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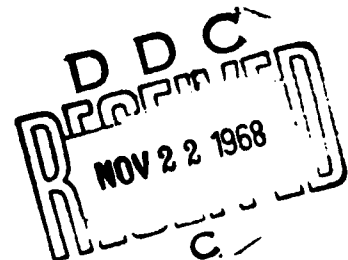
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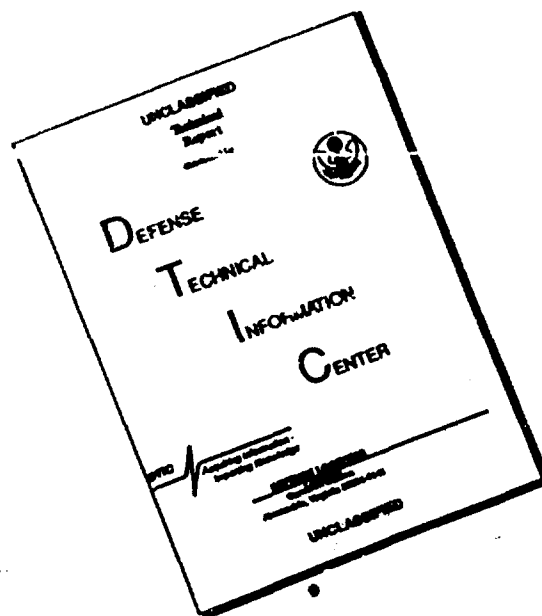
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## CHEMILUMINESCENCE IN SOLUTIONS

Uspakhi Fizicheskikh Nauk  
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R. F. Vasil'yev

### I. INTRODUCTION

Chemiluminescence is one of the least studied aspects of luminescence. "There can be no doubt," wrote S. I. Vavilov in 1932, "that the excitation of molecules or atoms, which is accompanied by chemiluminescence occurs as a result of the chemical energy released, however in no case is the mechanism of excitation in chemiluminescence precisely known." [5b]

Has the situation changed since the time when these words were written? For the past 20-30 years, thanks to the works of V. N. Kondrat'yev, A. N. Terenin, M. Polyani, and others great advances were made in the study of chemiluminescence in gaseous reactions\*). In liquid-phase reactions the luminescence mechanism has been investigated considerably less. However, interest in this phenomenon has grown considerably recently due to the fact that weak luminescence was discovered in various biological and chemical systems.

The purpose of the present work is to give a synopsis of the present condition of research of the mechanism of chemiluminescence and to discuss future developments in this field of physical chemistry. The

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\*) Investigation of the luminescence of gaseous reactions, particularly ignition, is a vast field of physical chemistry with clearly defined basic principles rich in experimental material and with usefully important applications [32, 49, 50, 115]. An examination of the gaseous phase of chemiluminescence goes beyond the scope of this review, but we shall refer to examples from this field in order to explain a series of principal peculiarities of chemiluminescence.

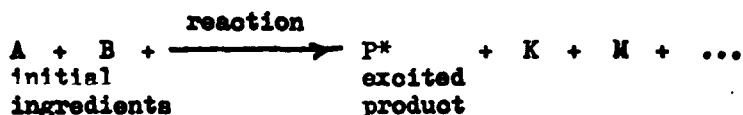
synopsis is concerned with liquid-phase systems, but the other aspects of chemiluminescence are briefly touched upon in it.

### 1. General Mechanism of the Phenomenon

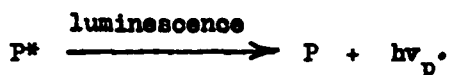
Chemiluminescence appears as superbalanced radiation, the intensity of which exceeds the intensity of thermal radiation. Deviation from equilibrium is caused by chemical reaction.

The chemiluminescence process may be separated into two stages:

1) The excitation stage — the formation in chemical reaction of abundant energy of particles (products of the reaction P) in such state ( $P^*$ ) from which a radiation shift is possible:



2) The luminescence stage:



Experimentally determined values — intensity of luminescence and speed of reaction — are connected with the equation

$$I = \eta_p \eta_p^{\text{excited}} w; \quad (1)$$

here the speed of reaction  $w$  is the number of molecules of the product formed in unit time in a unit volume; the quantum yield of excitation  $\eta_p^{\text{excited}}$  is the ratio of the number of excited molecules of the product to the overall number of molecules formed; the quantum yield of luminescence  $\eta_p$  is the ratio of the number of molecules  $P^*$ , which give off energy in the form of radiation to the overall number of excited molecules; the intensity of chemiluminescence  $I$  is the number of photons which radiate from unit volume of the reacting mixture for unit time.

The overall yield of chemiluminescence  $\eta_{\text{chl}} = \eta_p \eta_p^{\text{excited}}$  for various reactions differs over a wide range: from several per cent (for a small number of reactions) up to  $10^{-8}$  —  $10^{-10}$  and even  $10^{-15}$ .

Low yields of chemiluminescence are not surprising and they can be understood if the peculiarities of radiation are considered in their

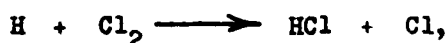
overall aspect.

Chemiluminescence is an unbalanced process. Deactivation of abundant surplus energy from the products of reaction proceeds intensively in the zone of chemical reaction. The reverse process — the accumulation of the energy of several elementary events in one particle — appears as a scarcely probable occurrence (especially in the liquid phase). Energy numerically equal to the sum of the thermal effect and the energy of activation of the reaction may be converted into excitation (Figure 1); therefore chemiluminescence should be observed in that spectrum range which corresponds to the energy of excitation or longer wave lengths.

Limitations, dictated by the law of conservation of energy, are not unique for chemiluminescence reactions. The law of conservation of the multiplicity of a system (Wigner's Law) must be observed in elementary chemical reactions which may be formulated by the following example: if the initial and final conditions of the system do not have identical values of the total spin quantum number, the exchanges between such conditions must be extremely improbable; other elementary processes for which, in the initial and final states, the resulting spins are identical [50,115]. A change in total spin may be one of the reasons for low emission of chemiluminescence.

Another reason may be the flow of processes which are competing with the luminescence of excited molecules: deactivation by suppressors, transfer of energy and internal deactivation. These processes make possible the establishment of equilibrium with the surrounding medium. It is true that equilibrium is not identically rapid for all states of freedom. In the general case, electron and circulation temperatures appear to vary and exceed the temperature of the experiment although, for each aspect of movement, there may be a Bol'tsmanovskiy distribution.

These peculiarities of chemiluminescence are manifested particularly clearly in gaseous phase reactions. For instance, in the exothermic reactions



infra-red chemiluminescence is observed which corresponds to shifts in the oscillating levels of HCl. The distribution of HCl by levels of the basic electron state was a Bol'tsmanovskiy one at a pressure of 0.2 mm standard mercury [92], however at  $10^{-2}$  mm of standard mercury a decided non-Bol'tsmanovskiy distribution was observed [93]. It is apparent that various oscillating states are created with a correspondingly different speed which increases with a drop in level. Collisions equalize distribution and make it a Bol'tsmanovskiy one. The experimental fact, which

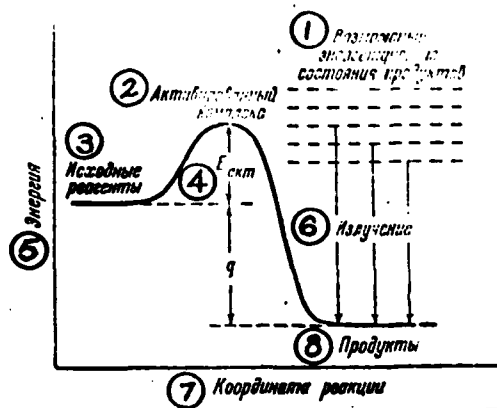


Figure 1. Diagram of the origin of luminescence in an exothermic reaction.

$E_{\text{event}}$  is the activation energy;  $q$  is the thermal effect.

Key: 1. Possible energy states of products; 2. Activated complex; 3. Initial reagents; 4.  $E_{\text{event}}$ ; 5. Energy; 6. Radiation; 7. Reaction coordinate; 8. Products.

is explained by this is very curious at first glance: at a high pressure much higher oscillating levels (up to  $v = 9$ ) are present than at a low pressure (only up to  $v = 4$ ).

In the example shown the change in oscillating energy due to collisions proceeds more rapidly than conversion of oscillating energy into progressive and circulating. Therefore the overall supply of oscillating energy hardly decreases during the lifetime of the excited state, and at a pressure of 0.2 mm of standard mercury the oscillating temperature turns out to be 2700°K; the intensity of chemiluminescence correspondingly exceeds equilibrium.

In the liquid phase, due to the great frequency of collisions, the oscillation excitation is very quickly dissipated and the circulating structure is absent. Probably, therefore namely cases of purely oscillation shifts in the presence of chemiluminescence in solutions were unknown before when spectra of chemiluminescence were obtained and interpreted and they appeared as electron spectra of emissions of reaction products (see below).

Thus, chemiluminescence appears to be a fairly complicated

phenomenon which is determined, on the one hand, by the kinetics and mechanics of a chemical reaction, and on the other, by luminescences and secondary physical processes in which excited molecules take part.

These questions are, respectively, subjects of research in chemical kinetics and the study of luminescence. Besides that, in order to study the rules of chemiluminescence which is often very weak it is necessary to employ sensitive light-measuring apparatus.

## 2. Brief Historical Outline

Chemical kinetics and the study of luminescence is a young science which was developed in the second quarter of the XX century. The same may be said of light-measuring techniques: it was literally in the last decade that convenient and sensitive detectors and recording circuits were developed.

It is therefore not surprising that essential progress in the study of the phenomenon was realized only in recent times, although the research of chemiluminescence has a history going back many centuries, on which we shall pause briefly (See also works [63, 103]).

Chemiluminescence in living nature, or bioluminescence (the glowing of fish, worms, insects, mollusks, mushrooms and rotting wood) held the attention of the scientists of the ancient world. The first references to bioluminescence are encountered in the works of Aristotle, and in greater detail in the descriptions of Pliny.

Medieval scientists were greatly interested in bioluminescence. Strange as it may seem, they were pursuing crudely practical goals — to develop sources of light to light streets, ships and especially powder magazines (explosion-proof!). They also tried ways of preserving living organisms in order that they could cause them to glow once more at any moment. They, naturally were unsuccessful in these attempts.

Robert Boyle was the first to develop a scientific approach to the phenomenon in modern times. He first established the fact of the stimulating effect of oxygen on chemiluminescence and came close to the notion of bioluminescence as a phenomenon that accompanied the process of slow oxidation. Boyle also investigated the glowing of phosphorus in detail. This research must be considered the first work on chemiluminescence itself — before that they studied only the glowing of living organisms or preparations obtained from them.

In the XVIII and XIX centuries many scientists were occupied in the research of chemiluminescence at one or another stage, including Reaumur, Lavy, Pel'tio, Becquerel, V. V. Petrov, Dewar, and at the beginning of the XX century — Trauts, P. P. Shorygin, Harvey and Lommel'.

By the third decade of the XX century a significant number of substances were already well-known which were able to give off comparatively intense glow in definite reactions, principally oxidation reactions with strong oxidizers, as well as oxygen. The high intensity of luminescence in these reactions were either connected with the high speed of the processes or with a high yield. Obviously, these conditions were not fulfilled in reactions proceeding at moderate temperatures (low speeds) forming products incapable of effectively glowing (low yields). One may expect, therefore, that many reactions will be accompanied not by intense, but slightly intense chemiluminescences.

The question of the broad extent of chemiluminescence has arisen each time new experimental capabilities have appeared. At the beginning of the XX century Trautz and Shorygin [151, 152] published voluminous research in which a great quantity of reactions of inorganic and organic compounds were enumerated, which were accompanied by chemiluminescences; luminescence was observed by the adapted eye. After a while, a photographic method \*) was introduced into the practice of researching chemiluminescence, however it was employed on reactions with more or less intense luminescence.

New confirmation of the broad extent of chemiluminescence was obtained in the works of Rene Audubert and his colleagues [55, 80, 81] who, with the aid of Geiger-Mueller counters, discovered an unusually weak ultra-violet emission from many reactions.

Toward the end of the Thirties Audubert finished research on chemiluminescence. One of his last works in chemiluminescence was closed with the words: "In the present situation of an unusually unfavorable and difficult method in terms of technique it is not surprising that the results obtained, for the present, are not very great. But advances in the technique of photoelectric counters will give, it must be hoped, possibilities to widely used the method which has already led to so many interesting results." [55]

In recent years photoelectron amplifiers have become more widely available. Their application has made it immediately possible to discover luminescence in many chemical reactions. These works were begun in 1958 in the Institute of Physical Chemistry of the Academy of Sciences of the USSR [7], and in 1960-1962 in Canada [108], Sweden [76], the United States [79], and the Federal Republic of Germany [142].

Luminescence in the visible range of the spectrum was registered in the following reactions:

- 1) the formation of hydrocarbons [6];

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\*) One of the first to use the photographic method was A. A. Greenberg [35] who investigated the oxidation of pyrogallol.

- 2) thermal decomposition of peroxides, hydroperoxides and azo-compounds in solutions [77];
- 3) thermal decomposition and oxidation in the gaseous phase of peroxides, hydroperoxides, alkyl iodides, alkyl nitrites, nitric acid, nitromethane, acetaldehyde [10, 71] and ethyl hyponitrite [108];
- 4) electrolysis of ethanol, acetic acid, potassium acetate [10, 71], sodium salts of acetic, propionic, citric and tartaric acids, Grignard reagents, amino acids and a number of other organic compounds [76];
- 5) oxidation by oxygen of hydrocarbons and other organic compounds in solutions [11, 43];
- 6) condensation of chloranhydrides of acids with amines, polycondensation (reaction yielding nylon) [73];
- 7) oxidation destruction of polypropylene and other polymers [79, 134];
- 8) oxidation of urea by cyanohalides [142], and others.

Thus, chemiluminescence was discovered in a great number of reactions of the most varied classes and types. Inasmuch as luminescence was observed also in the most important industrial reactions (oxidation, decomposition and poly-condensation) it is possible in principle, on the basis of photoelectric measurement of chemiluminescence, to create a method of constant automatic control and regulation of technical chemical processes [72].

## II. THE CHEMILUMINESCENCE MECHANISM

### 3. Oxidation of Luminol and Related Compounds

The intense glow of luminol was first observed by Albrecht [77] in 1928.

Chemiluminescence of luminol and related compounds had been studied, as a rule, in a complex mixture which consisted of water (the solvent), potassium and sodium hydroxide, hydrogen peroxide, a hydrazide and an "activating agent" of a strong oxidizer of the sodium hypochlorite type, or potassium ferricyanide, or even a metal having an alternative valence [62, 63].

The group that is capable of reacting is diacylhydrazine  $-O-NH-NH-O-$ . Substitutions in positions 3 and 4 are not touched by the reaction; they generally influence the stage of radiation in which an approximately identical reaction capability is evident (speed of oxidation) for hydrazides, and are even sharply separated according to luminescent intensity [57b, 96, 158].

Luminescence is reinforced with addition to the system of substances that decompose into free radicals (initiators) [87]. On the other hand, the introduction of compounds which intercept the radicals

(inhibitors), weakens chemiluminescence [87, 141, 149, 153]. These facts are treated as indications of the participation of free radicals in the reaction. From this point of view, the catalyzer necessary for luminescence aids the decomposition of hydrogen peroxide, or even any other intermediate reagent, into radicals. A. K. Babko [1, 2], using a physical chemical analysis method, has shown that luminol forms complexes with catalyzers (copper salts), which are active components of the excitation process, because they emit a fairly brighter light on reaction with  $H_2O_2$  than luminol itself. Besides, copper serves as an unusual catalyzer; taking part one time in the oxidation process it leaves the sphere of reaction (possibly joining in a complex with oxidation products). The study of chemiluminescence is made extremely difficult by the complexity and intricacy of the chemical mechanism.

Just the same, important data on the luminescence mechanism of luminol have been obtained in most recent years.

Selinger [138], once more has carried out careful comparisons of yields of chemiluminescence and fluorescence spectra for individual components of the system. He has obtained the following results:

1. The maximum chemiluminescence yield (at a pH of 11) is 0.02 photons per oxidized molecule of luminol.
2. The chemiluminescence yield depends on pH just like the fluorescence yield in luminol.

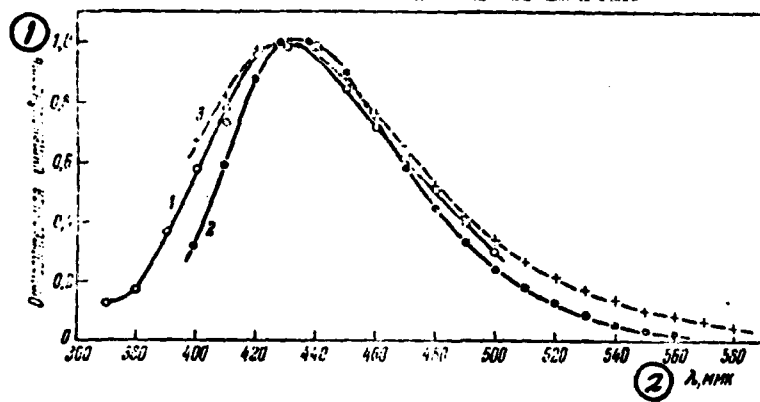


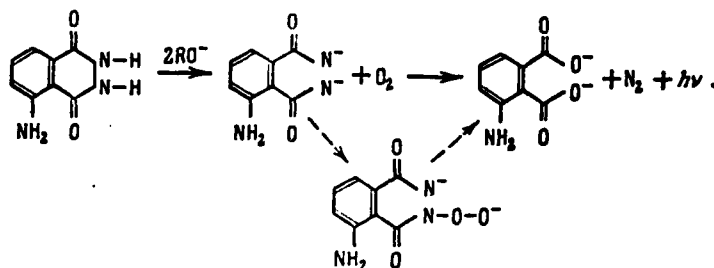
Figure 2. Spectrum of luminol chemiluminescence in an alkaline medium (1) and the spectra of luminol fluorescence in an acid medium (2) and of aminophthalic acid in an alkaline medium (3).

Key: 1. Relative intensity; 2.  $\lambda$ , in millimicrons.

3. The fluorescence spectrum of the acid is identical to the chemiluminescence spectrum. The luminol fluorescence spectrum also agrees with the chemiluminescence spectrum (Figure 2).

These and a series of other results point out the fact that aminophthalic acid serves as a chemiluminescence emitter.

Not long ago, White [154-156] pointed out that, in strongly polarized and weakly acid solutions (for instance, di-methyl sulfoxide and di-methyl formamide), only luminol, oxygen and a base are necessary for luminescence. The intensity of di-methyl sulfoxide is significantly higher than in water (quantum yield 0.1). The comparative simplicity of the chemical system has made it possible to investigate the mechanism of reaction and luminescence. Nitrogen and the aminophthalate-ion (up to 90%) were found in the products. Apparently the latter is also a product of the state in which energy is released and excitation occurs. On the whole, the mechanism of luminol chemiluminescence can be represented by the following diagram, according to White:

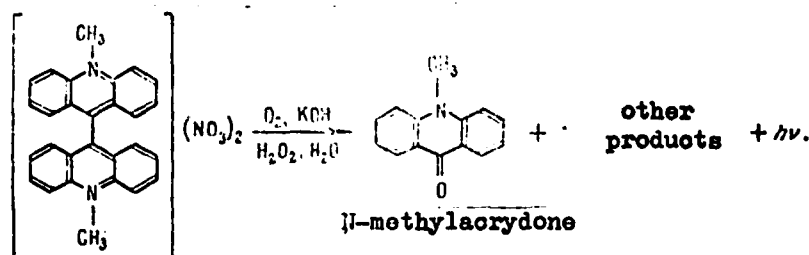


Still another possible path of the reaction is shown by the dotted line — through an intermediate ion of hydrogen peroxide. The energy effect of the reaction is approximately 90 large calories/mol. Basically, exothermy is involved in the formation of nitrogen molecules and therefore, the emitter is excited faster than ever in the state where nitrogen is formed. From this point of view, it is very probable that the excitation in the reaction is precisely the phthalate-ion.

The descriptions of Seliger and White were confirmed not long ago in the study of luminol chemiluminescence stimulated by electrolysis [114].

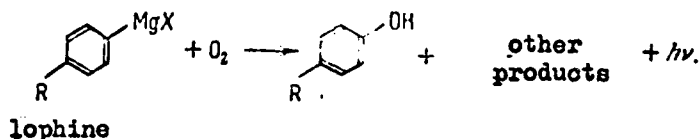
As yet, other clearly luminescent reactions have been studied considerably less than the oxidation of luminol.

The following is considered to be the most probable diagram in the oxidation of lucygenine [154]:

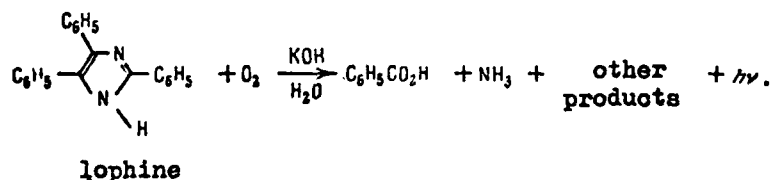


A. V. Karyakin [48] has shown that the chemiluminescence spectra for lucygenine and several of its analogs agree with their phosphorescence spectra and, consequently, triplet states of molecules may be excited.

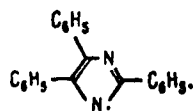
High intensity during the oxidation of Grignard reagents is connected solely to the great speed of reaction; the luminescence yield is lower and is approximately  $10^{-8}$  photons per molecule. The reaction proceeds at a uniform rate from +17 to  $-40^\circ\text{C}$  and it is possible to determine the speed of diffusion of  $\text{O}_2$  [87]. In general, the chemiluminescence diagram may be given in the following form [14]:



For chemiluminescence in the oxidation of lophine (2, 4, 5-triphenylimide azole) by hydrogen peroxide diagram [154] is given



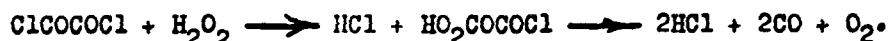
However, not long ago, the application of EPR (Elektronnyy Paramagnitnyy Rezonans; Electron Paramagnetic Resonance) in spectroscopic methods and the discovery of nitroso compounds has shown that, in the reaction, a free radical of 2, 4, 5-triphenylimidazyl is formed [104]:



Analogous data were obtained for the chemiluminescence of 2, 3, 4, 5-tetra-phenylpyrrole, a substance similar to lophine [104] in structure. It is possible that peroxide reactions are responsible for luminescence in these reactions, products of the interaction of radicals with oxygen. In a sample of 14 derivatives of lophine a clear connection has been demonstrated of chemiluminescence with chemical activity of the compounds: the logarithm of comparative intensity is linearly connected with the Khammet sigma-parameter which characterizes its reaction capability [126].

Chemiluminescence during oxidation by hydrogen peroxide in an alkaline solution of pyrogallol  $C_6H_3(OH)_3$  was concentrated in a narrow band of 630 millimicrons [86]. Apparently this is radiation from a complex of two molecules of  $O_2$  in  $\Delta_g$  states (See Article 6). Chemiluminescence of pyrogallol is reinforced by the fermenting of peroxidase [123].

A bluish-white chemiluminescence accompanies the oxidation of oxalyl chloride by hydrogen peroxide [91]:



The thermal effect of the reaction (70 large calories per mole) is sufficient for the emergence of luminescence in the visible region, however none of the products have adequate excitation levels. It is possible that a third particle is an emitter to which energy is transferred; for instance, non-reacted oxalyl chloride may be such a particle.

#### 4. Thermal Decomposition

In 1958 luminescence was discovered in the decomposition of peroxides, hydroperoxides and azo-compounds in solutions at 50-100°C [7].

Chemiluminescence was extremely weak and a highly sensitive photometric apparatus was assembled to measure it [9]. Further improvement in method led to the building of apparatus [23] (Figure 3) which is also used in investigating hydrocarbon oxidation reactions (See Article 5.).

Reaction occurs in vessel C which is warmed by water from the thermostat. The light from luminescence, passing through a light guide (polished glass or quartz blocks) SP, falls on the photoamplifier FEU<sub>1</sub>. The photocurrent is reinforced and recorded on a self-recorder. In recording the luminescence spectrum the light goes through a powerful light spectrometer and is focused by a condensing lens KL and the light guide SP on the photocathode of the photoamplifier FEU<sub>2</sub>. Scanning is accomplished by the rotation of a defraction grating. Spectra of photoluminescence may also be recorded on the apparatus. For this,

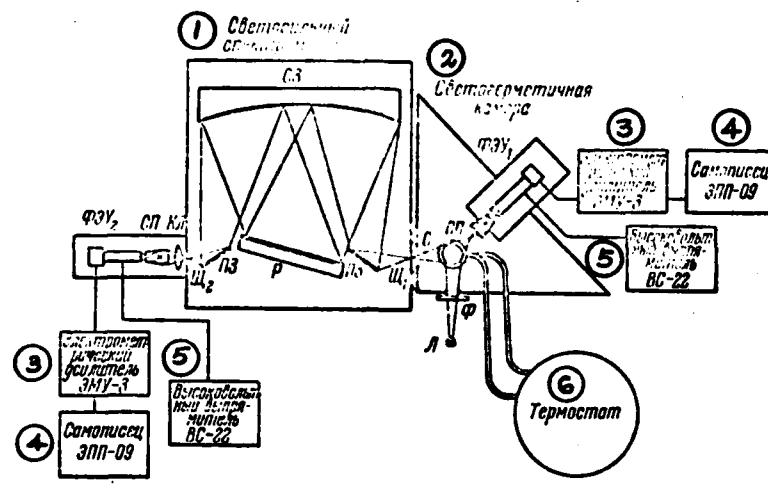


Figure 3. Diagram of apparatus for investigating chemiluminescence.

Key: 1. Light-powered spectrometer; 2. Light-tight chamber; 3. Electro-metric amplifier, EMU-3; 4. Self-recorder, EPP-09; 5. High-voltage rectifier, VS-22; 6. Thermostat.

the vessel C is lit up by a mercury lamp L through a light filter  $\phi$ . In the spectrometer [17] a replica is used of a defraction grating  $150 \times 140 \text{ mm}^2$  in size which has 600 lines per mm. The focal length of the objective, a spherical reflector, is 300 mm, candlepower is 1:1.5, height of slits is 70 mm. Due to the curved slits the spectrometer resolves, with 0.5 mm slits (spectral width of slit 1 millimicron), lines spaced two millimicrons apart. The high sensitivity of the photoamplifier is attained by its separation and cooling to minus  $50-60^\circ\text{C}$ . Sensitivity to total radiation (without decomposition in the spectrum) is 50 photons per second on the surface of the photocathode at a fixed time for the amplifier of 20-30 seconds under the most favorable conditions.

In thermal decomposition chemiluminescence is concentrated in the blue region of the spectrum. Luminescence intensity is proportional to the concentration of the decomposed substance and grows with temperature according to the law

$$I \sim \exp \left( - \frac{E}{RT} \right) \quad (2)$$

(Figure 4) wherein the parameter  $E$  agrees with the activation energy of decomposition of the compounds investigated [7, 10, 73]. These peculiarities point out the fact that excitation occurs during the recombination of radicals. Actually, the first event in decomposition of peroxides, hydroperoxides and azo compounds is the breaking of the bonds.

The radicals that are formed in this way may enter into further reaction producing new products and new radicals. At the same time, new collisions of radicals are inescapable and lead to recombination. In these processes considerable energy is given off (90-120 large calories per mole) equivalent to quanta from the visible region of the spectrum.

On the strength of the fixed state (radicals do not accumulate) the destruction speed of radicals,  $w_{rek}$ , is equal to the speed of their formation  $w_i$ :

$$w_{rek} = w_i \quad (3)$$

Radicals appear in the thermal decomposition of a substance Y with a speed of

$$w_i = 2f_{kl}k_0[Y], \quad (4)$$

where  $k_0$  is the speed constant of decomposition,  $f_{kl}$  is the effectiveness, taking into account the possibility of reverse recombination, just as radicals are formed ("exit coefficient from a cell"), the factor 2 reflects the fact that from the decomposition of one molecule two radicals are obtained. Inasmuch as excitation occurs during the recombination of radicals, the intensity of chemiluminescence is proportional to the speed of this process (See Formula (1)):

$$I = \eta_{khl} w_{rek} \quad (5)$$

From equations (3)-(5) it follows that the intensity is proportional  $[Y]$ :

$$I = 2\eta_{khl}f_{kl}k_0[Y]. \quad (5')$$

Further, the constant  $k_0$  may be written in the form of a product of the pre-exponent  $a_0$  and the exponent  $\exp(-E/RT)$ . Whence immediately follows a temperature relationship of chemiluminescence intensity (Formula (2)).

After excluding the recombination of radicals in thermal decomposition, there are no elementary events in which sufficient portions of energy would be isolated. It is true that the overall quantum yield of

chemiluminescence  $k_{hl}$  is very low, no higher than  $10^{-8} - 10^{-10}$  and the question naturally arises: Is not luminescence connected with the flow of some secondary process, the speed of which  $w'$  is irrationally smaller in comparison with the speed of the basic reaction, but which proceeds with high yield  $k_{hl}$ , so that the product  $k_{hl} w'$  would not appear to be too small? A good correlation between experimental and theoretical relationships and the possibility of obtaining correct activation energy show that the answer to the question must be in the negative.

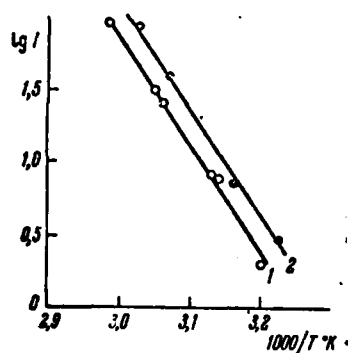


Figure 4. Ratio of the logarithm of luminescence intensity to inverted temperature during the decomposition of azo-bis-isobutyronitril in ethyl benzole (1) and di-acetyl peroxide in chlorbenzole (2).

At the same time, one may expect that, in some cases, the secondary processes of a type which has been mentioned above, may complicate the phenomenon. Thus, during the decomposition of difficult-to-analyze organic hydroperoxides [85] it is impossible to obtain clear quantitative rules.

The decomposition of peroxides is accelerated by catalyzers — metal salts of alternative valence (copper, zinc and cobalt). Intensity in these cases is comparatively high because the recombination speed of the radicals is high [42-44]. Whereas complex crystalline metal compounds serve as catalyzers — porphyrins and chlorophyll, the chemiluminescence spectra agree with the crystal fluorescence spectra [113, 116, 117].

Thermal decomposition of hydrogen peroxide in water also is accompanied by chemiluminescence, the intensity of which is proportional

to the speed of decomposition [57]. In distinction from the above mentioned cases this reaction proceeds by an ion mechanism; excitation, apparently, occurs during the act of decomposition of the complex formed from the  $H_2O_2$  molecule and the ion-radical  $HO_2^{\cdot-}$ .

#### 5. Oxidation by molecular oxygen in organic solvents

The intensity of chemiluminescence in the oxidation of hydrocarbons and their products is at least on a higher order than in thermal decomposition.

The liquid-phase oxidation of RH hydrocarbons and their products proceeds according to an insured mechanism. At moderate temperatures only the initial stage carries through — the formation of ROOH hydrogen peroxide, which occurs as a consequence of the following elementary acts \*):

1) The origin (initiation) of chains — the appearance of R or  $RO_2$  radicals with a speed of  $w_i$  (I)

2) Chain oxidation:

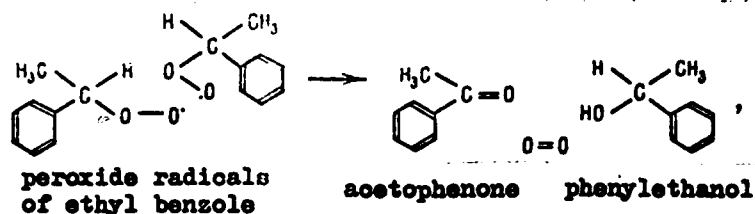


3) Breaking of chains (recombinations of radicals):

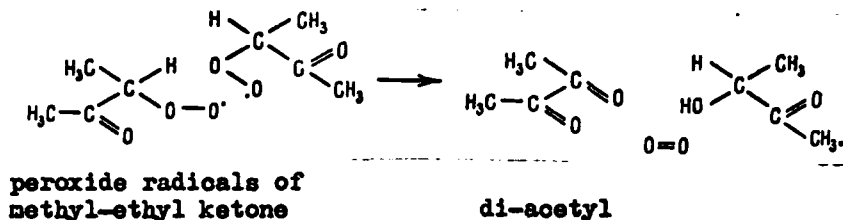


Just as in thermal decomposition, only reactions (IV), (V) and (VI) are sufficiently exothermic. Further, in the presence of a surplus of oxygen, the concentration of peroxide radicals  $RO_2^{\cdot}$  appears to be very much greater than the concentration of  $R^{\cdot}$  hydrocarbon radicals, and actually, reaction (VI) is a unique reaction in which an intermediate complex is formed which decomposes into  $O_2$  and molecular products [131], for instance, for the oxidation of ethyl benzole is a unique recombination reaction:

\*) Concerning the mechanism of liquid-phase oxidation, see for instance, the monograph [4].



for the oxidation of methyl-ethyl ketone:



The recombination of peroxide radicals does not require the energy of activation and the thermal effect, evaluated as the difference of the energies of formation and breaking of bonds which is no less than 100 large calories per mole and is sufficient for luminescence excitation in the visible region.

In a stationary situation the recombination rate is equal to the speed of initiation. If initiation is produced due to decomposition of a specially introduced initiator (Y), the luminescence intensity must depend on the temperature and the concentration Y just as in thermal decomposition reactions. This is carried out experimentally [10, 56] and serves as a confirmation of the recombination nature of excitation.

Recombination of peroxide radicals is amenable also for chemiluminescence which arises due to the action and consequences of thorough radiation in organic compounds [106].

In Figure 5 chemiluminescence spectra are shown in the oxidation of a number of substances [24]. The spectrum of methyl-ethyl ketone is characteristic — the structure is repeated in it which possesses the photoluminescence property of di-acetyl (Figure 5, Curve 4'). The latter is represented as a super state of fluorescence and phosphorescence, the basic path of radiation deactivation — phosphorescence [82, 133] (shift from the triplet condition; Figure 6).

The chemiluminescence spectra of other hydrocarbons are represented as broad, un-structured bands with sloping maxima from 420–450 millimicrons. If it is considered that ketones are excited under these conditions also, then this result is not unexpected: As A. P. Terenin

[65, 67] has pointed out, mono-carbonyl hydrocarbon products possess blue-violet luminescences which are represented as a triplet-singlet shift. However, in view of the absence of individuality of the band form only the spectral identification is not precise. "In solutions," S. I. Vavilov has stated, "the spectra are extremely uncharacteristic and diffused, and do not have thin components. Therefore, solely on the basis of spectra in the usual sense of the word, it is almost impossible to obtain sufficiently profound results. An understanding of the photoluminescence of solutions is markedly facilitated by drawing on other

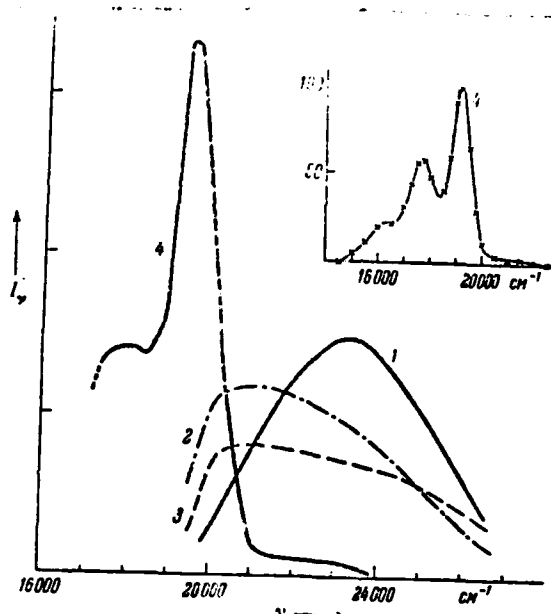


Figure 5. Spectra of ketone radiations excited in oxidation reactions of ethyl benzole (1), cyclohexane (2), n-decane (3) and methyl-ethyl ketone (4) at 60-65°C [24].

Width of entry slit is 7 mm., exit — 2 mm. and with a dispersion of 20 Å/mm. Curve 4' is the photoluminescence spectrum of di-acetyl (according to data from work [76]). Along the ordinate axis is the quantum spectral intensity on a frequency scale (in arbitrary units for each experiment).

optical properties of luminescence: intensity, polarity and persistence [5a]."

The direct determination of the persistence of the excited state (p.e.s.)  $\tau_p$  and the quantum results of radiation  $\eta_p$  during chemiluminescence is possible because, on the one hand, it is impossible to quickly shut off excitation, and on the other, the overall result of luminescence  $\eta_{khl}$  depends not only on the magnitude of  $\eta_p$ , but also on the result of  $\eta_p^{\text{excited}}$  (Compare equation (1)). However, it appears possible to employ direct methods.

P.e.s. was approximated by dampening with oxygen. Oxygen exerts a dual action in chemiluminescence [8]. In the region of low concentrations it reinforces luminescence because it facilitates the transformation of hydrocarbon radicals into peroxides (Reaction II), re-combinations which give a greater glow.  $[RO_2]$  depends approximately on  $[O_2]$  according to law [20]

$$[RO_2] = \sqrt{\frac{w_1}{k_6}} \frac{[O_2]}{[O_2] + s} \quad (6)$$

where

$$s = \frac{k_3}{k_2} \sqrt{\frac{k_4}{k_6}} [RH] + \frac{\sqrt{k_4 w_1}}{k_2}$$

If excited molecules are formed during the recombination of peroxide radicals, the intensity of chemiluminescence is proportional to the speed of that process and (by taking formulas (1) and (6) into account) is defined by the following expression:

$$I = \eta_p \eta_p^{\text{excited}} k_6 [RO_2]^2 = \eta_p \eta_p^{\text{excited}} w_1 \frac{[O_2]^2}{([O_2] + s)^2} \quad (7)$$

Reaction (II) proceeds at great speed ( $k_2$  is high), and already at  $10^{-6}$ - $10^{-5}$  mol/l. of oxygen all the hydrocarbon radicals present in the system are converted into peroxides (i.e.  $[O_2] \gg s$ ) and recombination only occurs with these latter ones. Therefore, a further increase in  $[O_2]$  still should not alter the intensity of luminescence. However, by experiment it appears that, as a rule, oxygen dampens

chemiluminescence in regions of high concentration. This effect is manifest particularly clearly if the solution is saturated with oxygen and the reaction vessel is hermetically sealed. Gradual diffusion of oxygen leads to a weakening of the dampening action and to an increase in intensity (Figure 7a). A marked weakening at the end of the process ("oxygen drop") is noted at the instant of complete disappearance of the oxygen in the solution. The oxygen diffuses at a constant rate [11, 21]

$$w_{O_2} = - \frac{d[O_2]}{dt} = \frac{k_3}{k_6} [RH] \sqrt{w_1} + \frac{1}{2} w_1 \quad (8)$$

Thus, temporary and simultaneous evolution in concentration of oxygen obtains and quantitative investigation of its influence is possible.

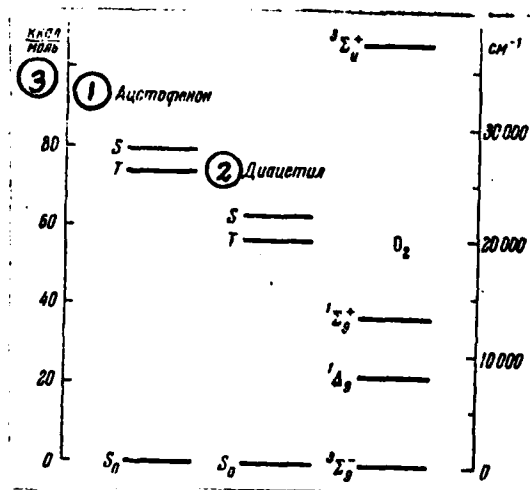


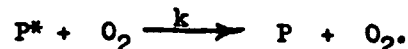
Figure 6. Diagram of the lower electron levels of acetophenone [39], di-acetyl [82] and molecular oxygen [33].

Key: 1. Acetophenone; 2. Di-acetyl; 3. Large cal./mol.

The ratio of intensity to  $[O_2]$  is subject to the Stern-Folmer equation (Figure 7b):

$$\frac{I_0}{I} = 1 + k\tau_p [O_2], \quad (9)$$

where  $\tau_p$  is the persistence of the excited state of the emitter  $P^*$  and  $k$  is the speed constant of the dampening reaction:



P.e.s. is determined with all  $P^*$  deactivation processes:

$$\tau_p = (f_p + d_p + \sum k_{Q_i} [Q_i])^{-1}, \quad (10)$$

where  $f_p$  and  $d_p$  are the probabilities of intra-molecular emission and non-emission exchanges, and  $k_{Q_i}$  are dampening constants with other dampeners  $Q_i$ , which are present in solution. After introduction of corrections the experimental value of  $k_p$ , which is found according to the Stern-Folmer equation, seems to be equal to  $2 \times 10^3$  l/mol. (in the oxidation of ethyl benzole). Assuming that  $k$  has a diffusion value of  $10^9$ - $10^{10}$  l/mol sec. it was found that  $\tau_p = 10^{-7}$ - $10^{-6}$  sec., which is close to the p.e.s of triplet acetophenone,  $3.6 \times 10^{-7}$  sec., obtained under the same conditions during photoluminescence [157].

Particularly strong dampening by oxygen sustains the chemiluminescence of methyl-ethyl ketone [15, 24]. This agrees with the large p.e.s. of this substance — up to  $10^{-3}$  sec. in well-purified solvents [82].

The quantum product of the luminescence of excited particles was determined according to activated chemiluminescence. The introduction of activators (A) into the solution leads to a transfer of energy [15, 16, 19]:



Radiation of the activator follows the transfer of energy:



In this regard, naturally, the spectrum, the product and the p.e.s. characterize the activator molecule and not a primary-excitation particle. For instance, in the addition of products of anthracene and oxazole the spectrum of luminescence becomes identical to the spectrum of fluorescence of activators (Figure 8) and the p.e.s. is shortened so

much that the luminescence dampening effect by oxygen [21] almost disappears ( $\tau_A$  is on the order of  $10^{-8}$  sec. [70]).

As a rule, activators reinforce chemiluminescence [15]. From Figure 9 it follows that the reinforcement action of activators grows with their concentrations according to the law obtained from work [16]:

$$\frac{1}{x-1} = \frac{P}{\eta_A - \eta_P} + \frac{1}{\eta_A - \eta_P} \frac{f_P}{k_{PA}} \frac{1}{[A]}, \quad (11)$$

where  $x$  is the coefficient of reinforcement or the ratio of the intensity of the activator. By means of formula (11), in the well-known fluorescence yield of the activator  $\eta_A$ , a quantum product was found from the radiation of the emitter in the oxidation of ethyl benzole and cyclohexane:  $\eta_P = 5 \times 10^{-4} \pm 60\%$  [25].

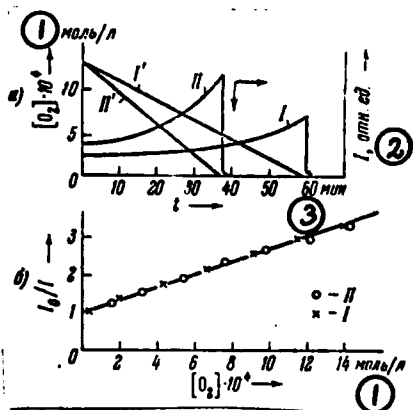


Figure 7. a) Kinetic intensity curves (I, II) and concentration of dissolved oxygen (I', II') in the oxidation of ethyl benzole for two experiments with different reaction speeds. b) Curves I and II were redrawn on coordinates of the Stern-Folmer equation.

Key: 1. Mol/l.; 2. I, in relative units; 3. Min.

The quantum yield and p.e.s. are measured independently. Their ratio should be equal to the probability of the radiation transfer in the product molecule:

$$\frac{\eta_P}{\tau_P} = f_P.$$

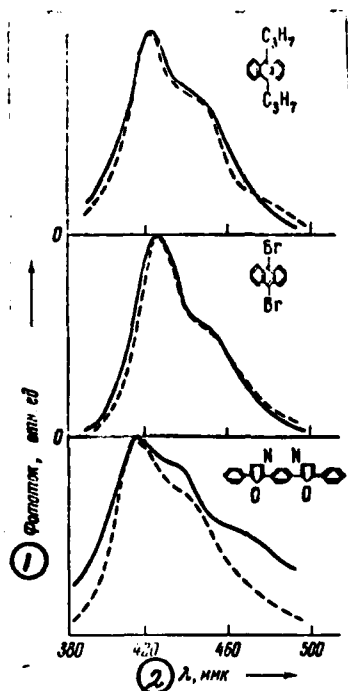


Figure 8. Solid lines are chemiluminescence spectra (oxidation of cyclohexane) activated by lumiphors.

Dotted lines are photoluminescence spectra (fluorescences) of lumiphors recorded on the same equipment.

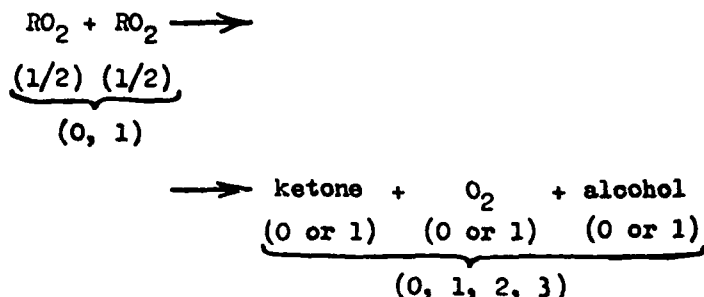
Key: 1. Photocurrent, in relative units; 2. , in millimicrons.

Estimation leads to a value on the order of  $10^3 \text{ sec}^{-1}$  [21] which is typical of the precision of triplet-singlet radiation transfers [39, 40].

A comparison of the quantitative characteristics of an excited particle with spectra and the chemical mechanism of reaction has led to the conclusion that carbonyl compounds in an electron-excited (principally, triplet) state are chemiluminescence emitters in the oxidation of hydrocarbons [21, 24, 25] \*). In the recombination of radicals

\*) In work [21] radiation in the region of 430-450 millimicrons with the oxidation of hydrocarbons is ascribed to an excited molecule

Wigner's law does not superimpose limits on the multiplicity of the products formed, which is easy to note from the level of the reaction.



(the numbers in braces are spin values).

Therefore, the products may be obtained both in the triplet and in the singlet state. That fact that the emitter in the oxidation of ethyl benzole is triplet acetophenone is connected only with rapid conversion from the singlet state to the triplet that is inherent to the substance [39], and apparently both states exist in the reaction. With the oxidation of methyl-ethyl ketone there are observed transfers both from the triplet and from the singlet states (See Figure 5).

The heat of recombination of peroxide radicals is also sufficient for excitation of levels  $^1\Sigma_g^+$  and  $^1\Delta_g$  of molecular oxygen (See Figure 6); its luminescence lies in the infra-red region of the spectrum (shown by means of light filters) [26].

The mechanism of luminescence in the visible region may be represented by the following diagrammatic Table 1 (symbols over the arrows are constants of the process speeds).

From the diagram is obtained the following expression for quantum intensity of chemiluminescence:

$$I = f_P [\overline{P^*}] + f_A [\overline{A^*}] = \{ \eta_P (1 - \eta_{PA}) + \eta_A \eta_{PA} \} \eta_P^{\text{excited}} w_{\text{rek}} \quad (12)$$

where  $w_{\text{rek}} = k_6 [\overline{\text{RO}_2}]^2$  is the speed of recombination of radicals;  $\eta_P = f_P (f_P + d_P + \sum_i k_{Q_i} [\overline{Q_i}])^{-1}$ , the quantum yield of radiation for  $P^*$ ;

of oxygen formed in reaction(VI). This interpretation gives rise to misunderstanding because of the population of the state  $^3\Sigma_u^+$  (106 large cal/mol; see Figure 6) which can give radiation in the visible region, doubtful even with the recombination of O atoms [89] and is hardly possible in comparatively weak reaction conditions (VI).

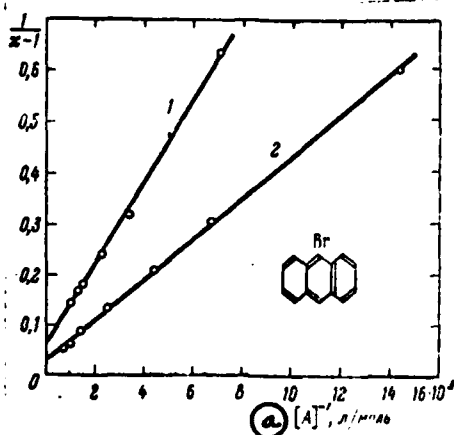


Figure 9. Ratio of the luminescence reinforcement coefficient to the concentration of 9-bromanthracine in the oxidation of ethyl benzole in benzole in equation (11) coordinates.

Initiators: 1. azo-bis-isobutyronitril ( $1.22 \times 10^{-2}$  mol/l) at  $50.0^\circ\text{C}$ ; 2. di-cyclohexylperoxy di-carbonate ( $4.3 \times 10^{-3}$  mol/l) at  $30.0^\circ\text{C}$ .

Key: a.  $[A]^{-1}$ , l/mol.

$\eta_P = f_A(f_A + d_A + \sum k'_i [Q_i])^{-1}$  is the quantum yield of radiation for  $A^*$ ;  
 $\eta_{PA} = k_{PA} [A] (f_P + d_P + \sum kQ_i [Q_i] + k_{PA} [A])^{-1}$  is the probable carry-over of energy.

According to (12) the intensity is proportional to the speed of reaction. However, the coefficient of proportionality depends on the concentrations of dampeners and activators. The role of dampeners, in particular, is played by some initiators, solvents and also reaction products, admixtures and oxidized hydrocarbons themselves [15, 25]. Therefore, the intensity of chemiluminescence often grows, not in proportion to the concentration of the initiators (like that demanded by formulas (3) - (5), but more slowly (Figure 10).

Equation (12) permits quantitative description of the action of the initiator-dampener Y; it is not difficult to obtain from it:

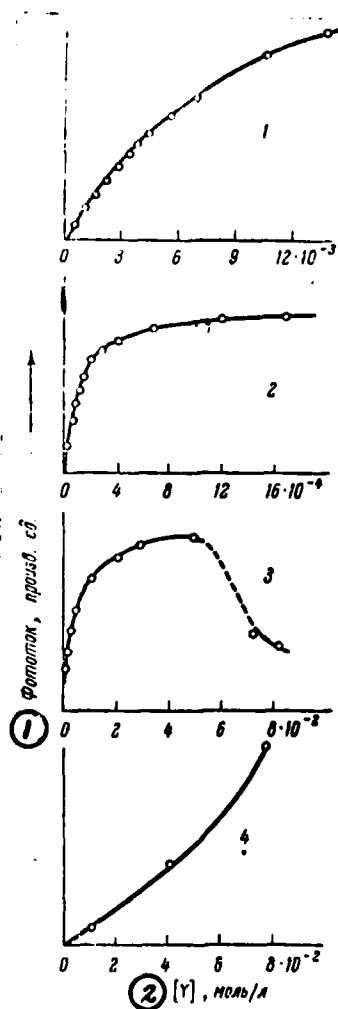


Figure 10. Ratio of luminescence intensity in oxidation reactions to concentration of initiators:  
 di-benzoyl peroxides in ethyl benzole (1); azo-bis-isobutyronitril in a mixture (ethyl benzole + acetic acid) (2) and ethyl benzole (3); di-cyclohexyloxy di-carbonate in a mixture (ethyl benzole + benzole) (4).

Key: 1. Photocurrent, in relative units; 2.  $[Y]$ , in mol/l.

Table I

## Chemiluminescence Mechanism in the Oxidation of (RH) Hydrocarbons in Solution

Process	Equation
Recombination of peroxide radicals with the formation of non-excited ketone	$2RO_2^{\bullet} \xrightarrow{k_6} O_2 + \text{alcohol} + \text{ketone (P)}$
The same with formation of ketone in the triplet state	$2RO_2^{\bullet} \xrightarrow{\eta_P^{\text{excited}} k_6} O_2 + \text{alcohol} + P^*$
Chemiluminescence	$P^* \xrightarrow{f_P} P + h\nu_P$
Internal deactivation $P^*$	$P^* \xrightarrow{d_P} P$
Deactivation $P^*$ by dampeners $Q_1$	$P^* + Q_1 \xrightarrow{k_{Q_1}} P + Q_1$
Carryover of energy of excitation to activator A	$P^* + A \xrightarrow{k_{PA}} P + A^*$
Luminescence of activator (activated luminescence)	$A^* \xrightarrow{f_A} A + h\nu_A$
Deactivation $A^*$	$A^* \xrightarrow{d_A} A$
	$A^* + Q_1 \xrightarrow{k'_{Q_1}} A + Q_1$

$$\frac{[Y]}{I} = \frac{[Y]}{I_0} (1 + k_Y \tau_P [Y]),$$

where  $k_Y$  is the deactivation speed constant with initiator. The relationship is well borne out by experiment (Figure 11). The values of  $k_Y \tau_P$  appear to be on the order of  $10^3$  l/mol, which, with assumption of the diffusion character of dampening ( $k_Y \approx 10^{10}$  l/mol sec.) leads to values of p.e.s. which agree with approximations on dampening by oxygen (on the order of  $10^{-7}$  sec.).

The carry-over of energy to luminescent components ("natural" activators) plays a minor role and is seldom observed. During initiation by di-cyclohexylperoxy di-carbonate the growth in intensity speeds the growth in concentration (Figure 11); it is possible that the initiator which has a C = O group will act as a weak activator [21]. Growth in intensity with time during the decomposition of di-tert-butyl peroxide in chlorbenzole [73] was connected with accumulation of well luminesced products.

Thus, secondary processes may essentially complicate the picture of the phenomenon and this must be borne in mind constantly\*).

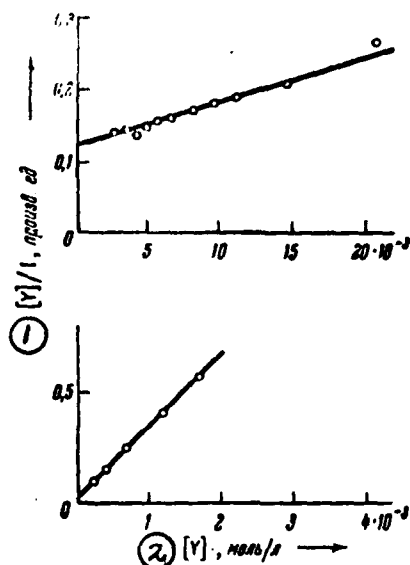


Figure 11. Function of the proportion of concentration of the initiator to the intensity of luminescence from the concentration of initiators for experiments 1 and 2, Figure 10.

Key: 1.  $[Y]/I$ , in arbitrary units; 2.  $[Y]$ , in mol/l.

\* ) The transfer of energy to specially introduced activators also has been observed in clearly luminescent reactions [39, 109, 121, 150]. The possibility of influence by "natural" activators on chemiluminescence in liquid-phase reactions was not considered earlier. The mechanism for the transfer of energy was not investigated.

When the characteristics of chemiluminescence (spectrum, product, p.e.) correspond to a primary excited particle, the carry-over of energy may not be taken into consideration and equation (12) takes on a simple form (1). Simultaneous measurement of absolute intensity and speed of reaction makes it possible to determine the overall quantum yield of chemiluminescence:  $\eta_{khl} = I/w = \eta_p \eta_p^{\text{excited}}$ . This value is small (on the order of  $10^{-10}$  for oxidation of cyclohexane and n-decane,  $10^{-9}$  for ethyl benzole, and  $10^{-7}$  for methyl-ethyl ketone [24]) and is basically determined by excitation yields. The low value of  $\eta_p^{\text{excited}}$  more than ever has been specified by the fact that the energy concentrated on the majority of molecules is insufficient for excitation.

In Figure 12 the distribution of product molecules by oscillation levels is shown qualitatively immediately following reaction and after a time sufficient for establishing equilibrium with the medium, but less than the persistence of the electron-excitation state. The distribution function has a maximum — with an increase in energy the numbers of oscillation levels fall, but density grows due to inharmonicity. For graphic purposes, only one system of oscillation levels is shown.

Whereas one product is formed in the reaction (for instance, in the recombination of hydrocarbon radicals) all of the energy released is concentrated in one molecule in each event (Case a)). The primary distribution is distinct and reflects only the Maxwell-Boltzmann distribution of original reagents (radicals). The probability of excitation may be high if the exothermy of the reaction is greater than the energy of excitation; it is equal to zero if a reverse correlation exists. If some products are formed during recombination (recombination of peroxide radicals) the distribution is more even (Case b)). Although the picture has a qualitative character, it clearly follows that it is difficult to expect great numbers at the level placed at a value of 70-75 large calories/mol, in the presence of heat of 100-120 large calories/mol dispersed among three molecules (alcohol, ketone and oxygen).

The second reason for low yield may be dampening by molecular  $O_2$  which, immediately after reaction, appears in the immediate vicinity of the excited product and may deactivate it.

For ethyl benzole and cyclohexane  $\eta_p^{\text{excited}} = 10^{-6}-10^{-5}$ ; correspondingly the stationary concentration of excited molecules is low — on the order of 10 molecules/cm<sup>3</sup> [24].

The quantum excitation yield has the sense of a formation probability for the products of an exothermic elementary event in a definite energy state. This characteristic is of great interest in the theory

of chemical reactions and for the understanding of processes which control the distribution and over-distribution of energy among products. Those questions have been intensively dealt with that are applicable reactions of simple molecules in the gaseous phase [124, 127, 128]. Applicable work has still not started on reactions in solution. It may be assumed that systematic measurements of yields of excited products of liquid-phase reactions (ketones and oxygen in the oxidation of single-type compounds) will give great value to the theory of elementary reactions in solutions.

#### 6. Oxidation in aqueous solutions.

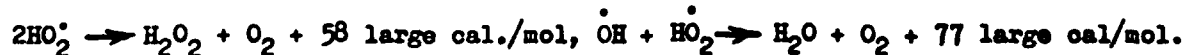
Not long ago Stauff and his colleagues [142-145] investigated weak chemiluminescence in the oxidation of many substances:  $N_2H_4$ ,  $H_2SO_4$ ,  $NaHSO_3$ ,  $K_3Fe(CN)_6$ , urea, gelatins, etc. Hydrogen peroxide, molecular oxygen (as a rule, with a catalyzer), hypochlorite  $NaClO$ , and hypobromite  $NaBrO$ , have served as oxidizers.

In the oxidation catalysis for aqueous solutions of  $NaHSO_3$  by molecular  $O_2$  the maximum luminescence takes place at 480 millimicrons. The kinetic curve of intensity has two peaks. The first peak, according to the opinion of the authors, is connected with a carry-over of an electron in the complex with the catalyzer and with the formation of an  $O_2^-$  ion, the second — with the recombinations of radicals  $HO_2^\cdot$ . The authors see support for this in the fact that inhibitors, the interceptors of free radicals, will dampen chemiluminescence [144, 145].

Spectra in oxidation reactions of hypo-halides have few characteristic maxima at 580 and 530 millimicrons — and in neutralization reactions, at 480 millimicrons. In a majority of reactions luminescence intensity grows quickly and then slowly decreases according to law

$$I^{-1/2} = I^{-1/2}_0 + at, \quad (13)$$

wherein the coefficient  $a$  is inversely proportional to  $[O_2]$ . Stauff considers that an excited particle is a complex of two molecules of  $O_2$  that are connected to the Van der Waals forces. The complex is formed when two electron-excited molecules of  $O_2$  encounter one another. The latter is obtained in the recombination of  $HO_2^\cdot$  and  $^{\cdot}OH$  radicals, the presence of which were discovered by the EPR method [145]:



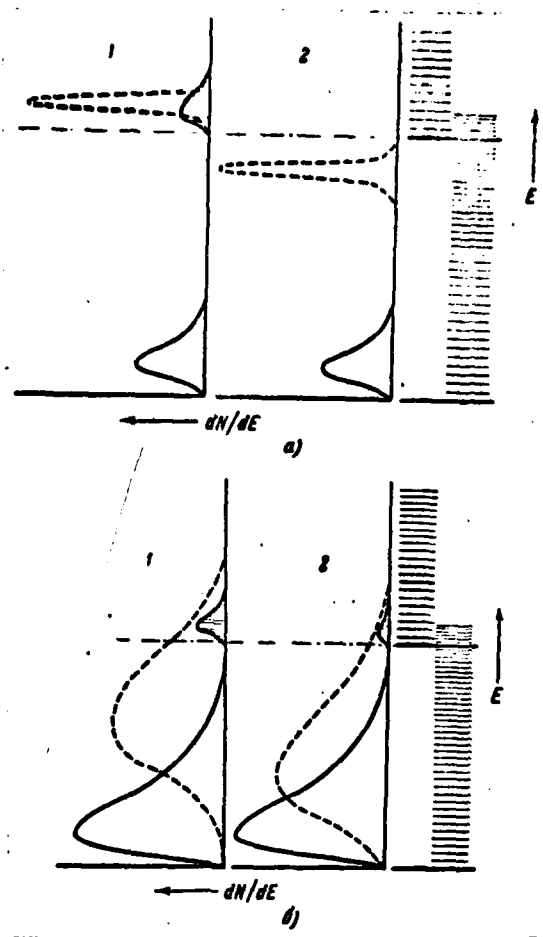


Figure 12. Distribution of radical recombination products by electron and oscillation levels (qualitatively). Dotted line — immediately following the reaction. Solid line — following establishment of thermal equilibrium with the medium. Ruled areas are proportional to the number of electron-excited molecules. Cases 1 and 2 correspond to the greatest and the least thermal effect of the reaction under very nearly identical conditions. In case a) one product is formed and the primary distribution is more abrupt than in case b) which corresponds to the formation of one product.

The energy given off in these reactions is sufficient for the excitation state  $^1\Delta_g$  and  $^1\Sigma_g^k$  (See Figure 6). Luminescence maxima in spectra may be added to conversions:  $^1\Sigma^+ \Delta \rightarrow ^3\Sigma^-$  (480 millimicrons),  $^1\Delta^+ \Delta + \omega \rightarrow ^3\Sigma^-$  (580 millimicrons),  $^1\Delta^+ \Delta + 2\omega \rightarrow ^3\Sigma^-$  (530 millimicrons), where  $\omega$  is the oscillation quantum of  $O_2$ ; they are close to the maxima of absorption of complexes  $(O_2)_2$ . Several kinetic schemes for the formation of  $O_2^*$  lead to a theoretical relationship of type (13) and to a proportionality between I and  $[O_2]$  observed by experiment.

Seliger [135] in 1960 discovered a 635 millimicron band and subsequently [136] two more bands in reactions of hypochlorite NaClO and  $Cl_2$  with  $H_2O_2$  in water: 703 millimicrons and (very weak) 578 millimicrons. Inasmuch as the difference in wave numbers,  $1570\text{ cm}^{-1}$ , is close to the frequency of oscillation in the  $O_2$  molecule ( $1580\text{ cm}^{-1}$ ), the authors [111] recorded bands with oscillation components (0, 0) and (0, 1) of the shift  $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$  (See Figure 6), and a short wave displacement of  $2600\text{ cm}^{-1}$ , in comparison with a shift in gaseous  $O_2$  is carried out due to the influence of the solvent. Although the possibility of such a great displacement has been illustrated by theoretical calculation [101], the prematurity of the given interpretation became clear after the very same bands were discovered in the gaseous phase (during electrical discharge in  $O_2$ ) [78]. Further, Browne and Ogryzlo [90] recorded the luminescence spectrum of the reaction  $Cl_2 + H_2O_2$  in a broad field (Figure 13) and gave the following interpretation: 12,700 and 10,700 Å (0, 0) and (0, 1) shift  $^1\Delta_g \rightarrow ^3\Sigma_g^-$ ; 7619, 8645 and 7700 Å — components (0, 0), (0, 1) and (1, 1) shift  $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$ . Three peaks in the orange-red region are recorded as components (1, 0), (0, 0) and (0, 1) of the electron shift  $^1\Delta_g^+ \Delta_g^- \rightarrow ^3\Sigma_g^-$  in the complex  $(O_2)_2$ .

Chemiluminescence spectra for many oxidation reactions in aqueous solutions are very similar [147]; this finds its explanation in the fact that the OH and  $HO_2$  radicals take part in the given processes, the reactions of which may give excited oxygen and its dimer  $(O_2)_2^*$ .

It should be noted, in the first place, that the concentration of the complex  $(O_2)_2^*$  must be very low inasmuch as, for its formation, an encounter of two excited molecules is necessary, and in the second place, the lifetime of the complex is very small (for an unexcited

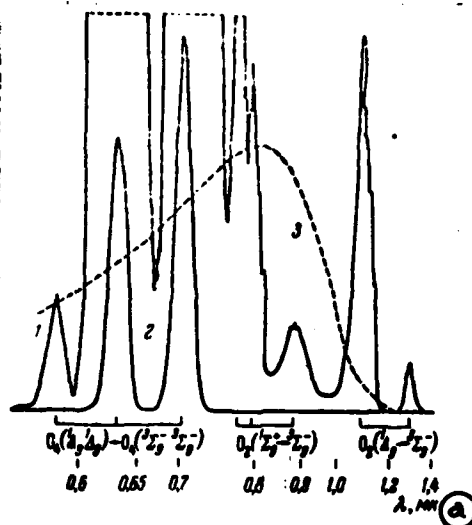


Figure 13. Chemiluminescence spectrum in the reaction of chlorine with hydrogen peroxide in an alkaline aqueous solution [90]. The scale of curve 1 is 1000 times larger than curve 2; 3 — is the curve of spectral sensitivity of the photoamplifier.

Key: a.  $\lambda$ , in microns.

complex it is, in all,  $10^{-13}$  sec. [38]). For this it follows that, with the excitation and luminescence of the complex  $(O_2)_2$  may compete with plug reactions. On the strength of both reasons the luminescence must be very weak, which is also observed in experiment.

### III. OTHER ASPECTS OF CHEMILUMINESCENCE

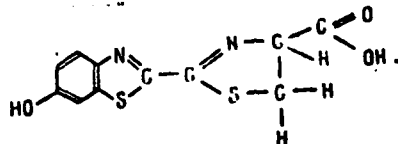
#### 7. Bioluminescence

The flow of complicated chemical processes (biochemical) in living organisms is sometimes accompanied by luminescence.

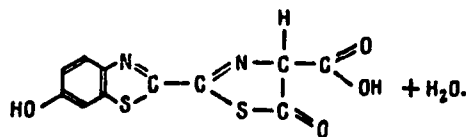
Many forms of fauna and flora possess an ability to luminesce: bacteria, fungi, radiolaria, sponges, sea worms, crustacea, mollusks, snails, centipedes, insects and ocean fish. At the same time, there are no luminescent forms among the higher plant life, amphibia, reptiles, birds and mammals. With the exception of a few forms, fresh-water

organisms do not luminesce, even those of them that are found close relationship with self-luminescent types that live in sea water.

The research of bioluminescence in various living organisms had already led to the conclusion a half-century ago that luminescence occurs during the oxidation of a substance called luciferine by oxygen and the reaction is catalyzed by ferment called luciferase. Both luciferines and luciferases are specified for different luminescing organisms. The structure of these compounds had not been established right up to very recent times. Not long ago [120, 137, 139] they were successful in separating luciferine and luciferase in pure form from the glands of the *Photinus pyralis* fly, identifying and chemically synthesizing luciferine, which had the following structure:



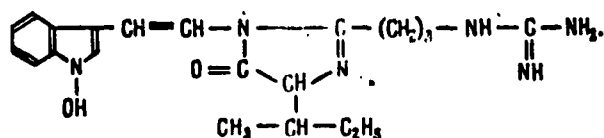
In the state responsible for luminescence, luciferine is oxidized by molecular oxygen and forms oxyluciferine and water:



Luciferase appears as a protein molecule which has in its make-up more than 1000 amino acid blocks. Adenosine tri-phosphate is a necessary component for luminescence. The ratio of luminescence intensity to the concentration of adenosine tri-phosphate serves as a basic method which permits measurement of an insignificant amount ( $10^{-10}$  -  $10^{-9}$  g/ml [69]) of this substance, a universal supplier of energy for bioluminescence processes that go on in living organisms.

A surprising result was obtained in the measurement of the quantum yield of the reaction. It appeared that, on an average, 0.88 photons were radiated for one oxidized molecule of luciferine [137]. Such a high quantum yield had never before been observed in a chemiluminescence reaction. Apparently, an oxidized molecule of luciferine is an excited particle. Before the oxidation event it is joined in the complex with ferment and adenosine monophosphate; the complex lowers the probability of deactivation during collisions with surrounding molecules.

Luciferine of Cypridina crustacea has the following structure [105, 140]:



According to the opinion of McElroy and Seliger the ability to luminesce is a rudimentary characteristic which was developed in the evolution of life forms on Earth [120]. It is possible that the first organisms which had appeared on Earth were capable of existing in the absence of oxygen. When oxygen began to appear in the Earth's atmosphere it exerted an unfortunate and poisonous influence on organisms. In the course of natural selection those forms were preserved that developed the ability to effectively "destroy" molecular oxygen which got into them, let us say, by converting it into water. The energy which was given off in this could provide excitation for molecules and radiation for light.

At the beginning of the Twenties the research of A. G. Gurvich and his colleagues [36, 37] was published, in which it was revealed that some plant and animal tissues give off weak radiation in the region of 190-325 millimicrons. They succeeded in pointing out that radiation is caused by mitosis — cell division. More than that, it appeared that mitosis in some cultures of tissues was reinforced under the influence of radiation \*). On this basis very sensitive biological radiation detectors were made, by means of which research was also conducted of so-called mitogenetics. As a consequence, this was also recorded by physical detectors, however the signals were almost always of the same order as noise too.

In recent times weak luminescence in the visible region was discovered in many biological systems, including living tissues and organs [31, 41] \*\*).

Research of weak chemiluminescent systems that are capable of photochemical reactions (particularly, photosynthesis [29]) has great significance in explaining the mechanism of photosensitized and fermentation reactions and accumulation and migration of energy.

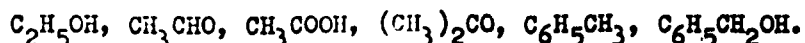
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\*) Not long ago S. V. Konev [51] reported on the acceleration of cell division of yeasts under the influence of weak streams ( $10^5$  photons per  $\text{cm}^2$  sec.) of ultra-violet light from a mercury lamp.

\*\*) See "Bioluminescence" Symposium (Symposium 3-6 June 1963), Moscow, "Nauka" Publishing House, 1965.

## 8. Heterogeneous Chemiluminescence

In 1945 A. N. Torenin and L. A. Kachur [66] discovered visible luminescence of the heated powder of magnesium oxide when air was passed over it that was saturated with the vapors of organic substances:



It was pointed out that the glowing appeared as chemiluminescence caused by oxidation reactions of organic substances on the surface of the magnesium oxide, which plays the part of a catalyzer. The highly concentrated products of oxidation or their groups serve as emitters; it is possible that they are excited as a result of a transfer of energy from the primary products of oxidation.

## 9. Candoluminescence

In 1925 Bonhoeffer [84] pointed out that crystal phosphors luminesce under the influence of atomic hydrogen. Subsequently analogous luminescence was observed also with the action of other free atoms and radicals, particularly those formed in flames. The phenomenon, called candoluminescence, is caused by recombinations on the surface of lumino-phosphor of free atoms and radicals [34, 132].

It should be noted that for a long time clear representations of the nature and mechanism of candoluminescence were absent. Some authors took the explanation of the phenomenon for oxidation-reduction processes, others generally disclaimed the high equilibrium character of luminescence and explained the experimental facts as peculiarities of purely temperature radiations of bodies under flame conditions. Only in recent years, thanks to the work of V. A. Sokolov and his colleagues [30, 34] uncontested experimental demonstrations of the recombination mechanism of the phenomenon were obtained.

In most recent times it has been brought to mind that crystal phosphor is a semi-conductor and at the same time a recombination catalyzer. The peculiarities of the phenomenon were considered on the basis of representations of electron theory of chemical absorption and catalysis and theoretical results qualitatively supported by experiment [30].

## 10. Luminescence during recombination of "frozen" radicals

In recent years means have been found for building up high concentrations of free, active radicals. For this purpose either precipitation on a cold surface of the products of electrical discharge or photolysis is employed, or photolysis or radiolysis of frozen solutions or of solid substances. In freezing or liquifying samples, the radicals regulate one another. In this, luminescence is often observed.

Thus, sparks of yellow-green light appear during the freezing of solutions of aromatic compounds exposed to gamma rays [94], and blue-green in the heating of products from the interaction of atoms of H with  $\text{HN}_3$  or  $\text{N}_2\text{H}_4$  [125]. The formation of excited ethylene is shown during the freezing of products of the photolysis of di-azo methane  $\text{CH}_2\text{N}_2$  [99].

Weak chemiluminescence is observed during the solution of exposed desoxy ribonucleinic acid [75], protein [61, 148] and polymethyl methacrylate [61].

It is necessary to distinguish other forms of luminescence from chemiluminescence during the recombination of "frozen" radicals, which occur during the heating of exposed samples, for instance, the recombination of electrons with openings [54].

#### 11. Luminescence during electrolysis

In electrochemical reactions the primary products of oxidation and reduction, as a rule, are unstable and are extremely capable of reacting. Therefore, a portion of the energy given off in reactions between the active products of electrolysis may be sufficient for excitation with visible luminescence. Actually, weak luminescence was observed during the electrolysis of ethanol, acetic acid, potassium acetate [10, 73], salt of carbonic acids, a number of organic substances and Grignard reagents [76].

The authors of work [74] conducted electrolysis of a 0.1 normal NaOH solution on platinum electrodes, a solution to which had been added  $5 \times 10^{-5}$  mol/l of fluoresceine or eosin. At room temperature, a potential of 10-30 v., and a direct current of several milliamperes, an intense chemiluminescence was observed at the anode. The application of electrolysis with alternating current of various frequencies made it possible to discover supplementary chemiluminescence processes and to estimate the life time of active anodic products (on the order of 1 sec.).

#### 12. Sonoluminescence

It is well-known that cavitation (destruction of compactness) of some liquids acted on by ultra-sonics is accompanied by a weak luminescence. The radiation mechanism (so-called sonoluminescence) has not yet been established conclusively. Along with theories that assume thermal excitation (under compression) or electrical discharge, indications exist to the effect that chemiluminescence, which occurs in reactions is caused by ultra-sonics [100, 102].

#### IV. APPLICATIONS OF CHEMILUMINESCENCE

##### 13. Analytical applications of reactions with intense luminescence

Already in an earlier stage of investigation of the liquid-phase of chemiluminescence various uses of the luminescence of luminol, lucigenine, lophine, etc., were proposed.

It has been noted above that, for luminescing luminol, hydrogen peroxide and a catalyzer (for instance, copper) were necessary. In decreasing the concentration of any of the indicated substances below a definite limit, intensity is decreased and this may serve as a basis for the quantitative analysis of the given compound. Besides that, it is also possible to define those compounds which regulate with luminol, with  $H_2O_2$  or with a catalyzer. In particular, such compounds may be determined by the chemiluminescence method as hydrogen peroxide; sodium hypochlorite; copper; acetaldehyde; glucose; vitamin C; phenol; pyrocatechin; resorcylic; pyrogallol; aniline; nitroanilines; methyl, ethyl, and propyl alcohols; and so on [57a, 58]. The sensitivity of the method to  $H_2O_2$  may be brought to  $10^{-7}$  mol/l [118]. Sensitivity with respect to metals is  $10^{-8}$ - $10^{-6}$ , which exceeds the sensitivity of the radioactivation method [2, 3]. The development of alkaline solutions of luminol with gases which contain the CN and PF groups (nerve-paralyzing toxic compound), cause chemiluminescence. Intensity depends on their concentration linearly [98].

Reinforcement of luminol chemiluminescence with small quantities of hemin was proposed for use in criminology for uncovering traces of blood at the scene of a crime [52].

Those substances, the chemiluminescence of which depends markedly on the pH of the medium, serve reliably as indicators in quantitative analysis by titration [52, 57b].

Thus, any empirically established influence of any reagent on intensity or the luminous whole of luminescence may be the basis of a quantitative method of analysis of the given substance, even if there are little data concerning the mechanism of chemiluminescence. In work [97] the chemiluminescence which occurs in a mixture of luminol and alkali was used as a method of solving hydrodynamic problems concerning the limit of a liquid jet flowing into another liquid.

##### 14. Obtaining kinetic characteristics of oxidation reactions

In the oxidation of hydrocarbons excited states appear with the recombination of radicals and the intensity of luminescence, according to the law, seems to be connected with a kinetic reaction. On this basis chemiluminescent methods were developed of the quantitative

measurement of the characteristics of oxidation reactions \*).

Thus, for instance, according to the chemiluminescence "oxygen drop" (See Article 5 and Figure 7) one may succeed in measuring the absolute speed of oxidation, the concentration of oxygen in a liquid and in a gas, the relationship of elementary constants  $k_3/\sqrt{k_6}$  and  $k_2/\sqrt{k_4}$ , the speed of initiation [12-14, 18]. From measurements of the intensity of chemiluminescence were obtained relative [12] and absolute [46, 47] values of constants which characterize the activity of inhibitors, and also new data on the decomposition mechanism of azo-compounds [18] and hydrogen peroxide [42-44]. According to the temperature rate of intensity a rapid determination of the energy of activation [10, 73] is possible, and according to the kinetic curve — the obtaining of absolute constants of radical recombinations [28].

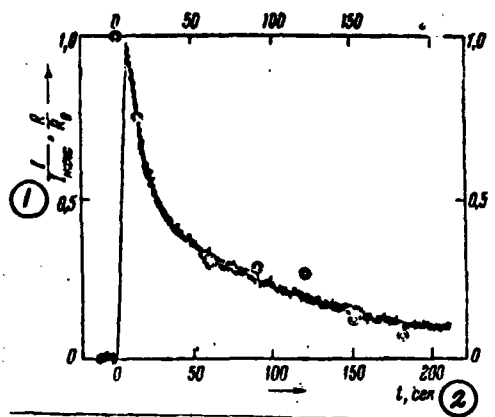


Figure 14. Drop in chemiluminescence intensity (curve) and electron paramagnetic resonance signals (points) in the period following solution of exposed polymethyl methacrylate in di-chlor ethane [61].

Key: 1.  $\frac{I}{I_{\max}}$  ,  $\frac{R}{R_0}$  ; 2.  $t$ , in sec.

The possibility of obtaining valuable quantitative information shows that chemiluminescence may serve as an effective physical method of investigating the kinetics of reactions.

The intensity of light is the value measured in experiments.

\*) These methods are considered in detail in survey [56].

Therefore, the chemical part of the installation is very simple and consists of a thermostat and a vessel with a thermal jacket. Intensity is constantly and automatically recorded by standard instruments. With these features the method is connected with high productivity, precision and reliability of the results obtained. Increased precision (1-2%) is attained in those methods where not the intensity of luminescence is measured, but the time from the beginning of the reaction to a particular point on the kinetic curve of intensity (for instance, "oxygen drops"). Measurements do not introduce any kind of changes in the chemical system. The sensitivity of chemiluminescence methods may be increased by the introduction of activators.

Chemiluminescence methods have a particular value for research of the chemiluminescence mechanism itself. During chemiluminescence radiation (intensity, spectrum, and their change in time) it is very important to carry out a parallel control of the speed of reaction (i.e. speed of excitation). This is conveniently given with the aid of chemiluminescence methods, because in this regard, the necessity of conducting individual experiments in chemical equipment falls away and, consequently, the question of identical experimental conditions does not obtain.

In radical reactions chemiluminescence is connected to re-combinations of free radicals. It is interesting to compare chemiluminescence methods with another physical method of recording free radical conditions — electron paramagnetic resonance. It is not difficult to see that these methods supplement one another. A high breakdown rate of radicals promotes a successful application of chemiluminescence methods, i.e. their high reaction capacities. A high stationary concentration of radicals promotes successful application of the electron paramagnetic resonance method, i.e. their chemical stability. So much as the sensitivity of both methods is increased so will the situation become even less alternative, and their simultaneous application, it is necessary to suppose, will permit obtaining interesting results. Work [61] in which weak luminescence was discovered in the solution of exposed protein and polymethyl methacrylate serves as the first example of this type. The kinetics of the drop in intensity coincided with the kinetics of the decrease in free radicals measured on the electron paramagnetic resonance spectrometer (Figure 14). Important data concerning the protective action of inhibitors on a radiated system (model for investigating radiation sickness) were obtained by both methods.

#### 15. Study of the properties of excited molecules

The fate of excited molecules need not depend on excitation capability. Besides, each property has its peculiarities which can make the interpretation of results difficult. Therefore, in the investigation of excited states the attraction of other excitation methods is also

expedient. If, in a practical reaction, an excitation product is identified, it is permissive in that case to speak of chemiluminescence as a method of obtaining a given excited particle and of investigating its properties.

Chemical excitation which is applicable to gaseous-phase systems [32, 33] is widely used. Only by this means has there ever been success in obtaining spectra of physically stable, but chemically unstable particles (for instance,  $C_2$ , HCO, ClO, JF and so on), inasmuch as they may be accumulated in noticeable quantities only under conditions of an intensively rapid chemical reaction.

This method has never been employed in liquid-phase reactions up to the present time. Intermolecular transfer of energy from the triplet level of ketones formed during the oxidation of hydrocarbons, to the singlet (fluorescent) level of activators which produce anthracene is considered in the nature of a first example in works [15, 16, 22]. The fact of transfer itself was indicated spectrally (See Figure 8) and, depending on the intensity of activated chemiluminescence to the concentration of the activator (See equation (11)), relative and absolute constants of the rate of transfer of energy  $k_{PA}$  were obtained.

For anthracene and alkyl- and phenyl-anthracenes the  $k_{PA}$  constants do not exceed  $10^7$  l/mol sec., but they increase on the order of 1-3 when the heavy atoms — chlorine and bromine are introduced into the molecule. Thus, for di-bromanthracene  $k_{PA} \approx 10^9$  l/mol sec. which, in all, is one-half to two times lower than the number of collisions calculated according to diffusion theory formulas.

The transfer of energy during contact of the electron shells of molecules is theoretically considered by Dexter [95] (See also [40]). From the region of overlap an excited electron of the donor may transfer to the acceptor, and an unexcited electron of the acceptor — to the donor. The probability of transfer is distinct from zero only in that case where the multiplicity of excited states of the donor and of the acceptor are identical. It is not difficult to see that this rule of selection is not fulfilled in the case under consideration because the excited state of the donor is triplet and the acceptor is singlet. Therefore, the energy transfer constant  $k_{PA}$  is small (on the order of  $10^7$  l/mol sec.) in the case of anthracene and its alkyl- and phenyl products.

Introduction into the acceptor of halogens reinforces the interaction of the electron spin and orbital magnetic moments, and this leads to a "mixture" of triplet and singlet conditions. Now the transfer of energy becomes critical and, in a greater degree, the more the addition of triplet to singlet. The  $k_{PA}$  constant grows. For quantitative

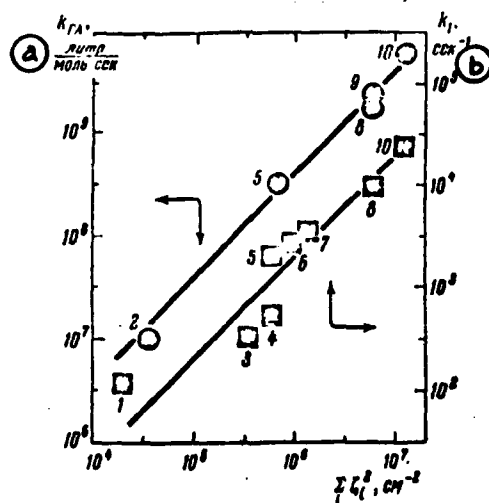


Figure 15. The influence of substitution on  $k_{PA}$  and  $k_1$  constants. The constant  $k_{PA}$  is taken from experiments on the oxidation of cyclohexane at  $50^\circ$  in benzole [22],  $k_1$  — from work [107].

1. Anthracine (A); 2. 9, 10-diphenyl-A; 3. 1-chlor-A; 4. 1, 5-di-chlor-A; 5. 9, 10-dichlor-A; 6. 2, 9, 10-trichlor-A; 7. 1, 5, 9, 10-tetrachlor-A; 8. 9-brom-A; 9. 9-brom-10-phenyl-A; 10. 9, 10-dibrom-A.

Key: a.  $k_{PA}$ , in liters/mol sec.; b.  $k_1$ , in  $\text{sec}^{-1}$ .

evaluation of spin-orbital effects an approximation is often sufficiently good in which the constants of a spin-orbital bond of isolated atoms are used [119] which, in a well-known sense, are equivalently introduced to a crude model of a molecule like systems in which individual atoms independently influence an excited electron. The contribution of each atom may be approximated by the value  $\zeta_i^2$  where  $\zeta_i$  is the radial part of the matrix element of the operator in a spin-orbital interaction of an isolated atom — a value that is well-known from atomic spectra. Within the framework of the model adopted it may be expected that the  $k_{PA}$  constant is proportional to the sum of the values  $\zeta_i^2$  for all atoms that enter into the molecule (the greatest contribution, in this regard,

is made by heavy atoms, because  $\zeta_C = \zeta_H = 28 \text{ cm}^{-1}$ ,  $\zeta_{Cl} = 587 \text{ cm}^{-1}$ ,  $\zeta_{Br} = 2640 \text{ cm}^{-1}$ ). This is actually observed by experiment (Figure 15).

It is necessary that, with the introduction of halogens the probability of intra-molecular non-irradiated triplet-singlet transfer  $k_1$  [107] also increases, whereas at the same stage the constant of intermolecular transfer increases somewhat. This is explained by the fact that simultaneously with the appearance of an addition of a triplet character to the singlet state there is approximately the same addition of the singlet character to the triplet state and intercombination prohibition is weakened for both transfers.

Thus, in the case under consideration, a modified form of triplet-triplet energy transfer takes place, first observed by A. N. Terenin and V. L. Yermolayev [68] in solid solutions. In liquids the triplet-triplet transfer is realized with constants equal to the diffusers [82, 129, 133], which agrees with quantitative laws of activated chemiluminescence.

The example shown indicates the prospects for using chemiluminescence of reactions with a radiation mechanism for radiating excited states.

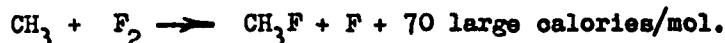
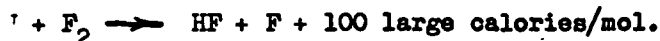
The chemiluminescence method possesses the following advantages: 1) excitation is the same with respect to volume; 2) a background for the source of excitation exists and it is possible to regulate radiation with very low yields; 3) the actual portions of energy are not large (2-4 ev.); 4) the absorption capability of other components play no role and do not hinder excitation; 5) well-luminesced components are not excited (they may be excited only due to the transfer of energy); 6) excitation occurs by a "shaded" method; therefore the usual rules for the selection and the possibility of effective population of "prohibited" levels. In particular, during photoexcitation it would have been very difficult, if generally possible, to investigate the transfer of energy from a poorly-luminesced donor (ketone) to a well-luminesced activator; in this regard, certainly, not only would the ketone be excited, but also the anthracene inasmuch as they absorb in one and the same region of the spectrum. In the case of activated chemiluminescence, the excited states were caused by the chemical, shaded method and well-luminesced components may be excited only as a result of a transfer of energy which has also been studied in work [22].

An obvious disadvantage of the method is that it is specific — not every compound can be synthesized by far, which was obtained in the excited state in the synthesis reaction. Other features of the method that may be discussed of an undesirable type are the necessity for the presence of definite reagents and low luminescence intensity.

## V. CONCLUSION

Already the material presented above indicates that research on chemiluminescence now consists of a sufficiently broad, interesting and rapidly developing field of science at the junction of physics and chemistry. The phenomenon of chemiluminescence is characterized by a series of general laws which govern any reaction (See Article 1). On the other hand, chemiluminescence is a very specific phenomenon and the conversion of chemical energy into light energy may go by different paths in different reactions. Moreover, in one and the same reaction not only one product may be excited, but several products may radiate identically, whether in different spectral regions. The nature of the excitation reaction itself may be different in different chemical systems.

These circumstances are not always taken into account in works on chemiluminescence. Some authors, for instance, develop representations concerning the radical character of chemiluminescence reactions [87, 154]. Moreover, they propose to consider the existence of luminescence as a demonstration of participation of radicals in a reaction [83, 130], whereas they persist even by the fact that chemiluminescence in the short-wave (blue and shorter) region may be the result only of reactions with the participation of two free radicals [87]. Actually, effective conversion of chemical energy into radiation is more probable and should be encountered more often in the recombination of radicals. Just the same, it would have been incorrect to deny the possibility of excitation in other reactions as well, reactions distinct from recombination. For instance, bright flares were observed during the introduction of molecular fluorine in a stream of  $H_2$  or  $CH_4$  [45]. In these reactions there are elementary events



They are sufficiently exothermic, but they include one free radical in the form of an original reagent.

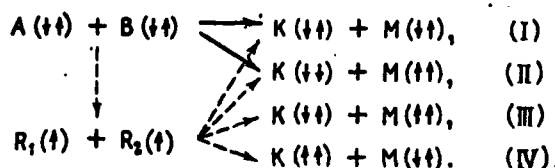
From our point of view, there exist only two conditions necessary for chemiluminescence phenomenon;

- a) the reaction must be sufficiently exothermic (the law of conservation of energy);
- b) the product must have a suitable energy level, the radiation from which occurs with sufficient probability.

The carrier of excitation in solutions is the electron state, inasmuch as in a liquid wave excitation is rapidly lost. The structure of the spectrum is determined by the luminescent properties of the excited state, and is not a part of the energy given off (the latter, it stands to reason, must correspond to the emitted quantum of light).

In those cases where the products of exothermic reaction have a triplet level, its excitation undoubtedly favors the fact that for a majority of molecules it is disposed lower and requires less energy than the excited singlet level. The question of the multiplicity of the excited particle sometimes may be well-defined decided on the basis of the rule of the preservation of the system's total spin (Wigner's rule). However, in using Wigner's rule, it is necessary to keep in mind that it is applicable to an elementary event and not to the Brutto-reaction.

For instance, if a reaction between saturated molecules A and B goes in one elementary event, then both products K and M must be obtained either in the singlet or in the triplet state (combinations I and II):



If the reaction flows by the radical path, then other combinations (III and IV) are possible. In view of what has been discussed, yields during the oxidation of luminol [154] and oxalyl chloride [91], with respect to the triplet nature of the excited state, are represented as being premature.

The reaction may go with the breaking of Wigner's rule, inasmuch as it is not very strict. In this case the excitation process must have a low probability (low yield). And conversely: if, by experiment, a high chemiluminescence yield is obtained, it is difficult to expect that the elementary act of excitation goes with a change in multiplicity. This is why, during reasearch of the chemiluminescence mechanism, it is important to measure the luminescence yield correctly. In this connection the following should be emphasized.

1. In determining chemiluminescence yield the intensity of luminescence is necessary not only with reference to the speed of the Brutto-reaction, but to the speed of formation of that product which serves as an emitter.
2. The chemiluminescence process flows in two stages, and correspondingly, the overall luminescence yield depends on the excitation yield  $\eta_p^{\text{excited}}$  and radiation yield  $\eta_p$ . These values have a completely different physical meaning and variously depend on the structure of a molecule, medium, conditions of the experiment, and so forth.

A majority of chemiluminescence reactions are essentially oxidation reactions. Connected with this, probably, is the fact that the products of oxidation reactions (ketones, aldehydes, and  $O_2$ ) have lowly disposed levels of energy which may comparatively effectively

populate a reaction (i.e. the yield of  $\eta_p^{\text{excited}}$  is comparatively great); besides that, oxygen-bearing compounds luminesce relatively well in the visible region of the spectrum (i.e. the yield of  $\eta_p$  is comparatively great).

Institute of Physical Chemistry  
Academy of Sciences of the USSR

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