with radiation. Irradiation at -196°C of palmitic acid, tripalmitate and potassium palmitate, which differ only by substitution in the carboxyl group, leads to the formation of radicals of a different structure with different radiation yields. These results agree with the known data about the different radiation stability of a fatty acid, its salt and ester, and they confirm the existing point of view about the migration of absorbed energy along a molecule and on its localization near a definite bond.

A comparison of the EPR spectra at -196°C (Fig. 1) and the radiation yields G radicals formed at the same temperature in an acid, a salt and an ester under the effect of radiation (see the table) shows what presence of oxygen during irradiation causes no changes as compared to the evacuated samples in the case of the acid, but leads to a decrease in G for the ester and the salt and to a change in the character of the spectrum for potassium palmitate: along with EPR signals of the alkyl radicals a single symmetric line appears with $\Delta H = 10$ oe, which is ascribed to the radical

$$-CH_2-CH_2-C\overset{O}{\underset{O\cdot}{<}}$$

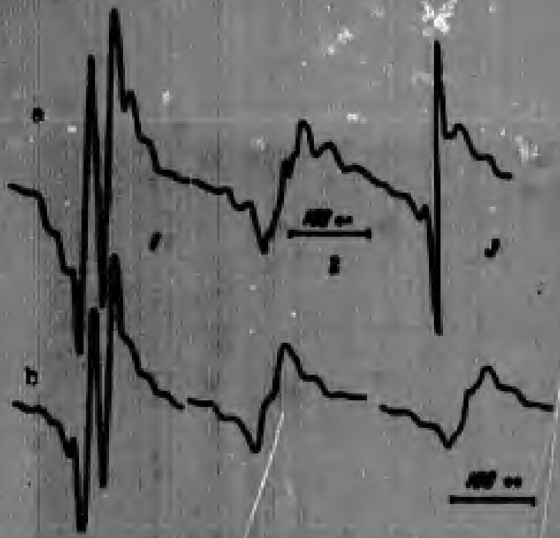
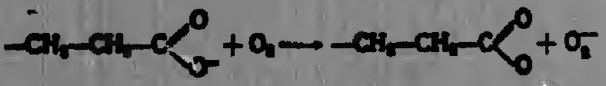


Fig. 1. EPR spectra of palmitic acid (1), tripalmitate (2) and potassium palmitate (3) irradiated at -196°C: a) in a vacuum; b) in oxygen.

Radiation Yields of Radicals Formed During Radiolysis of Palmitic Acid, Its Ester and Its Salt

[illegible]	G, 1/100 ev	
	In vacuum	[illegible]
Acid	20	20
Ester	12	7
Salt	8	7

The absence of this radical during radiolysis in a vacuum and during radiolysis of two other compounds forces us to connect its appearance with the presence of an anion and with the presence of oxygen near it, which is ensured by the structure of the ionic-molecular crystal of palmitate. The formation of the radical can be explained by the reaction



$$-\overset{-}{C}H_2-CH_2-C\langle^{O}_{O^-}+O_2\longrightarrow -CH_2-CH_2-C\langle^{O}_{O}+O_2^-$$

with transition of an electron to the O_2 molecule in the primary act.

Analysis of the EPR spectra of piperidine irradiated at -196°C in a vacuum and in the presence of oxygen also allowed us to make certain conclusions about the character of the primary processes. A sharp distinction from the spectra of the nearest analog, cyclohexane, agrees with the difference in yields of the final products of radiolysis and radiation oxidation of these two compounds. The character of the EPR signal of piperidine irradiated in a vacuum cannot be explained by the formation of the radical due to breaking of the C—H or N—H bonds. The structure of the EPR spectrum, which is a dublet of triplets (ΔH dublet ~40 oe, ΔH triplet ~7 oe), is kept with an increase of temperature up to fusion and corresponds to the interaction of a free electron with one proton and with nitrogen. From this it follows that the signal should be caused by the $C_5H_{10}NH+$ ion-radical. The formation of tetrahydropyridine and molecular hydrogen during radiolysis in accordance with this can be explained by the sequence of processes according to the diagram

$$C_5H_{10}NH \longrightarrow C_5H_{10}NH^{+\cdot}_{\cdot} + e \rightarrow C_5H_{10}NH^{*} \rightarrow C_5H_9N + H_2.$$

This diagram is confirmed by the ratio between the destruction of radicals and the formation of H_2.

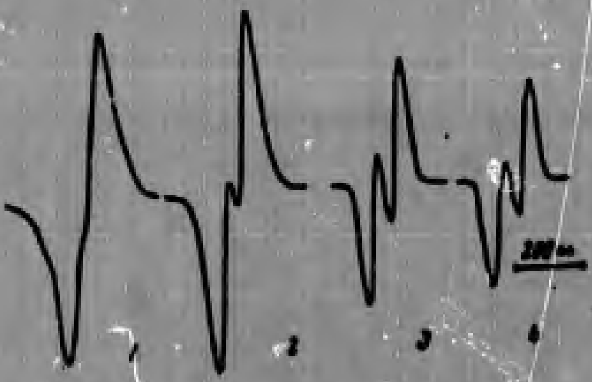


Fig. 2. EPR spectra of irradiated piperidine: 1) in vacuum at -196°C; 2) after a stay in vacuum at -78°C for 66 hours; 3) after a stay in vacuum at -19°C for 50 minutes; 4) irradiation in the presence of O_2, a stay at -17°C for 30 minutes. The temperature of recording the spectrum, -196°C.

In the presence of oxygen the radiation yield of radicals is lowered (from 5.5 to 2 1/100 ev) without a change in their structure. In spite of the absence of peroxide radicals the process of radiation oxidation occurs, leading to the formation of hydrogen peroxide. In developing the above diagram, we can assume the following mechanism of the formation of the peroxide compound:

$$C_5H_{10}NH + O_2 \longrightarrow C_5H_{10}NH^+ + O_2^- \rightarrow$$
$$\rightarrow [C_5H_{10}NH \cdot O_2]^* \rightarrow C_5H_{10}NOOH$$

According to this diagram the presence of oxygen leads to its introduction into the piperidine molecule without radical stages of the process. The observed decrease in the yield of radicals in the presence of oxygen thus indicates their decomposition with the formation of hydrogen peroxide.

Discussion

V. L. Karpov. I want to ask a question concerning the technology of the experiment: how was the small yield of hydrogen determined at low temperatures, before melting or after melting?

A. A. Revina. The small yield of hydrogen was determined before melting, i.e., at the temperature of liquid nitrogen.

V. L. Karpov. Can hydrogen get stuck? Such phenomena have been observed.

A. A. Revina. There can be certain difficulties with diffusion of hydrogen at -196°C, but at -80 or -100°C hydrogen diffuses very easily; nonetheless, the observed yield of hydrogen at these temperatures was lower than after melting.

V. V. Voyevodskiy. Were the mechanisms with the introduction of oxygen in the case of nitrous compounds confirmed by kinetic methods, or were your conclusions made only on the basis of an analysis of the final products?

A. A. Revina. The assumptions about the mechanism were made on the basis of an analysis of the EPR spectra and the final products of radiolysis.

V. V. Voyevodskiy. Were there quantitative coincidences?

<u>A. A. Revina.</u> The radiation yield of hydrogen peroxide during irradiation of piperidine in the presence of oxygen in the liquid phase is equal to 5 moles/100 ev, which is very close to the yield of radicals determined at the temperature of liquid nitrogen.

If determine hydrogen peroxide after melting the piperidine irradiated at the temperature of liquid nitrogen, its radiation yield is lower: it is equal to 1.8. This is obviously connected with the deficiency of O_2 in the solid crystalline phase. The ion-radical $C_5H_{10}NH^+$ in this case is expended on the competing reactions of the formation of hydrogen peroxide and disintegration on hydrogen and tetrahydropyridine.

<u>V. V. Voyevodskiy.</u> What can you say about the variation in the quantity of oxygen during transition of one effect into the other?

<u>A. A. Revina.</u> We hope to obtain these results in our next experiments.

THE SPECIFIC CHARACTER OF RADIATION SOLID-PHASE POLYMERIZATION DURING IRRADIATION

I. M. Barkalov, V. I. Gol'danskiy, N. S. Yenikolopov,
and G. M. Trofimova

The problem of radiation polymerization in the solid phase has obtained considerable interest both for possible practical applications so also for the development of general theoretical presentations of chemical kinetics. In the usual method of investigating the kinetics of radiation solid-phase polymerization the polymer yield and polymerization rate are determined upon completion of not only the actual irradiation, but also after strong heating of the sample accompanied by fusion and often by phase transitions. As a result the obtained data turn out to be very indefinite since it remains vague whether polymerization occurs in the solid phase (it can occur during irradiation as a result of "after effects") or during thawing in region of phase transitions, or at the time of fusion [1-4]. Meanwhile, to establish the mechanism of the process of polymerization of every given monomer the question of just when it occurs has great importance.

We investigated solid-phase radiation polymerization of acrylonitrile (AN) and vinyl acetate (VA) under the effect of electrons with an energy of 1.6 Mev with calorimetric measurements of the liberation (absorption) of heat both during thawing of irradiated samples of monomers and also in the course of the actual irradiation and with observation of the [EPR] (ЭПР) signals (under the beam and after termination of irradiation). A description of the method of purifying the monomers, regulating the dosimetry and determining the yields of polymers is given in the detailed report [5]. To determine just when the effective reaction of polymerization occurs, in the solid phase or during thawing, we designed and applied a diathermic calorimeter, the principle of which is offered in work [6]. This calorimeter allowed us to determine thermal effects (both signs) with an accuracy of ±1 cal/g during thawing of the irradiated monomer. Thermal effects were measured directly under the beam on a calorimeter with a higher sensitivity, one that was based on the same principle and described in work [7].

Acrylonitrile. As thermographic analysis has shown in the temperature range from -196 to -75°C, there is one thermodynamic equilibrium phase transition, "crystal-crystal," at -130°C. The melting point of AN is -82°C. The effect of a different phase state of irradiated solid AN was observed on all kinetic regularities. At temperatures below -130°C (the point of the phase transition) we observed a "limiting" of the polymer yield at large doses, which was especially clearly expressed at -196°C. Brief irradiation by large doses (8 Mrad) with thawing of the irradiated monomer above the point of phase transition, the sample not necessarily fusing, and reverse freezing after every irradiation led to an increase in polymer yield proportional to the number of irradiations. The molecular weight of the polymers obtained at temperatures above the point of phase transition was more than for polymers obtained at lower temperatures for using the same doses. And finally, post-polimerization of AN was observed only at temperatures above the point of phase transition.

The form of the EPR signal of irradiated solid AN under the beam and after termination of irradiation is identical.[1] In the temperature range from -196 to -130°C the intensity of the signal also does not change and only after the phase transition do we observe a decrease in the concentration of paramagnetic particles, which drops to zero during fusion of the sample. Calorimetric measurements showed that no changes in the heats of phase transition and fusion due to liberation of the heat of polymerization during thawing of the irradiated sample were observed. Inasmuch as the post-polimerization rates are low, a noticeable quantity of the polymer also cannot form during fast thawing of irradiated sample. Also, measurements conducted on the more sensitive calorimeter allowed us to directly observe liberation of the heat of polymerization during irradiation. Thus,

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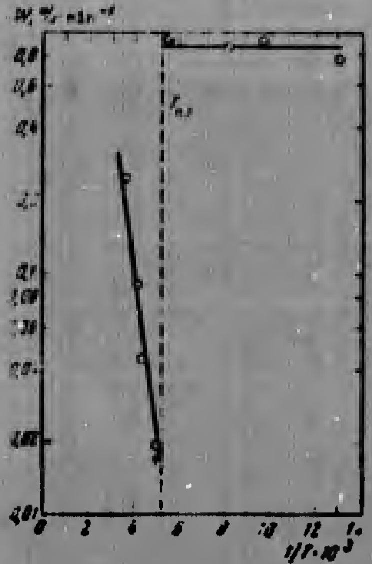
[1] V. N. Shemshev participated in these experiments; the authors express their sincere gratitude to him.



Temperature dependence of the initial polymerization rate of acrylonitrile. Dose rate of irradiation, 0.3 Mrad/min.

polymerization of AN at $t < -130°C$ was complete, and at $t > -130°C$, after subtracting the insignificant contribution of slow aftereffects occurs in the solid phase during irradiation.

Vinyl acetate. In solid state this monomer can be obtained in a glasslike state and in the form of crystals

The temperature of devitrification is about -129°C. We studied the polymerization of VA in two these states. In the glasslike state VA is polymerized at a rate almost one order greater than in the crystal state. The molecular weight of the polymers obtained from glasslike VA are also somewhat higher. As compared to AN, the polymerization of VA requires larger doses; post-polimerization of VA is lacking at all temperatures in the glasslike and crystal states. The form of the EPR signal for VA during irradiation and after its termination is identical. During thawing of irradiated glasslike VA the intensity of the signal remains practically constant up to the point of phase transition (-129°C), after which the signal disappears. A comparison of the calorimetric data for irradiated and unirradiated samples of VA, as in the case of AN, leads to the conclusion that the reaction of polymerization occurs in the solid phase in the course of irradiation.

The sharp difference in fast polymerization of solid AN in the course of irradiation from its slow post-polimerization and the fast polymerization of solid VA under the beam in the absence of after effects testify to the specific character of radiation solid-phase polymerization in the course of irradiation. One more characteristic of such solid-phase polymerization "under the beam" is the practical absence of a temperature dependence of the polymerization rate for both AN and VA. As it is known, a similar phenomenon can be explained in the framework of the hypothesis of N. N. Semenov about the flow of solid-phase polymerization by means of the development of energy chains, [8, 9]. In this short report we can only consider one natural assumption following from the presented results.

It is possible that the basic cause of the effective flow of the process just in the course of irradiation is the appearance of short-lived molecules, which are naturally destroyed rapidly after the beam is turned off in the solid phase, and in the liquid phase they are stored in much smaller stationary concentrations due to an increase in the rate of "quenching." Such centers, playing the role of energy "depots" that compensate for useless scattering of energy, can have more importance than "ordinary" ions or radicals for the development of energy chains that lead to the polymerization of a solid monomer. A second possible cause of acceleration of solid-phase radiation polymerization can be the presence of hot active centers during irradiation. As work [10] shows, local heating up along the track of a primary electron does not exceed several degrees and therefore cannot play a role. However, "loosening" of substance along the tracks primary particles and δ-electrons, which is apparently responsible for the phenomenon of radiation acceleration of diffusion [1], [2], can have definite value. The possibility of molecule displacements in a solid body under the effect of electron impact, short-term releasing of internal rotation and excitation of all possible oscillations brings the properties of an irradiated solid body close to those observed near the points of phase transitions or fusion and promoting, as is known, effective polymerization.

Literature

1. V. A. Kargin, V. A. Kabanov, and V. N. Zubov. High-molecular compounds, 1, 265 (1959).

2. V. A. Kargin, V. A. Kabanov, et al.. High-molecular compounds, 3, 426 (1961).

3. H. A. Rigby, C. J. Danby, and C. Hinshelwood. J. Chem. Soc., 1948, 234.

4. R. E. W. Norrish and J. C. Bevington. Proc. Roy. Soc., A196, 363 (1949).

5. I. M. Barkalov, V. I. Gol'danskiy, N. S. Yenikolopov, S. F. Terekhova and G. M. Trofimova. High-molecular compounds, 6, 92 (1964).

6. A. F. Kapustinskiy and Yu. P. Barskiy. Transactions of the Conference on Thermography. M., Publishing House of Academy of Sciences of USSR, 1955.

7. I. M. Barkalov, V. I. Gol'danskiy, and V. B. Rapoport. DAN USSR, 162, No. 1 (1965).

8. N. N. Semenov. Chemistry and technology of polymers, No. 7-8 (1960).

9. N. N. Semenov. Pure and Appl. Chem., 5, 353 (1962).

10. V. I. Gol'danskiy and Yu. M. Kagan. Internat J. Appl. Radiation and Isotopes, 2, 1 (1960).

11. M. A. Mokul'skiy, Yu. S. Lazurkin, M. B. Fiveyskiy, and V. I. Kozin. DAN USSR, 125, 1097 (1959).

12. N. S. Tikhomirova, Yu. M. Malinskiy and V. A. Karpov. DAN USSR, 125, 1084 (1960).

Discussion

V. V. Voyevodskiy. What direct experimental proof do you have that polymerization occurs namely in the solid phase?

I. M. Barkalov. Our work was set up just to produce direct proof. We measured the heat given off during thawing. If polymerization passed at the point of phase transition or the point of fusion, we would have observed additional liberation of heat due to polymerization. The thermal effect at the observed percent of polymerization had to be increased by 150% with respect to the heat of phase transition (the accuracy of our method was ±10%). We did not observe additional heat emission. We conducted direct measurements of the heat liberated in the course of irradiation for acrylonitrile. These measurements were conducted on a more sensitive calorimeter with two measuring cells. After the beam was turned on heat emission due to polymerization.

V. V. Voyevodskiy. Did you measure the heat during polymerization at various depths and was heat emission proportional to the percent of polymerization?

I. M. Barkalov. During polymerization of acrylonitrile at -196°C we observed the following: after achievement of 4.5% polymerization increasing the dose by one order does not lead to additional formation of the polymer. Heat emission under the beam also corresponds to 4.5% polymerization and stops after that.

On the linear section we have not yet succeeded in obtaining a kinetic curve with respect to heat measurements under the beam due to deficiencies of the method (long relaxation time).

N. D. Sokolov. Is there a dependence of the effects upon the energy of the particles?

I. M. Barkalov. We have experimental data only for the process of polymerization under the effect of an electron beam with energy of 1.6 Mev. Bensasson and Marx [1] conducted polymerization of acrylonitrile under the effect of γ-radiation. They observed the same slope of the kinetic curve; the activation energy for the process in the solid phase is practically absent; the magnitude of the limiting yield also coincides with our data.

V. L. Karpov. What is the difference in the structure of acrylonitrile below and above -150°C? Why is the polymerization rate higher for vinyl acetate in the glasslike state than in the fine-crystalline state?

I. M. Barkalov. We conducted only a thermographic analysis of a frozen sample.

It is known that at -150°C in acrylonitrile there occurs an equilibrium transition of the "crystal-crystal" type.

For vinyl acetate there is an evident dependence of the polymerization rate upon diffusion processes, which naturally flow faster for the glasslike state.

L. S. Polak. What diffusion are you speaking of?

I. M. Barkalov. Diffusion of the formed polymer radical. The difference in the specific volumes of the crystal monomer and polymer is great and the formation of a polymer in a crystal of vinyl acetate requires a substantial deformation of the crystal. Naturally, this is not required in the glasslike state.

S. Z. Roginskiy. Is it possible to obtain a multiple increase of the polymer yield if an irradiated monomer is thawed and then frozen and again irradiated?

I. M. Barkalov. This leads to a multiple increase in the yield. We showed that it is not necessary to thaw the sample to the liquid state. It is sufficient to carry out a phase transition and to freeze sample again. The same multiple increase is obtained as in heating to the liquid state.

S. Z. Roginskiy. Does this signify that there is some limited quantity of "intermediate products" or do breaks, microdisturbances, form in the structure of the crystal? Why does polymerization stay at 4.5%?

I. M. Barkalov. In all probability the limiting concentration is connected with a limiting concentration "intermediate products," from which polymerization occurs in the crystal. For the formation of new "intermediate products" it is necessary to raise the temperature above the point of phase transition.

Yu. L. Khait. Is it possible to say that a moving electron "loosens" the crystal lattice? How can different motions be released in the lattice (this releasing being connected with the motion of heavy particles) if it is known that the cross section of such processes is very small?

I. M. Barkalov. During the effect of radiation on a substance there is releasing of rotations and, thereby, diffusion is sharply accelerated in the substance at the time of irradiation. I expressed the assumption about releasing of motions in the lattice as a speculation.

Yu. L. Khait. On the basis of your experiments is it possible to refute the data that indicate that the yields and rates of different reactions of radiation polymerization are very great in the region of the melting point?

I. M. Barkalov. The peaks at the points of phase transition pertain not to radiation polymerization, but to polymerization of frozen mixtures of catalyst-monomer. The literature contains data about explosive polymerization formaldehyde at the point of phase transition. I should say that we did not observe explosive polymerization, even for formaldehyde.

A. Ya. Temkin. Are the distances between atoms in the crystal lattice kept during formation of new chemical bonds in the process of polymerization?

I. M. Barkalov. No. The difference in the specific volumes of polymer and crystal acrylonitrile is around 15%.

A. Ya. Temkin. Does the polymerization rate depend upon the type of symmetry of the monomers?

I. M. Barkalov. The vinyl acetate sample was fine-crystalline. The monomer was frozen to 77°K; we obtained a sample in the glasslike state; it was further heated above the point of phase transition and then it passed into the fine-crystalline state. The sample was then kept at the studied temperature and irradiated. We also obtained a large crystal of vinyl acetate by keeping the sample several degrees below the melting point. In such well organized crystals polymerization occurred at an even lower rate; the molecular weight was lower than in the case of fine-crystalline samples.

V. V. Voyevodskiy. How should we understand the fact that polymerization of the monomer in glasslike state flows at a higher rate than in the crystalline state? Does this mean that the growth rate constant of a chain in the amorphous state is larger, or can this be caused by a lower yield of radicals in the crystal sample with a higher growth rate constant of the chain?

I. M. Barkalov. The yield of radicals was measured by the EPR method directly under the beam. We found that the yield of radicals in the crystalline state is somewhat lower than in the amorphous state? However, this difference cannot be explained by the observed difference in the polymerization rates in the amorphous and crystalline states.

S. Z. Roginskiy. Did you press the sample strongly after polymerization of [illegible] Will this not maintain the process? In topochemical reactions it is frequently observed that a reaction stops due to a break in contact between the initial and forming phases.

I. M. Barkalov. We did not try this.

L. S. Polak. What are the molecular weights of the obtained products of polymerization?

I. M. Barkalov. The molecular weight of the polymer obtained during irradiation of glasslike vinyl acetate is approximately 15,000, in the case of acrylonitrile, it attains 100,000.

M. A. Bruk. V. A. Kargin, et al., [2] and Bensasson and Marx [1] observed a phase transition in acrylonitrile at -160°C. Do you have any data about such a transition?

I. M. Barkalov. Bensasson and Marx did not observe a phase transition at -160°C. V. A. Kargin and others worked with mixtures obtained by condensation of molecular beams. Molecular-dispersed metals and monomer crystals during thermographic analysis naturally can give a transition at -160°C. We conducted thermographic analysis of a pure monomer.

M. A. Bruk. Investigators [3] conducted solid-phase polymerization of acrylonitrile and gave a graph of the dependence of the logarithm of the rate upon the magnitude of inverse temperature not in the form of a straight line, but in the form of a broken line. These authors consider that at several points the activation energy passes from positive to negative. In particular, they consider the activation energy negative near the point of phase transition of acrylonitrile, whereas your data indicates the absence of a temperature dependence of the polymerization rate in the solid phase.

I. M. Barkalov. In the work of Sobue and Tabata [3] this dependence is not given in the form of a broken line, but in the form of straight line where the value of the activation energy of solid-phase polymerization of acrylonitrile equal to 0.4 kcal/mole lies practically within the limits of experimental error. This permits affirming that activation energy is absent. Bensasson and Marx obtained precisely the same data.

N. D. Sokolov. According to the theory of N. N. Semenov in hard-phase polymerization excitions corresponding to certain excited states play a large role. Do you plan to study this process during irradiation of frozen monomers by ultraviolet light of a definite wavelength?

I. M. Barkalov. Yes, we do.

V. I. Lakhvitskiy. Did you observe a limiting value of polymer yield during irradiation of vinyl acetate in the crystalline and glasslike states?

I. M. Barkalov. No, not in either case.

S. Z. Roginskiy. What was the dose rate in your experiments?

I. M. Barkalov. For acrylonitrile, 0.3 Mrad/min; for vinyl acetate, 5 Mrad/min.

Yu. A. Chikin. Did the form of the EPR spectrum change at the point of phase transition?

I. M. Barkalov. At the phase transition point for acrylonitrile we observed only a drop in the signal intensity without a change in its form.

Yu. V. Pepelyayev. What is the difference in the molecular weights of polymers when the reaction was carried out in different phases?

I. M. Barkalov. In the case of polymerization of acrylonitrile in the liquid phase the molecular weight continuously increased up to full cross-linking at a dose near 8 Mrad. In the solid phase (in both states) we observed an increase in the molecular weight up to a definite limit.

Literature

1. R. Bensasson and R. Marx. J. Polymer Sci., 48, 53 (1960).
2. V. A. Kargin, V. A. Kabanov and others, High-molecular compounds, 3, 421 (1961).
3. H. Sobue and Y. Tabata. J. Polymer Sci., 43, 459 (1960).

PECULIARITIES OF THE FLOW OF PHOTOCHEMICAL HYDROBROMINATION OF ETHYLENE IN THE SOLID PHASE

G. N. Kovalev and G. B. Sergeyev

A mixture of hydrogen bromide and ethylene was frozen at 77°K and illuminated by ultraviolet light for a definite time. After thawing, in the reaction products we found ethyl bromide and dibromomethane in the ratio of 500:1. The depth of transformation attained 70%.

With thermographic analysis we show that the reaction of hydrobromination of ethylene begins at about 77°K and has an explosive character. A peculiarity of the reaction developed during continuous illumination of the sample at 77°K, is the presence of an induction period (τ = 4-50 sec), during which the reaction occurs at a depth on the order of several percents.

The fast exothermic process has a thermal nature since a decrease in heat removal from preliminarily illuminated samples leads to gradual self-heating of the mixture, and after a certain temperature is achieved, to a stormy reaction.

The ratio of the yields of products and a direct appraisal of quantum yield of the reaction show that in the described conditions hydrobromination of ethylene occurs through a chain mechanism with the length of chain being several hundreds of sections.

Experimental data and an analysis of the possible elementary reactions lead to conclusion that bromine atoms and possibly π-complexes of bromine atoms with ethylene can be stored in the illuminated mixture.

A study of dependence of the induction period upon the intensity I during continuous illumination of the mixture up to the moment of explosion reveals an interesting peculiarity of the reaction. With a decrease in I the induction period increases so that the product $I\tau$ remains constant over a considerable interval of intensities, i.e., for an explosion to develop at 77°K a definite dose of irradiation is necessary.

The following explanation of the found facts is the most probable. Under the effect of light there occurs a dissociation of hydrogen bromide into H and Br atoms. Due to their mobility at 77°K the H atoms easily recombine, giving hydrogen, whose liberation we recorded. The bromine atoms stored during irradiation at 77°K are durably secured in their cells and cannot enter into the reaction. However, in rare cases during specially favorable conditions due to point liberation of heat during recombination a bromine atom is joined to a neighboring molecule of ethylene and thus a single chain of the reaction can develop. The thermal wave of a single chain of the reaction spreads along the solid mixture and, attaining the nearest stabilized bromine atom, it can make it possible for it to start a chain reaction in turn. Inasmuch as the temperature in this thermal wave drops rapidly with distance, the appearance, under the effect of the thermal wave, of a second chain is possible only if a second bromine atom is less than a certain critical distance from the first. N. N. Semenov calls this mechanism the development of single chains branched with help of elementary thermal waves. As the concentration of stabilized bromine atoms increases the probability of "thermal branchings" increases, leading to an increase in the reaction rate, which appears in a gradual at first smooth and then all more accelerated, increase in temperature. During illumination the reaction rate attains a certain critical magnitude at which influx of heat from the reaction becomes equal to heat removal. When the reaction rate exceeds a critical number of acts of "thermal branchings" and straight chains an avalanche-type explosion develops, during which all the bromine atoms accumulated before the explosion are involved in the reaction.

In the same conditions of heat removal an explosion starts at the same critical reaction rate. This rate depends upon the concentration of stabilized bromine atoms, which, independent of intensity, is attained only after illumination of a definite critical dose.

Thus, the described phenomenon manifests the traits of thermal and chain explosions and we consider it as a confirmation that "thermal branchings" do occur in the solid phase.

Discussion

V. L. Karpov. Did you study the dependence of the magnitude of the induction period upon the average dimensions of the crystallites? Do you think that this dependence should occur if the mechanism of the reaction is connected with a special method of retaining the bromine atoms?

G. N. Kovalev. Both are possible. The main thing is that the energy subtracted during chemical reaction is expended on ejecting the bromine atom from its trap, which then starts the reaction.

S. Z. Roginskiy. Do you consider that heating up at least its start, is caused by absorption of light?

G. N. Kovalev. Our control experiments showed what this heating up is not connected with absorption of light.

CAN DISPLACEMENT OF A STITIAL ATOM INTO THE INTERSTICE BE ACTIVATED AS A RESULT OF IONIZATION OF THE K-SHELL?

S. V. Starodubtsev and A. Ye. Kiv

The formulation of this problem is connected with the appearance of a large quantity of experimental data indicating the possibility of the appearance of structural disturbances in crystals under the influence of radiation with an energy lower than the threshold necessary for elastic displacements.

The time a stitial atom is inside a potential well is determined by the expression

$$t \propto \frac{1}{\nu_0} \exp\left(\frac{E}{kT}\right). \qquad (1)$$

where ν_0 is the effective frequency of oscillations of the atom; E is the height of the potential barrier.

As a result of ionization of the K-shell stitial atoms of not very heavy elements obtain a positive charge thanks to Augier-transitions. Their potential energy in the crystal increases and they turn out to be in an activated state, which in certain cases can lead to their going into an interstice.

Let us consider this question with reference to valence crystals. We can consider that the potential energy of an atom in such crystals is basically caused by Coulomb repulsion of the cores and exchange interaction of the valence electrons. If one of the atomic cores obtains an additional charge, the potential energy of the atom can grow by a magnitude sufficient for the atom to be above the potential barrier [1]:

$$\Delta V_i = \sum_k \sum_j \frac{(z_i^* - \sigma_i)(z_j - \sigma_j)e^2}{r_{ij}^k} -$$

$$- \sum_k \sum_j \frac{(z_i - \sigma_i)(z_j - \sigma_j)e^2}{r_{ij}^k} - (z_i^* - z_i)e \int_{r_0}^{\infty} \left(1 - \frac{1}{\varepsilon}\right) \frac{e}{r^2}\,dr. \qquad (2)$$

Here $z_1 e$, $z_j e$ are the charges of the atomic cores in the crystal; σ_i, σ_j are the screening constants caused by valence electrons; r_{ij}^k is the distance from the examined i-th atom to all j-th atoms of the k-th coordinate sphere; ε is the dielectric constant; r_0 is the radius of the sphere inside which the additional charge provoking polarization of the medium is located; $z_1^* e$ is the charge of a repeatedly ionized atomic core.

In general, the process of displacement is determined by the magnitude [2]:

$$\tau = \min(\tau_m, \tau_a). \qquad (3)$$

where

$$\tau_a \simeq \frac{3\pi n^{*4} a_0 \sqrt{a_0 a^3}}{z^{*4}} \exp\left(\frac{2}{\hbar}\sqrt{2m\Delta\varepsilon a}\right). \qquad (4)$$

Here n^*, $z^* e$ are the effect quantum number and the charge for the given shell; a_0 is the Bohr radius; a is the lattice constant; $\Delta\varepsilon$ is the ionization energy of a valence electron; τ_m is the lifetime of the ionized state of the given atom.

During passage of a fast charged particle through a crystal ionization of the K-shells of two neighboring atoms can occur, which will lead to an even larger value of ΔV_1. The probability of this process is expressed by the formula:

$$W = 1 - \exp\left(-\frac{a}{\lambda}\right). \qquad (5)$$

where

$$\lambda = \frac{1}{\sigma N_0};$$

N_0 is the concentration of atoms; σ is the ionization cross section.

The cross section of the process of displacement can be written in the form:

$$\Sigma = \sigma_k \prod_i (1 - \eta_i) \frac{\tau}{T}, \qquad (6)$$

where σ_k is the ionization cross section of the K-shell; η_i is the yield of fluorescence of the l-series of the X-ray spectrum.

Appraisals show that this ionization mechanism of atom displacement can also play an important role when the energy of radiation is sufficient for elastic displacement of atoms in a crystal.

Literature

1. S. V. Starodubtsev and A. Ye. Kiv. DAN USSR, 151, 550 (1963).
2. A. Ye. Kiv and S. V. Starodubtsev. News of the AN UzSSR, 3 (1963).

General Discussion

N. V. Kulyupina and A. M. Kabakchi. Under the effect of ionizing radiation on multicomponent systems it is usually taken that the energy of radiation absorbed by every component is proportional to its electron share in the mixture. In accordance with this, an additive law is formulated according to which the yield of primary products of radiation-chemical transformation of each of the components of the mixture must be proportional to the electron share of the component. Deviations from the additive law are considered as a result of secondary processes caused by an intermolecular transfer of energy.

Distribution of Absorbed Energy of Radiation (in %)
Between Components of a Mixture

System	Component	Average excitation potential, v	Calculated from electron shares	Calculated from the contribution to stopping power during the effect			
				protons (2 Mev)	electrons, Mev		
					0,02	0,2	2
Methyl methacrylate – ethyl acetate (1:1 by weight)	MMA EA	65,2 64,0	50,5 49,5	50,2 49,8	50,2 49,8	50,2 49,8	50,2 49,8
Styrene – carbon tetrachloride (1:1 by weight)	Styrene CCl_4	60,8 156,0	52,8 47,2	54,5 45,5	57,8 42,2	55,9 44,1	57,1 42,1
Aqueous solution of sodium chloride (2 mole/l)	H_2O NaCl	68.0 163,5	88,5 11,5	90,5 9,5	90,8 9,2	91,3 8,7	92,8 7,2

According to the Bethe theory the energy dispersed by a particle per unit length of the path as a result of nonelastic collisions depends, in a determined way, not only upon the electron density of the medium, but also upon the average excitation potential of the entering particle. If the primary particle is an electron with energy greater than 1 Mev, we must also consider polarization of the medium. Therefore, calculation of the energy of radiation absorbed by the components of mixture from electron shares can carry only an approximate character. It is obviously more accurate to base the calculation on the assumption that the absorbed energy is distributed proportional to the contribution of every component to the stopping power of the medium with respect to the given form of radiation.

The table gives values of the energy of radiation absorbed by the components of the mixture calculated from electron shares and from the contribution of every component to the stopping power of the medium for certain systems studied in the radiation-chemical sense. The energy of radiation absorbed by the components of the mixture was calculated from their contribution to the stopping power of the medium for protons with energy of 2 Mev and for electrons with energies of 0.02; 0.2 and 2 Mev. For electrons with energy of 2 Mev we introduced a correction for polarization.

From the tabular data it follows that when the average excitation potentials of the components differ little from each other, calculations from the electron shares of the components and from their contribution to the stopping power of the mixture give coinciding results regardless of the form and energy of radiation. When the average excitation potential of one component essentially exceeds that of another component, the results of calculations from electron shares and from contribution to stopping power noticeably differ from each other. The divergence between the results exceeds the usual error of radiation-chemical experiments. For an aqueous solution of sodium chloride (2 mole/l) under the effect of electrons with an energy of 2 Mev the divergence between the results of calculations both methods is approximately 40% with respect to the energy absorbed by sodium chloride. It is obvious that the divergence will be even larger for such systems as concentrated aqueous solutions of potassium bromide or mixtures of rubbers with different fillers, which are very common objects of radiation-chemical investigations.

V. L. Tal'roze. I would like to consider this question: To what degree can the difference in atomic numbers of elements affect the process of primary absorption of energy during radiolysis. First, we must consider that in the formula for the energy losses by charged particles (the Bethe formula) there is a logarithmic term that depends upon the excitation potential of the molecule. It is possible, however, to show that for most organic systems, including those that contain oxygen, this correction does not play an essential role. Thus, for electrons with an energy of 200 kev this correction is one percent of the full energy for a cyclohexane-benzene mixture and 4% for water.

However, it is always possible that a difference in radiation effect on molecules will start to have effect at small electron energies (100-1000 ev), when the Bethe formula is practically inapplicable. This difference can be essential if just slow electrons play the main role in chemical-radiation processes. Apparently the only method to approach such questions is to compare the experimental data on the interaction of slow electrons (with energy of $\sim$100 ev) with various individual molecules in the gaseous phase. These questions have been studied in detail in mass spectroscopy[1] and we can now consider it fixed that the ionization cross section caused by such electrons increases directly proportional to the polarizability of the molecule. It is very significantly that the electrons of a molecule or atom play the main role in the process of ionization. To clarify this, with Ye. L. Frankevich we compared the dependence of the ionization cross section of different molecules (organic compounds, inert gases and NO, HCl, CO_2, H_2O, etc.) upon the full number of electrons in the molecule n, and also upon the number of peripheral electrons $n_{\text{пер}}$. We found that the ionization cross section of organic molecules (saturated and unsaturated aromatic hydrocarbons) increases proportional to n. For all inert gases and those that do not contain hydrogen, the ionization cross section also increases proportional to n, however, for each of these substances the ionization cross section is approximately 2 times less than for a molecule of an organic substance with an identical number n.

If we construct an analogous dependence of the ionization cross section upon $n_{\text{пер}}$, ($\sigma_{\text{иониз}}$ increases proportional to an increase in $n_{\text{пер}}$) the ionization cross sections for all organic compounds and most inert gases lie on one curve. The exceptions are only argon, neon, CO, O_2, N_2 and H_2O, whose cross sections are about twice reduced. Consequently, for organic substances with large hydrogen contents practically to the smallest energies of primary electrons it is necessary to consider all the electrons.

A difference can appear only in such mixtures as a mixture of xenon with organic molecules. Then we must consider that for xenon approximately half of electrons will be effective and the others not. Apparently, this must also be considered during radiolysis of hydrogen-free compounds with large oxygen contents.

V. V. Voyevodskiy and Yu. N. Molin. The clarification of the nature of active particles, the precursors of some form of primary chemical disintegration during

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[1] J. L. Franklin, F. H. Field, and F. W. Lampe. J. Am. Chem. Soc., 79, 6129 (1957).

radiolysis, are of very great interest. Although we cannot yet solve this problem in the common form, it is expedient to express certain qualitative considerations on this matter, which can be useful in setting up this general problem.

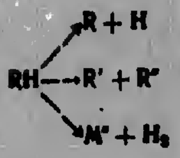
According our previously expressed hypothesis [1, 2], the effectiveness radiolysis in the condensed phase is determined by the difference of energies ΔE between the energy of first excited level of the molecule E_1 and its energy of dissociation D. When $E = E_1 - D < 0$, dissociation from the lower excited state is doubtful and the substance should have increased radiation stability. This hypothesis is valid if that the disintegration probability of molecule from the highest excited states is small as compared to the probability of transition into the first excited state. In the condensed phase this condition is usually fulfilled. From the point of view of this hypothesis a consideration of the data on the formation of radicals during radiolysis of solid hydrocarbons permits us to explain the regular change in the yield of radicals with a change in ΔE, and also to express an assumption that the direction of the reactions of hydrogen atoms formed during dissociation is determined by magnitude of excess energy ΔE.

An analysis of the totality of processes occurring during radiolysis requires more a detailed consideration of the question about the nature and paths of disintegration of molecules in the lower excited states. During radiolysis, along with the first singlet S and T levels of excitation, we must consider the state of ionization I. Considering each of these states as a precursor of some chemical disintegration

$$S \xrightarrow{k_S} (\text{product})_S;$$
$$T \xrightarrow{k_T} (\text{product})_T;$$
$$I \xrightarrow{k_I} (\text{product})_I,$$

in the most general form we can affirm that the yield of a certain product of disintegration will be determined by the rate constants of the corresponding process and the stationary concentration of the precursor. Affecting the concentration of one or another precursor by different additions, in principle we can establish that the precursor is responsible for one or another decay. However, application of this method, even for the simplest class of organic compounds, hydrocarbons of different structure, encounters essential difficulties due to a series of complicating side effects. In connection with this there is great interest in experiments on photochemical decay, in which we can obtain a precursor of one type (for instance S) and thus model one of paths of radiation-chemical transformation.

Experiments on photolysis of different hydrocarbons in the gaseous phase in recent years led to the conclusion that the basic means of decay of singlet-excited molecules is detachment of molecular hydrogen [3]. These experiments can serve as an indirect indication that during radiolysis of saturated hydrocarbons in the condensed phase, of the three basic processes of disintegration



the last is caused by singlet-excited molecules. Recently reported data on photolysis of solid ethane [4], as it were, confirm this assumption. However, for final proof more experimental data are needed on photolysis in the condensed phase. Direct application to the condensed phase of results of numerous experiments carried out in the gaseous phase would be too risky, inasmuch as the path of transformation of excited states can essentially depend on the phase state of substance.

In recent years interesting data have been obtained through the [EPR] (ЭПР) method indicating that even very insignificant changes in the structure of a solid can affect the direction of the primary processes of chemical disintegration. Thus, the yield of alkyl radicals in cyclohexane can change by 2-3 times depending upon the conditions of freezing [5, 6]. Even stronger effects were observed in our experiments conducted jointly with I. 1. Chkheidze and N. Ya. Buben during radiolysis of frozen $(C_6H_5)Si(CH_3)_3$. The conditions of freezing in this case affected not only the yield of radicals, which changed from experiment to experiment within limits of one order, but also the direction of primary chemical disintegration, which was indicated by a change in the form of the EPR spectrum. At this symposium B. N. Shelimov and N. V. Fok reported that photochemical processes in the aromatic hydrocarbon-saturated hydrocarbon system stopped almost completely with an increase in the temperature of the mixture frozen at 77°K by only several tens of degrees. Probably, in this case the structure of the substance influences the effectiveness of chemical disintegration.

It is doubtful whether we can consider it random that the sharpest changes in the direction and effectiveness of the processes of primary chemical disintegration are observed in systems that contain aromatic rings. In such systems the transition of excitation energy of the π-system into dissociation energy of σ-bonds should be strongly inhibited and, therefore, we can expect that very insignificant structural changes in the substance (deformation of chemical bonds, a change of mutual location of molecules, etc.) can influence the probability of certain primary processes.

From the point of view of the hypothesis that in the processes radiolysis we must consider only the lower excited states, substances with large systems of conjugated bonds must be subjected to radiation destruction. However, destruction in these cases nevertheless occurs although with a small yield. One of possible paths of chemical disintegration in these systems can be quadratic processes, in which the energy of two excited states is expended on one act of dissociation. Data on increased radiation yield of the products of radiolysis of aromatic hydrocarbons with a shift to irradiation by heavy particles, which were given by I. V. Vereshchinskiy,[1] evidently confirm such a possibility. In the tracks of particles the density of ionized and excited molecules is very great and therefore the probability of quadratic processes should increase sharply in this case.

Literature

1. Yu. N. Molin, I. I. Chkheidze, Ye. P. Kaplan, N. Ya. Buben, and V. V. Voyevodskiy. Kinetics and catalysis 3, 674 (1962).

2. V. V. Voevodskii and Y. N. Molin. Radiation Res., 17, 366 (1962).

3. H. Okabe and J. McNesby. J. Chem. Phys., 37, 1340 (1962).

4. M. D. Scheer, J. McNesby, and R. Klein. J. Chem. Phys., 36, 3504 (1962).

5. H. Szwarc and R. Marx. J. chim. phys., 57, 680 (1960).

6. Yu. N. Molin, I. I. Chkheidze, N. Ya. Buben, and V. V. Voyevodskiy. Kinetics and catalysis 2, 192, (1961).

A. Ya. Temkin. Will you please say on what you based the conclusion you made in the very beginning about hydrogen formed during disintegration of the C-H bond being hot. After all, first the transfer of excess energy into a vibrational degree of freedom of the same molecule is possible; secondly, inasmuch as the matter in crystalline, this energy can be transfered to the lattice. It would be very important to have experimental proof of this.

V. V. Voyevodskiy. First of all, we proceeded from the experimental fact that when transition with energy release occurs, i.e., transition from a higher level

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[1] See this collection, p. 287.

to a lower one, huge yields of molecular hydrogen are obtained; these yields are absent when such transitions do not occur. It is known that the primary act in both cases is identical, the breaking of the C-H bond. However, during radiolysis of one group of compounds molecular hydrogen forms and during radiolysis of another group, it does not. This fact requires some explanation. We originated from a simple consideration: a light particle is detached from a heavy one. Light and heavy particles distribute the energy among themselves and the light particle receives the main share of energy.

A. Ya. Temkin. It is certainly true that the main part of the energy goes to the light particle. However, the fact is that in the actual process of breaking away of a light particle energy can be converted to a vibrational degree of freedom.

V. V. Voyevodskiy. Certainly.

A. Ya. Temkin. The question is what energy can the light particle receive. It is fully possible that a greater part of the energy released during transition can be converted into a vibrational degree of freedom of the lattice. This consideration apparently does not exclude the actual fact of energy release.

V. V. Voyevodskiy. Our reasonings are these: there is a qualitative physical concept that the light particle receives the major part of the energy and this simple concept allows us to explain a very large number of previously unexplained data. Before our work, as far as I know, there was no explanation of why comparatively little molecular hydrogen is formed during radiolysis of aromatic compounds and why a lot is formed during radiolysis of aliphatic compounds.

S. Ye. Kupriyanov. You said that during photolysis in the far ultraviolet a hydrogen molecule can detach from one carbon atom. But it can also detach from two carbon atoms. What can you say about the ration of these processes?

V. V. Voyevodskiy. Works carried out by the American Bureau of Standards with tagged atoms show that in the region of wavelengths 1400-1300 A the basic path of the formation of hydrogen is the breaking away of two H atoms from one C atom as a molecule. But this does not preclude the possibility of molecular breakaway of two H atoms from two C atoms.

S. Ye. Kupriyanov. We should note that there are data on photolysis of propane and butane. The basic mechanism of the formation of molecular hydrogen is the breaking away of a hydrogen molecule directly. A comparison of these data indicates that the process of breakaway of a hydrogen molecule from two C atoms is more probable than from one C atom.

V. V. Voyevodskiy. No, I nevertheless cannot agree with such a conclusion. If we consider data with tagged atoms in a detailed analysis for just ethane, in which it has been proved that H_2 breaks away from just one carbon atom, on the basis of analogy with other substances it is impossible to affirm that these data are incorrect. Data on different substances must be compared through one method and in every case the mechanism must be shown. I think that in various cases, for instance, for methane and other hydrocarbons, there can be different mechanisms. Therefore, the question about the mechanism of H_2 breakaway cannot be posed in any other manner.

I. V. Vereshchinskiy. Recent investigations convincingly showed that the radiation-chemical yield of the products of radiolysis of liquid aromatic hydrocarbons essentially depends upon the nature of the ionizing radiation, i.e., upon the magnitude of linear energy transfer (LET). In other words, during radiolysis of liquid aromatic hydrocarbons there are track effects. In discussing the nature of track effects, it is expedient, apparently, to be limited to a consideration of radiolysis of the simplest aromatic hydrocarbons, those that do not contain alkyl groups, benzene, diphenyl and terphenyl.

The available data are very incomplete. In the case of radiolysis of liquid rarified benzene a considerable dependence of the magnitude G upon the LET magnitude is observed [1]. A similar dependence was found during radiolysis of terphenyl [2]. It is interesting to note that magnitude of the ratio of radiation-chemical yields of the products of radiolysis found at two different values of the LET depends little upon the nature of the hydrocarbon.

During radiolysis of o-terphenyl under the action of α-particles of Po^{210} in the whole investigated interval of temperatures (60-300°C) a linear dependence lg G upon inverse temperature is observed. The lack of a deviation from the linear dependence indicates the insignificant role of pyrolithimic processes at these temperatures. The activation energy is ~0.5 kcal/mole, i.e., close to the activation energy of the process of diffusion.

The known presentations do not seem convincing. The assumptions of Gaeumann [3] about the simultaneous formation of intermediate radicals and their reaction with each other until they diffuse does not agree with the noted temperature dependence. The Burns model [4], according to which active particles and accepting or deactivating particles are produced from the same molecule of substratum, ignores the mechanism of formation.

In discussion track effects it is apparently necessary, first of all, to consider the interaction of excited molecules. In order of magnitude the time molecules are in the excited state is 10^{-9} sec. In the first approximation we rightly consider that at the same LET magnitude the distribution of the primary products of radiolysis is equal for all aromatic hydrocarbons. The magnitudes of the corresponding coefficients of diffusion cannot considerably differ from each other.

The discussed effects can be explained if we accept the hypothesis of V. V. Voyevodskiy and Yu. N. Molin, which establishes a correlation between the magnitudes radiation-chemical yield of radicals and the position of the lower level of excitation of the corresponding compounds [5]. In the case of diphenyl and terphenyl the position of the lower level of excitation is somewhat below the magnitude of the energy needed to break the C-H bond.

If the lifetime of a molecule in the excited state is greater than or equal to (in order of magnitude) the time necessary for diffusion to another molecule, the effectiveness of radiolysis increases. It is clear that the effectiveness of this process increases for high local concentrations of excited molecules, i.e., for large LET.

Further investigations of the radiolysis of a series of aromatic hydrocarbons at various values of LET and at different temperatures can give proof of the correctness of the presentations developed here.

Literature

1. I. V. Vereshchinskiy and A. K. Pikayev. Introduction to radiation chemistry. M., Publishing House of the Academy of Sciences of the USSR, 1963, p. 364.

2. J. J. Jang and F. C. Goodspeed. Chem. and Ind., No. 23, 1018 (1962).

3. J. Hoigne and T. Gaeumann. Second Internat. Congress of Radiation Research. Harrogate, August 1962. Abstracts of Paper, p. 85.

4. W. G. Burns. Ibid, p. 124.

5. V. V. Voevodskii and Yu. N. Molin. Radiation Res., 17, 366 (1962).

V. M. Agranovich. The phenomenon of solid-phase polymerization deserves the most serious study. It is interesting to clarify what role the excited states of the monomer molecules stay here. At present, as far I know, there is no specific diagram of the participation of excitons in such a process. Therefore, I will try to say several words about the possible mechanism of polymerization with participation of excitons.

The heat of polymerization for one molecule is ~20 kcal/mole, i.e., during breaking of a π-bond and formation of a σ-bond energy on the order of 1 ev is liberated. Where does this energy go? It is clear that this process primarily concerns the electron subsystem. Energy transfer from electrons to ions is weakened due to the difference in their masses. If we can indicate any process in which the released energy is converted into any exciton, we could present a diagram of polymerization with participation of excitons as "initiators" of the process of polymerization. Can such energy be turned into energy of excitons that are available in a solid? The question immediately arises about the energy of an exciton that exists in a monomer.

The lower excited state of a monomer presents greatest interest. Possibly, the first such state is the triplet state, and the next, the singlet. We must clarify the role of these exciton states in such processes. First of all this question is vague; What excited state is necessary for explosive polymerization? This question cannot be answered on the basis of experiments on irradiation by fast electrons since we can consider that under the action of fast electrons among all the formed molecules about 30% are molecules in the triplet excited state, and the others, in the singlet state. Let us assume that the process of polymerization requires a triplet excited state. From the point of view of power balance this state is of great interest because its energy is less. When a π-bond breaks and a σ-bond forms in any single process exactly 1 ev of energy will be released. If this energy is sufficient to excite the triplet state, at this place would be formed a triplet exciton will form at this place that at any other place may cause the process of polymerization. However, apparently energy of 1 ev is insufficient to excite the triplet state. If such process does occur, the monomer exciton does not participate in it and the energy should be turned into heat. It is possible to devise another process that is considerably less probable. If two σ-bonds form immediately, the probability of such a collective process would be considerably less, since it would occur through intermediate virtual states.

I only indicated a possible role of the triplet state. For singlet excitons the diagram is approximately the same; however, one should expect what if a singlet exciton is formed and a triplet is needed that the singlet exciton can go to the triplet level and the reaction will go further. The participation of excitons could "branch" the reaction, i.e., give many polymerization centers. In this case it is possible, by introducing impurities that capture excitons, to somehow regulate the rate of explosive polymerization.

V. I. Gol'danskiy. Calorimetric measurements during thawing of irradiated solid monomers and calorimetric measurements in process of irradiation show that in these monomers the process of polymerization occurs in the course of irradiation and practically without activation energy. To clarify the role of excited states in such reactions, I want to speak of the possibility of conducting experiments with the introduction into monomers of different additions that extinguish luminescence. If excited states are responsible for polymerization, a decrease in their stationary concentration with the introduction of extinguishers will lead to a deceleration of polymerization.

Let me say several words about the properties of a substance under an electron beam. There are a number of processes, for instance, diffusion, that sharply accelerate under the beam; this acceleration is not explained by an increase in the temperature of the sample. It is clear that the passage of rapid polymerization under the beam and acceleration of diffusion can be analogous. However, both these phenomena have not yet found a good explanation. It is known that polymerization often occurs especially rapidly near the points of phase transition and fusion. V. A. Kargin and his colleagues explain this by the fact that in a frozen monomer there are ordered intermediate products that are close to the future structure of the polymer and, in addition, near the point of fusion their mobility is increased, thanks to which these intermediate products can have a form somewhat different from that required for polymerization "to be corrected."

In this connection I want to speak about one experiment that illustrates a unique similarity of an irradiated solid and a liquid. I have in mind experiments conducted in our laboratory and in certain foreign laboratories on annihilation of positrons in solids and liquids. A positron can form a positronium atom, which is an analog of the hydrogen atom. This positronium atom exists either in a state with antiparallel spins and a lifetime of 10^{-10} sec, or in a state with parallel spins and a lifetime of 10^{-7} sec in vacuum. The "long-lived" state enters into various kinds of interaction in the solid phase. Different reactions with participation of the positronium atom and different paths of the formation of positronium affect the lifetime of positrons and the probability of the formation of positronium. In particular, the formation and behavior of positronium depend upon the state of the substance. Thus, in solid napthalene and anthracene the long-lived component practically will not be formed because in these substances there is no "free volume" for a positronium atom, whose dimensions are twice that of a hydrogen atom, to be formed and retained. In melted napthalene and anthracene the long-lived component is observed. It is interesting to note that polymers and substances like napthalene that are subjected to irradiation behave like a liquid: the long-lived component of positronium forms in them. Thus, here is possible to speak about changes in the properties of a solid, bringing it near, in a certain sense, to a liquid. Possibly, this plays some role in the kinetics of solid-phase polymerization, brings polymerization under the beam close to polymerization near the points of phase transition.

A. Ya. Temkin. The assumption about the role of excited states in the process of solid-phase polymerization, which was expressed by V. I. Gol'danskiy, can be checked by introducing inhibitors. If these inhibitors effect only the process of chain initiation when they are introduced the average length of the chain and the average molecular weight will not change. If, however, the excited state plays a role in chain development, in each elementary act of bonding molecules of the monomer, introducing an inhibitor should lead to a change in the molecular weight of the obtained polymer.

I want to make a second remark concerning the energy development of the chain. There are two types of monomers that polymerize at low temperatures. In some cases polymerization requires only a change in the electron shells; the distance between nuclei do not change; in other cases, in the process of polymerization a change occurs in the distances between nuclei. In attempting to apply the presentation about the energy development of chains to the second case we must be careful since here it is required that the electron-excited state exists long enough for the nuclei to approach the necessary distance. However, there is a possibility that the energy of an electron-excited state will be converted into energy of motion of the nuclei and thus the excitation dissipates and the process of polymerization ceases. This possibility must be considered.

A. N. Ponomarev, V. L. Tal'roze, D. A. Kritskaya and I. K. Larin have developed a calorimetric method of studying radiation solid-phase reactions during irradiation by electrons of the kilovolt range.

The general diagram of the installation consists of the following.

The studied substance was frozen on an adiabatic calorimeter; it was then irradiated by electrons with an energy of several kilovolts. From the temperature change of the calorimeter (at its known heat capacity) the quantity of heat separated in irradiated layer as a result of absorption of the energy of bombarding electrons and the chemical reactions occuring was measured. The excess of the measured heat emission above the energy of absorbed radiation naturally constitutes the heat of chemical reactions in the solid layer. The basic merits of this method are the possibility of easy control of the electron beam, which particularly allows work on the sector method with a high frequency, and the possibility of creating very high dose rates in the irradiated layer. For instance, it was possible to work at a dose rate up to 10^9 rd/sec.

To check the possibilities of this experimental method we conducted calorimetric measurements of a thin film of acrylonitrile at 130°K during irradiation. We obtained a clear excess of the recorded heat above the heat given off by the electron beam; the excess equaled 100% of the latter. It is interesting that this result was obtained at an electron energy of 2 kev and a dose rate of $2 \cdot 10^6$ rd/sec. The calculated radiation reaction yield of polymerization is 100 elementary acts per 100 ev of absorbed energy. We consider these results to be a confirmation of the phenomenon observed by V. I. Gol'danskiy, et al. In our case the radiation reaction yield turned out to be two orders below that of their work. This result can be explained either by accelerated recombination of active particles at high doses or by track effects.

V. S. Pshezhetskiy. In a study of solid-phase polymerization we must consider the structure of the crystal lattice. In particular, it was revealed that the position of molecules in the crystal lattice of frozen acetaldehyde is almost the same as the position of monomeric sections in the polymer formed from it. We determined the temperature at which polymerization occurs thermographically. For acetaldehyde we showed that the temperature of polymerization changes depending upon the dose. As the dose increases the temperature of polymerization drops and it attains a limit at a certain definite dose. The thermal effect accompanying polymerization also increases with the dose and it also attains a limit at the same dose as the temperature of polymerization. To connect this thermal effect just with polymerization and not with other processes, we introduced inhibitors (acetone) and showed that the thermal effect decreases with an increase in the concentration of the addition.

<u>I. M. Barkalov.</u> I want to make certain remarks because of the report of V. S. Pshezhetskiy. 1. Acetaldehyde does not belong to vinyl monomers, which our report was dedicated. The polymerization of acetaldehyde is postpolymerization; we spoke about the specific reaction during irradiation; therefore our results do not contradict what V. S. Pshezhetskiy said. 2. One of the causes of fast polymerization in the course of irradiation, which we considered in our report, is the increase in mobility in a solid during irradiation. During γ-irradiation this reaction also apparently occurs. Bensasson and Marx, and also the Japanese researchers Sobue and Tabata, consider that polymerization of frozen acrylonitrile occurs directly during γ-irradiation, and not during subsequent thawing.

<u>V. B. Kazanskiy.</u> Recently in our laboratory G. B. Pariyskiy observed the disappearance of the EPR signal of hydrogen atoms that were stabilized on the surface of silica gel at -196°C under ultraviolet light. If one were to irradiate silica gel with fast electrons γ-rays at the temperature of liquid nitrogen, as is known the bonds of the hydroxyl groups covering the surface of this substance break and hydrogen atoms are formed that are stabilized on the surface. Simultaneously there is weak coloring of the samples as a result of the formation of F-centers. The adsorbed hydrogen atoms and the color centers give the EPR signals.

After illumination of irradiated silica gel by ultraviolet light there is discoloration of the samples and the EPR signals of both the adsorbed hydrogen atoms and also the F-centers disappear. We consider that under the light there is a transfer of electrons from the adsorbed hydrogen atoms to the color centers with the formation of protons and the disappearance of color centers. The formed proton is stabilized at a negatively charged aluminum atom that is introduced into the grid of the silica gel. It seems to me that a transfer of the energy absorbed by the solid to that adsorbed on the surface of molecules, as reported by Yu. A. Kolbanovskiy and others, can occur in a similar manner.

<u>V. A. Roginskiy.</u> During the study of hydrobromination of ethylene in the solid phase under ultraviolet light and γ-radiation we obtained certain new facts along with results that agree with the data of G. N. Kovalev and G. B. Sergeyev [1].

During irradiation of an equimolecular mixture of C_2H_4 and HBr in a quartz ompule (4 mm in diameter) by filtered ([PS-11] (ПС-11) filter) light from a [SVDSh-250] (СВДШ-250) lamp at the temperature of liquid nitrogen, after the first thermographic peak corresponding to a transition of the reaction into the explosive regime, we observed several more similar peaks (up to four). A similar picture was noted during irradiation, at the temperature of liquid nitrogen, of the mixture from a Co^{60} source (intensity, 500 rd/sec), but the number of peaks decreased to two with a simultaneous increase in the maximum heating up. These facts obviously confirm the hypothesis of D. A. Frank-Kamenetskiy [2] about the possibility of a regime of thermokinetic oscillation of the reaction rate for multistage processes.

The conclusion [1] about the independence of the product of induction time and intensity from intensity is strange inasmuch as this can be comprehended as the independence of the probability of bromine atoms obtained during photolysis of HBr getting out of the stabilized state from the intensity of illumination. The reaction rate of chain development, which determines the probability of transition of the process into the explosive regime, depends upon the concentration of stabilized bromine atoms, the conditions of heat exchange, and also the intensity of irradiation. At a sufficiently low intensity, the rate of chain development can be insufficient for a transition of the reaction into the explosive regime.

Indeed, with a decrease in the intensity of ultraviolet light by tens of times, transition into the explosive regime is not carried out at all, but with subsequent full light intensity this transition occurs very rapidly. During γ-irradiation of the mixture at the temperature of liquid nitrogen from a Co^{60} source (intensity, 50 rd/sec) the transition into the explosive regime is also not carried out, although the reaction occurs completely in the field of radiation. This is confirmed by the fact that during thermographic control of the processes of thawing the irradiated mixture exothermic effects are not observed.

Literature

1. G. N. Kovalev and G. B. Sergeyev. This collection, p. 353.

2. D. A. Frank-Kamenetskiy. Diffusion and heat transfer in chemical kinetics. M.-L., Publishing House of the Academy of Sciences of USSR, 1947.

G. N. Kovalev. In a brief report at this symposium it is not possible to consider the whole series our experimental data on low-temperature photochemical hydrobromination of ethylene in detail.

First of all one should note that the reproducibility of the results strongly depends upon the method of preparation of the samples and the conditions of heat removal. In developing our experimental method we also observed several peaks in conditions of poor heat removal from samples.

The constancy of the product I_1 in a definite interval of intensities is an experimental fact. At low intensities we also did not observe an explosion. The causes of this are insufficiently clear; however, the totality of obtained data permits assuming this can be explained by energy inequivalences of stabilized bromine atoms and a change in the average length of single chains during illumination.

Stabilization of bromine atoms also occurs and at low intensities of illumination since during subsequent thawing a rapid exothermic process is fixed. In light of this, the absence of overheating at low doses of radiation, observed by V. A. Roginskiy, is interesting. In our opinion this difference is connected with the formation of hot bromine atoms during radiolysis, which in a reaction capable matrix of ethylene and hydrogen bromide cannot stabilize and immediately initiate single chains of reaction. Therefore, during radiolysis thermal branchings of the type we described apparently should not occur and critical phenomena characteristic for photolysis will not appear.

B. V. Ershler. Since today is the last day of the symposium, I must note that the experience of such an organization is very positive. Preliminary formulation of questions subject to discussion and distribution of reports on these questions facilitated the work very much. I think we have to express gratitude to the organizing committee for such organization.

On the other hand, the wide subjects of discussed questions leads to the participants of the symposium having the most diverse profile. In connection with this several survey reports on different regions would help all participants to follow the work of the symposium.

Let me also note that this symposium heard a great number of different models of radiation effect, a number that significantly exceeds the amount of factual material presented.

Now I will go to the radiation chemistry of aqueous solutions, which was presented at this symposium only by our report. The essential difference in this region is that here there is no doubt about the existence under irradiation of different active particles, both oxidizing and reducing, or of the formation during radiolysis of a definite quantity of molecular products. The accuracty of determining the quantity of active particles in aqueous solutions, in contrast to organic substances, is about 1%. In connection with this I want to turn your attention to the value of the criterion we suggested. The most diverse acceptors give identical yields, which are fixed with great accuracy. There is also a region of acceptor concentrations in which yields do not depend upon concentration. In those regions where the dependence of yield upon acceptor concentration is observed there is competition between recombination of active particles and their capture by an acceptor. Within these limits the advantages of our criterion is that it is valid regardless of the nature of active particles and the character of their formation.

Let me say something with respect to equal distribution of particles in the medium. If particles are distributed evenly, this criterion must be in effect. It consists of the fact that in the region of the dependence of yield upon acceptor concentration the curve of the dependence shifts during a change in the radiation intensity by a strictly defined magnitude. We do not need to know what processes flow in the solution, the type of active particles, etc.; it is only important that the active particles are distributed evenly. If this shift is proportional to $I^{1/2}$, the distribution of these particles should be uniform. This criterion allows us to reject a series of mechanisms of the appearance of molecular products in the solution and to make certain conclusions about the nature of the active particles. An example is the exception of the hypothesis about energy migration in water.

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III. CHEMICAL REACTIONS AS POSSIBLE SOURCES OF INDUCED RADIATION

GENERATION OF COHERENT RADIATION IN CHEMICAL REACTIONS

V. L. Tal'roze

Recently researchers have tried to find paths for the creation of a "purely chemical" quantum generator of radiation, i.e., a generator in which the energy released during a chemical reaction or transmitted in the form of heat of the reaction mixture will be converted into coherent radiation. Experimental search in this direction should precede theoretical consideration of problem on the whole.

This report gives the results of a very general theoretical consideration of the conditions of self-excitation and the efficiency for a hypothetical generator working on a gas reaction and a transition between electron-excited levels. The derivation is made in terms of the chemical kinetics of chain reactions. The system is depicted on the figure. Here, X, X' are the products in the states between which induced transition occurs; k_B is the rate constant of the process of excitation in cm^3/sec; k_E is the rate constant of the process of induced radiation; α is the total rate constant of spontaneous radiation and loss of excitation during collisions of X' with other particles or with the walls with transition of X' into X; W', W are the rates of formation of the products X' and X ($W_x = W + W'$); k_x is the total rate constant of the transformation of X' not into X, but into other products; k_x' is the total rate constant of "destruction" X in chemical

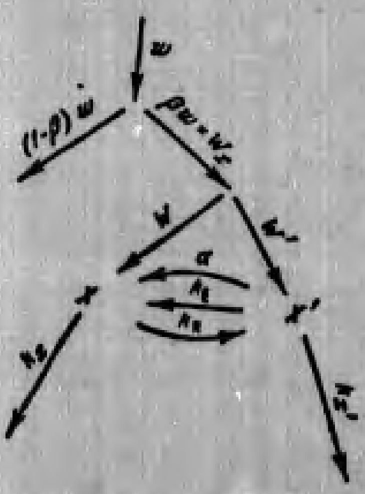

Diagram of the processes in a chemical laser.

reactions, on the wall, and also, if X is an excited state, through spontaneous radiation and collisions of the second kind; w is the full chemical reaction rate; β is the "fraction" of the reaction leading to the formation of X and X'. We show that the efficiency of this system, i.e., the ratio of the energy of coherent radiation to Q, the heat given to the system (for an endothermic reaction) or to the thermal effect (for an exothermic reaction,)[1] is

$$\varkappa = \frac{\varepsilon_c}{\varepsilon_r+\varepsilon_c}\cdot\frac{\mu\beta q}{Q}\left\{\frac{w'}{w_x}-\frac{k_x'+a}{k_x'+k_x\frac{g}{g'}}\left[1+\frac{4gk_x(\varepsilon_c+\varepsilon_r)}{g'\psi l\lambda^2\beta w}\right]\right\}, \qquad (1)$$

where μ is the obtainable depth of the reaction; q is the energy of the "working" quantum; g and g' are the statistical weights of X and X'; ε_c transmittance of the mirror; ε_r is the "absorptivity" of light by the mirror; l is the length of the laser; λ is the wave length; $\psi = a_0/\Gamma$, where a_0 is the radiation and Γ is the full line width for a "working" transition.

The following cases are considered: 1) X is an excited molecule; 2) X is an unexcited atom or a "small-atom" free radical; 3) X is a nonatomic radical; 4) X is an excited molecule or radical. It is shown that case 4 is optimum for fulfillment of the conditions of self-excitation; however, in cases 2 and, to a lesser degree, case 3, these conditions can be carried also out if "removal" of the radicals is produced as a result of fast elementary reactions of acceptance or exchange.

Let us discuss the requirements presented by the conditions of self-excitation to the chemical reaction rate. When a working transition occurs in the atom, a relative rate of transformation of 10^{-4} -10^{-2} sec^{-1}; if, however, the working transition occurs in a radical or a molecule, a relative rate of transformation of 10^{-1} -10^{+2} sec^{-1} (due to "smearing" of the electron transition line into a band).

Let us recall that the last values of the rate are practically accessible at not too large temperatures only in chain chemical reactions.

Let us consider the specific kinetic regularities of simultaneous flow in a system of chemical and "quantum" ("wave") chain reactions for the cases of unbranched and branched chemical reactions. The specific nature of these regularities permits us to determine such, now hypothetical, jointly flowing chain reactions as "chemical-wave" chain reactions. It is shown, in particular, that for an unbranched chain

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[1] Correspondingly, the concepts of thermo chemical and chemical quantum generators are introduced.

chemical-wave reaction the requirements presented by the conditions of self-excitation to the chemical reaction rate lead, with certain assumptions, to the expression

$$\frac{\tilde{k}_{обр} k_{обр}}{k_B W_0} \leqslant 10^{-1}, \tag{2}$$

where k_B is the rate constant of induced radiation; $\tilde{k}_{обр}$ and $k_{обр}$ are the rate constants of breaking for wave and chemical chains; W_0 is the rate of generation of chemical chains.

Critical phenomena are predicted for "chemical-wave" chain reactions (limits of self-excitation with respect to pressure, temperature, diameter and length of the reactor, the mixture ratio, etc.) and their character is considered.

The rational nature of photochemical or radiation-chemical initiation of chemical chain reactions that are proposed for use in quantum generators is shown.

Consideration of the possible values of the efficiency in chemical quantum generators leads to the conclusion that it is doubtful whether they can exceed 10^{-3}.

Discussion

S. S. Butsko. You spoke about the efficiency of a chemical laser. Can you definitize what you implied by this and can you give its approximate numerical values?

V. L. Tal'roze. By efficiency we mean the fraction of introduced thermal energy (for an endothermic reaction) or the fraction of thermal effect of an exothermic reaction that is converted into energy of coherent radiation. With such a determination the case of a thermoneutral reaction proceeding practically without heat addition appears very paradoxical. Then the denominator of formula (1) turns into zero and we obtain infinite efficiency. However, this difficulty is purely formal. A consideration of the known processes shows that we need reactions with strongly exothermic elementary acts. In reality, such acts apparently can exist in fast exothermic reactions. What magnitudes of efficiency are obtained? Rough estimates lead to upper boundary of 1-0.1%, and if we actually manage to obtain such values, this would be very well.

S. S. Butsko. If I comprehended correctly, only about 1% of the energy of a chemical reaction can be converted into energy of light. On the other hand, it is known that in certain reactions more than 1% of the chemical energy is turned into light. How should we understand this fact?

V. L. Tal'roze. We are talking not simply about obtaining more light, but about obtaining coherent radiation. For this it is quite insufficient to simply have more light, but a whole series of conditions must be fulfilled, which was the essence of the whole report.

V. V. Voyevodskiy. What transitions did you consider: from oscillating-excited or electron-excited states?

V. L. Tal'roze. Electron-excited states. In examining oscillatory or rotary levels whole series of new problems appear.

S. Z. Roginskiy. Is the requirement that the rate of removal of particles from the ground state be greater than from excited states still in force?

V. L. Tal'roze. To continuously support inversion of the population density particles must be removed from the lower state as rapidly as from the upper. Identical removal rates of particles is the generation limit.

THE APPEARANCE OF NEGATIVE TEMPERATURES DURING CHEMICAL REACTIONS

A. N. Orayevskiy

In a number of chemical reactions the compounding of separate reagents into one molecule occurs with participation of excited electron states [1]. For the appearance of states with negative temperature is necessary so that the number of excited particles, which are products of the reaction, exceed the number of analogous particles that are in the unexcited state. If in initial state products of reaction are lacking, the appearance of a state with negative temperature it is necessary and sufficient that

$$\frac{1}{g^+}\cdot k^+ > \frac{1}{g^-} k^- . \qquad (1)$$

where $k^+(k^-)$ is the specific rate of the reaction leading to the appearance of excited (unexcited) electron states in the products of reaction; $g^\pm$ is the statistical weight of the states.

It is known [1], that the reaction

$$Na_2 + Cl = NaCl + Na \qquad (2)$$

leads to the appearance of excited Na atoms and the appearance of the yellow line of luminescence (D-line) characteristic for Na. As experiments show, [2] at sufficiently low pressures ($\sim 10^{-3}$ mm Hg), when quenching of the luminescence due to collisions is absent, 80% of the sodium atoms appearing as a result of the reaction radiate. Consequently,

$$\frac{k^+}{k^+ + k^-} = 0{,}8. \qquad (3)$$

The ratio of the statistical weights $g^+/g^- = 3$, and from (3) it follows that condition (1) is fulfilled.

The fulfillment of relationship (1) guarantees the appearance of states with negative temperature only at the initial moment of time.

For an analysis of the appearance of negative temperatures in a steady-state operation we shall consider the simplest kinetic equations describing the change in the number of particles in different states:

$$\frac{dn_+}{dt} = C^+ - w_{cn} n_+ - w^+ n_+;$$
$$\frac{dn_-}{dt} = C^- + w_{cn} n_+ - w^- n_-, \qquad (4)$$

where n_+ and n_- are the numbers of excited and unexcited products of reaction; C^+ and C^- are the reaction rates; w_{cn} is the probability of radiation decay of the excited state; w^+ and w^- are the probabilities of removal of the products of reaction from the system.

In the steady state $dn_+/dt = dn_-/dt = 0$ and the condition of the appearance of negative temperature $\frac{n_+}{g^+} > \frac{n_-}{g^-}$ leads to the inequality

$$\frac{g^-}{g^+} > \frac{w_{cn}}{w^-} \cdot \frac{C^+ + C^-}{C^+} + \frac{w^+}{w^-} \cdot \frac{C^-}{C^+}. \qquad (5)$$

If $w^+ \ll w^-$, and C^+ and C^- satisfy relationship (1), for condition (5) to be fulfilled it is necessary that the ratio w_{cn}/w^- is sufficiently small. If the excited state appearing as a result of the reaction is not metastable, then $w_{cn} \simeq 10^8$ sec^{-1} and w^- should be on the order of 10^9 sec^{-1} or larger. This rate of removal of unexcited particles is difficult to ensure by ordinary evacuation. For this purpose it is best to use adsorption or a chemical reaction, as a result of which products are formed that do not have spectral lines that coincide with line of radiation. In particular among such reactions are chain reactions, similar to the reaction of sodium with chlorine, which are developed according to the diagram [1]:

$$Na_2 + Cl = NaCl + Na;$$
$$Na + Cl_2 = NaCl + Cl. \qquad (6)$$

For such reactions relationship (5) takes on the form:

$$\frac{g^-}{g^+} > \frac{w}{kX} \cdot \frac{k^+ + k^-}{k^+} + \frac{k^-}{k^+} \cdot \frac{w^+}{k}. \qquad (7)$$

where X is the concentration of Cl_2; k and k^* are the specific rates of the reactions $Na + Cl_2 = NaCl + Cl$ and $Na^* + Cl_2 = NaCl + Cl$ (Na^* is an excited atom of sodium). Since for the D-line of sodium $w_{cп} = 6 \cdot 10^7$ sec^{-1}, and $k = 6 \cdot 10^{14}$ $cm^3 \cdot mole^{-1} \cdot sec^{-1}$ [2], fulfillment of relationship (7) requires pressures on the order of one atmosphere.

According to diagram (6) the reaction Cs + Cl can be more favorable, since for it $k^* \approx 0$.

If as a result of the reaction atoms appeared in the metastable state, with help of sufficiently fast evacuation it would be possible to remove the "processed" atoms from the system. From this point of view thermal dissociation of CO_2, N_2O, the ground state of which is $^1\Sigma$, is of interest. Since the ground state of oxygen is ^3P, it is possible to expect that during dissociation:

$$CO_2 \rightarrow CO(^1\Sigma) + O;$$
$$N_2O \rightarrow N_2(^1\Sigma) + O, \qquad (8)$$

oxygen will be formed in the excited state ^1D [1, 3]. The state ^1D is metastable since it is singlet and the ground state ^3P is triplet. Evacuation rates of 1000 l/sec are fully sufficient to remove the products of reaction from a volume of 1 cm^3 in 10^{-6} sec.

Let us remember that many biochemical reactions occur with participation of excited electron states [4]. Therefore, it is fully possible that negative temperatures play a definite role in biological processes.

Literature

1. S. Glesston, K. Leydler and G. Eyring. Theory of absolute reaction rates, M., IL, 1948.

2. J. Magee. J. Chem. Soc., N 8, 638 (1940).

3. K. Laidler. The Chemical Kinetics of Exited States. Oxford, 1955.

4. S. Rid. Excited electron states in chemistry and biology. M., IL. 1960.

Discussion

S. S. Butsko. In the reaction you wrote, as is known, a large part of the light is given off in the form of sodium D-lines. But along with this in spectrum of this luminescence there is a whole series of other lines, including a line located in the region of 2000 A. What components, what products of reaction are responsible for this radiation and what is the mechanism of the appearance of this reaction?

A. N. Orayevskiy. I cannot specifically answer this question since I did not study this reaction. A study of these questions would be very interesting.

V. L. Tal'roze. You are not confused by the fact that at any conceivable temperature in an equilibrium mixture of Na_2 vapor there is always not more 0.3% Na_2? This indicates that more than 99% of the sodium is in the atomic state at the zero level, the actual one to which you want to pass, i.e., you preliminarily pump to the lower level almost 1000 times more particles than to the on upper.

A. N. Orayevskiy. This is one more argument for using molecular beams on the first stage. According to Ramsey, in a molecular beam approximately 0.5%, or, in the best case, about 1% Cs_2 can be obtained. If we calculate that 10^{19} atoms depart per second, we obtain 10^{17} for Cs_2. Furthermore, in molecular beams we can separate Cs from Cs_2 atoms comparatively simply in a nonuniform magnetic field: Cs is deflected by a magnetic field and Cs_2 is not.

V. L. Tal'roze. This separation in magnetic field is the only means; all the remaining, disregarding the application of a molecular beam, cannot help since in molecular beam gas is fed from a furnace where it is in the equilibrium state.

A. N. Orayevskiy. I know of no data about the probabilities of formation of higher states in this reaction.

V. L. Tal'roze. Indeed, perhaps higher electron states will be obtained and we will start to work on a multilevel diagram. But I doubt that the heats of reaction will be sufficient for this.

A. N. Orayevskiy. I also doubt this, but I have no data favoring or opposing this assumption.

V. N. Kondrat'yev. I have more of a comment than a question. To stop speaking about Cs_2 and Na_2, I must say that such a process as

$$Na_2 + Cl \rightarrow NaCl + Na^*$$

does not exist. Sodium can be excited a second time; all the energy in the beginning is concentrated apparently on NaCl, which then collides with a Na atom and excites it.

A. N. Orayevskiy. Perhaps I have old data, but according to Magee, this is not so.

V. N. Kondrat'yev. I myself studied this reaction. Therefore, I am not talking about molecular beams.

A. N. Orayevskiy. According to Magee, the rate of the appearance of Na in the excited state is considerably more than the rate of its formation from the unexcited state during collisions of excited NaCl with Na. Moreover, according to the same data for cesium the channel of the formation of unexcited state is practically closed. If these data are refuted, a series of additional difficulties appear when molecular beams are used.

V. V. Voyevodskiy. I have a question about terminology. It is necessary, in general, to introduce the term "negative temperatures" and does it characterize a system?

A. N. Orayevskiy. This term has already been introduced, it is in wide use, although he does not always have deep meaning. In this case "inverse population density" is more preferable.

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OBTAINING "NEGATIVE" TEMPERATURES DURING REVERSIBLE PHOTOCHEMICAL REACTIONS

M. G. Kuz'min

One of the existing methods of creating "negative" absolute temperatures consists of optical excitation of substances having several excited levels. The substance does not change its own chemical structure and only passes through a series of excited energy states.

However, it is easy to obtain a system with "negative temperature" with help of optical excitation if we use the difference in the chemical properties of the ground and excited states. Let us consider the equilibrium system:

$$A \rightleftarrows B \qquad K = \frac{[B]}{[A]}; \qquad (1)$$
$$A^* \rightleftarrows B^* \qquad K^* = \frac{[B^*]}{[A^*]};$$

where K and K^* are the respective equilibrium constants. In many cases the constant K and K^* differ by several orders. By changing the conditions (medium, pH and so forth) it is possible to select the constants such that $K \ll 1$, and $K^* > 1$. Then, at a sufficiently great (as compared to the effective lifetime of the excited state τ) rate of establishing equilibria (1), a large part of the unexcited molecules will be in form A, and the excited, in form B^*:

$$[B] = K[A] \quad [B^*] = K^*[A^*].$$

At a rate of photochemical excitation W and quantum yield φ

$$[B] \approx [A^*] + [B^*] = W\tau\varphi.$$

Then, to produce "negative temperature" with respect to the transition $B \rightleftarrows B^*$ it is necessary that

$$[B^*] > [B], \text{ i.e., } W\tau\varphi > K[A], \text{ or } W > \frac{K[A]}{\tau\varphi}.$$

To create "negative temperatures" by this method the fast reactions of dissociation into ions, recombination of ions, isomerization, dimerization, polymerization, compounding-detachment and oxidation-reduction can be useful. Especially convenient are organic luminescent compounds since, by modifying their structure it is almost always possible to select the necessary parameters.

As an example we will consider the reaction of electrolytic dissociation. The dissociation rates and constants of certain organic compounds in aqueous solutions are known. In the singlet excited state the dissociation constants are increased by 5-7 orders (for instance, for α-naphtol pK = 9.23, and pK^* = 2). Calculations show that to produce "negative temperature" in aqueous solutions of such compounds (for α-naphtol $C \approx 10^{-4}$ mole/1, pH = 4) the easily attainable (especially in the pulses regime) rate of excitation $W \approx 10^{20}$ molecules/cm^3·sec is sufficient. We should note that the absorption and emission spectra A, A^* and B, B^* essentially differ from each other. The difference in the frequencies of luminescence maxima is equal to

$$\nu_A - \nu_B = \frac{\ln K^* - \ln K}{hRT}.$$

Let us now consider the question of the possibility of the realization of amplification and generation of light in such systems. Obviously, for this it is necessary that the optical density of the system

$$D_\lambda = l\Sigma\varepsilon_i C_i = \ln\frac{I_0}{I} < 0,$$

here l is the thickness of the sample; C_i is the concentration; ε_i is the coefficient of absorption by substance i of light with wavelength λ; I_0 is the intensity of incoming, and I, of outgoing light. For many organic compounds the forces of oscillators of singlet-singlet transitions are very great ($\tau_{\text{излучат}} \approx 10^{-8}$ sec, $\gamma = 10^{-2}$ cm^{-1}). Therefore, even in liquid solutions, in spite of the large width of the spectral bands ($\Gamma \approx 10^3 \text{см}^{-1}$), the coefficients of absorption are sufficiently great ($\varepsilon \approx 10^5$ l/mole·cm). The coefficient of forced emission B^* is equal to the coefficient of absorption ε_B; ε_A at the frequency of the emission maximum B^*, ε_A is sufficiently small. Then, in the absence of absorption by excited molecules

$$(\varepsilon_{B^*} < \varepsilon_B) — W > \frac{K[A]}{\tau\varphi}.$$

$$D \approx -\varepsilon_B W_0 \tau \varphi l.$$

For the typical case $D \approx -10^{-23} W$. At the attainable in the pulsed regime $W = 10^{21}$ molecules/cm^3·sec, $D = -0.01$, i.e., the amplification factor $\frac{I - I_0}{I_0} = 2.3\%$. If we place the sample between parallel mirrors (Fabry-Pero interferometer), with losses in the optical system smaller than this magnitude self-excitation and generation of light will be observed.

The presented principle makes possible a wide selection of various systems for the creation of a four-level quantum generator profitably differing by the lack of the necessity to convert a larger part of the initial molecules into the excited state. A change in the structure of the utilized compounds and the introduction of different substituents permit us to select a substance with practically any emission spectrum, from the infrared to the ultraviolet region.

Discussion

V. L. Yermolayev. How do you plan to study the absorption spectrum of excited molecules; this is obviously impossible?

M. G. Kuz'min. For singlet excited states it is indeed impossible to determine the absorption spectrum experimentally, but this is not necessary. The absorption spectra of triplet states are easily determined with the help of pulse photolysis.

V. L. Yermolayev. How does the offered diagram differ from the usual diagram of fluorescence of complex organic molecules? I see no difference. For complex organic molecules the high oscillatory levels to which the molecule passes during fluorescence are also strongly impoverished. In my opinion, this idea was already offered.

M. G. Kuz'min. This is the diagram of usual fluorescence of complex molecules, when isomerization or some other chemical reaction of particle occurs in the excited state. I suggested using this diagram for quantum generators.

V. V. Voyevodskiy. You said that removal from the lower level B with respect to the equilibrium $B \rightleftarrows A$ is ensured with a sufficiently high rate. The time of removal should be on the order of 10^{-7} sec or less. You suggest recombination of ions. The times for recombination of ions are determined not only by the constant, which is sufficiently great, but also by the concentration of secondary ions. What calculations can you give?

M. G. Kuz'min. A time of removal of about 10^{-9} sec is ensured.

DECISION OF THE SYMPOSIUM ON ELEMENTARY PROCESSES OF HIGH-ENERGY CHEMISTRY

Taken at the concluding session of the
Symposium, 22 March 1963.

The symposium on elementary processes of high energy chemistry (radiation chemistry, plasma chemistry, photochemistry, chemistry of the ionosphere, cosmochemistry, and of high-temperature chemistry) took place in Moscow on 18-22 March 1963, prepared by these scientific councils: on the use of atomic energy in chemistry of the OKhN of the Academy of Sciences of the USSR; on the theory of chemical structure, kinetics, reactivity and catalysis of the OKhN of the Academy of Sciences of the USSR; on complex problem of "High-temperature thermophysics" of the Academy of Sciences of the USSR.

Scientists of 59 organizations from 11 cities of the Union participated in the work of the symposium. In all, 495 scientists participated in the sessions of the symposium. Sixty reports were heard and there were more than 120 appearances in debate. The program of the symposium was prepared by preliminary correspondence with 100 scientists working in the specified regions. Besides the program of reports, in this a list of 134 specific questions was prepared for discussion and clarification at the symposium. Many of these questions were discussed and new data were presented. The following problems were subjected to especially detailed discussion:

1) the mechanism of disintegration of molecule during electron bombardment;

2) the role of ionic-molecular reactions in processes occurring in the ionosphere of Earth;

3) the role of energy and charge transfer in all regions of high-energy chemistry.

4) the kinetics and mechanism of accumulation of free radicals and ions under radiations on solids.

One of the ten sessions was specially dedicated to the processes in quantum light generators.

Many scientists participated in discussing these problems.

On one of the discussed problems, the mechanism of excitation transfer during radiolysis and photolysis of condensed systems, a group from competent scientists prepared specific conclusions from the discussions and recommendations for further works in this region.

The participants of symposium consider the exchange of mutual information and systematic investigations in the region of elementary processes and the mechanism of transformations in high-energy chemistry exceptionally useful and they emphasize the great generality of many types of elementary processes for many regions of high-energy chemistry. Just this generality makes their joint consideration useful.

The symposium considers the rapid publication of the materials of the symposium necessary with a circulation of at least 3000 copies.

To strengthen mutual communication and exchange of information the symposium considers it necessary to carry out the following measures:

1. To conduct symposia on the elementary processes of high-energy chemistry regularly two or three times a year.

2. To conduct, during the next two years, a conference restricted to the problem of energy transfer, considering the interests of biologists and scientists studying the utilization of solar energy.

3. To ask the Presidium of Academy of Sciences of USSR to consider creating a journal to publish work on chemical the mechanism and elementary processes of radiation chemistry, photochemistry, plasma chemistry, high-temperature chemistry, of the chemistry of the ionosphere. The creation of such a journal will allow, in the opinion of the participants of the symposium, to lift level the state of the theory in these regions to a considerably higher level and it would have huge practical value. The name of the symposium, "High-Energy Chemistry" could serve as a tentative name for this journal.

The participants of the symposium ask scientific organizations in which work on elementary processes of high-energy chemistry is conducted to more widely invite the scientists working in regions adjacent to high-energy chemistry to their seminars and meetings.

The participants of the symposium consider it expedient:

to conduct experiments to clarify the mechanisms of the processes of energy transfer in super-pure substances;

to conduct in various laboratories exact measurements of the limiting concentrations of free radicals stored in organic substances under the effect of radiation.

Symposium turns to the Council on physics chemical methods of investigation and instruments with a call to consider improving the technical base of experiments (especially the [EPR] (ЭПР), [YaMR] (ЯМР), mass, and optical spectrometers).

Participants of symposium express gratitude to the scientific councils for the initiative that made it possible to carry out this symposium.