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STUDY OF THE INFLUENCE OF MOLECULAR STRUCTURE ON THE VELOCITY OF IONIC AND ATOMIC REACTIONS OF ISOTOPE EXCHANGES

- USSR -

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STUDY OF THE INFLUENCE OF MOLECULAR STRUCTURE ON THE VELOCITY OF IONIC AND ATOMIC REACTIONS OF ISOTOPE EXCHANGES

IV. Investigation of the Radical-Chain Reactions of Isotope Exchanges of Iodide Alkyls with Elementary Iodine.

[Following is a translation of an article by M. B. Beuman, V. B. Miller and Yu. M. Shapovalov in Zhur. Fiz. Khim. (Journal of Physical Chemistry), No. 3, Moscow, 1956, pages 492-499.]

Modern theories, clearly formultated by N. N. Semenov [1-5], state that homogeneous reactions in solutions can follow both ionic and radical-chain mechanisms.

The mechanism of the process determines, in some cases, the direction of the reaction. For instance, when the reaction $CH_3CH = CH_2 + HBr$ takes place according to the radical mechanism (in the presence of peroxides), propyl bromide is formed. But if the reaction takes place according to an ionic mechanism, HBr is added in accordance with V. V. Markovnikov's rule, and isopropylbromide is formed [6].

We may assume that the reverse dependence is also true, namely that the change of molecular structure influences the velocity of ionic or radical-chain reactions differently. The confirmation of this hypothesis would -- in our opinion -- confirm A. M. Butlerov's theory concerning the influence of elements of molecular structure nn the velocity of reactions with various substances [7].

In connection with these considerations and in addition to our investigation of the influence of molecular structure on the velocity of ionic reactions of isotope exchange [8-11], we studied the effect of the change of structure of several alkyl iodides on the velocity of their isotope exchance with iodine molecules in a cyclohexane solution. The isotope exchange reaction was carried out between alkyl iodide RI,

$$I_2 + h\nu \xrightarrow{k_1} 2I \tag{1}$$

marked as radioactive isotope I^{131}, and elementary iodine.

When the solution is illuminated with visible light, according to the reaction iodine atoms are formed, which are initially active centers in the chain reaction. They develop according to the scheme [12]:

$$I + RI^{*} \xrightarrow{k_2} R + II^{*}, \tag{2}$$

$$I_2 + R \xrightarrow{k_3} RI + I. \tag{3}$$

The chain is broken because of a recombination of iodine atoms, according to the equation:

$$I + I \xrightarrow{k_4} I_2. \tag{4}$$

If we assume, according to Bodenstein's method, that the wtationary reaction $d(I)/dt = d|R|/dt = 0$, will produce the following expressions for the values of $|I|$ and $|R|$.

$$[I] = \sqrt{\frac{2k_1}{k_4} i_{абс}}, \tag{5}$$

$$[R] = \frac{k_2[RI]}{k_3[I_2]} \sqrt{\frac{2k_1}{k_4} i_{абс}}. \tag{6}$$

Here, i_{abc} is the number of light quanta absorbed by iodine. If we assume $|I_2| = a$, $|RI| = b$, $|RI^*|_0 = c$; $|RI^*|_t = c-x$; $[I_2^*] = \frac{1}{2}x$, we shall obtain the following equation for the velocity of increase x:

$$\frac{dx}{dt} = \frac{k_2}{k_3 a} \sqrt{\frac{2k_1}{k_4} i_{абс}} \left(c - x - \frac{b}{2a} x\right). \tag{7}$$

Let us introduce the values of specific activities alpha = x/a and beta $_0$ = c/b. Then (7) gives us:

$$\frac{dx}{dt} = \frac{k_2 b}{k_3 a} \sqrt{\frac{2k_1}{k_4} i_{абс}} \left\{\beta_0 - x\left(\frac{1}{b} + \frac{1}{2a}\right)\right\}. \tag{8}$$

We will make a note of the ratio of activities α/β_0 = Z, and equation (8) becomes

$$\frac{dz}{dt} = \frac{k_2 b}{k_3 a} \sqrt{\frac{2k_1}{k_4} i_{абс}} \left\{1 - \frac{x}{c}\left(1 + \frac{b}{2a}\right)\right\}. \tag{9}$$

It is clear that in the case of small conversion depths, when

$$\frac{x}{c}\left(1+\frac{b}{2a}\right) \ll 1,$$

we can assume

$$\frac{dz}{dt} \approx \frac{k_2 b}{k_3 a} \sqrt{\frac{2k_1}{k_4} i_{\text{абс}}} = \text{const.} \qquad (10)$$

In the current study, we were determining the relative magnitude of the velocity of the atomic exchange dz/dt in the same manner as we did it in our preceding study [13]. Since a and b have had a constant value in the majority of experiments and the conditions of temperature and light did not vary, the values dz/dt, which we obtained, permitted us to characterize the relative velocity of the isotope exchange of alkyl iodides of various structures.

The concentration of iodoform in the experiments diminished ten times, because it exchanges very rapidly. In this case, a correspnnding correction was introduced in the value of dz/dt, which we determined experimentally. It was increased tenfold in accordance with equation (10).

In the current study, we examined the effect on the velocity of the isotope exchange of RI* + I_2, which follows the chain mechanism. The elongation of the carbon chain and the isomerization of the alkyl radical R, as well as the substitution of hydrogen in CH_3I with methyl radicals and iodine atoms, were also examined in the same context.

Methodology of the Experiment

The velocity of atomic exchange in cyclohexane solutions of alkyl iodides and iodine was studied. Active alkyl halide, identified by isotope I^{131}, and an inactive iodine solution were used, in contrast with experiments on the study of ionic exchange reactions. Marked alkyl halide was obtained by means of an exchange of RI with NaI* at 100° C. The concentrations of alkyl halide and of iodine solutions, mixed for the exchange, were respectively 0.01 and 0.005 equiv/l. Alkyl halides do not exchange with molecular bromine in darkness, as wasshown by the studies of S. Z. Roginskiy and his collaborators in the case of bromine exchange [14].

We carried out many experiments on the isotope exchange of several marked alkyl iodides RI with elementary iodine in a cyclohexane solution in darkness at room temperature. These experiments showed that no noticeable exchange takes place even over a period of 10 hours. The generation in the reacting mixture of atoms capable of provoking the chain process is necessary in order that the exchange may take place.

A diagram of the apparatus, which we utilized to study the reactions of the isotope exchange, is shown in Fig. 1.

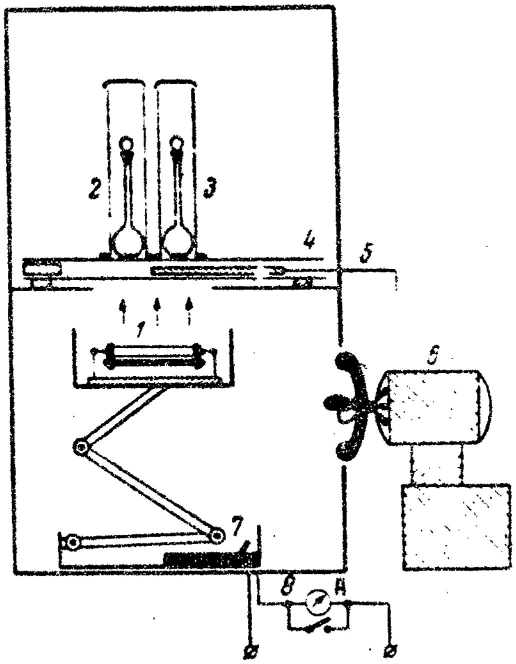


Fig. 1. Diagram of the installation for the study of reactions of isotope exchange.

1) Mercury lamp;
2, 3) reaction flasks;
4) glass light filter;
5) sliding plate;
6) motor with blower;
7) starting push button;
8) ammeter with a switch.

A mercury lamp 1, serving as a source of light, and flasks with solutions 2 and 3, put into special nests, were installed in a lightproof box. The mercury lamp was cooled by an air draft produced by the blower 6. The radiations from the mercury lamp passed through glass filters 4, which absorbed the ultraviolet part of the spectrum. This radiation initiated a reaction in the solution $RI^* + I_2$.

Special experiments, during which the cyclohexane solution of RI* was exposed to illumination for a long time, showed that the radiation of the mercury lamp, which passed through glass filters, does not decompose alkyl iodides.

About one hour passed after the lamp was switched on before it became a stable source of light. When the light intensity became regular, which was determined by readings on the ammeter 8, the shiding plate 5 was opened; the reaction of the atomic exchange commenced inside flasks 2 and 3 under the influence of the light. Stopping the process at various times (this stoppage can be achieved either by closing the sliding plate 5 or by turning off the lamp), we extracted iodine in an aqueous solution of Na_2SO_3. Ions of I*, which were formed in the aqueous layer, were reacted to form AgI*, the activity of which was measured on a recorder.

The experiments were carried out with a constant light intensity, and their duration was selected in such a way that the conversion depth would not surpass seven to eight percent. Under such conditions, the reaction depth of the isotope exchange is proportional to the duration of light.

The Effect of the Elongation of the Carbon Chain of the Alkyl Radical Reaction on the Velocity Of the Atomic Exchange

We selected for this study the same series of alkyl iodides which was used for the ionic exchange, namely: methyl, ethyl and propyl iodides. The results of our experiments follow:

Isotope Exchange $CH_3* + I_2$. Cyclohexane solutions of iodine with active methyl iodide were illuminated during various periods of time, ranging from one up to eight hours. The results of experiments on the study of the velocity of atomic exchange of $CH_3I* + I_2$ are given in Table 1.

The magnitude of the ratio x/c, which characterizes the velocity of the exchange in the unit of time, was expressed in percentages. In spite of the prolonged illumination, the exchange took place to the extent of 0.15 percent; whereas the equilibrium activity distribution in accordance with the concentration of substances $|CH_3I*| = 0.01$ equiv/l and of $|I_2| = 0.005$ equiv/l, corresponds to x/c = 33 percent.

Isotope Exchange $CH_3CH_2I^* + I_2$. The results of experiments on the study of the exchange of ethyl iodide with iodine atoms are given in Table 2.

The concentrations of reagents were $|CH_3CH_2I^*|$ = 0.01 equiv/l and $|I_2|$ = 0.005 equiv/l. Therefore, the limiting value of the ratio x/c is also equal to 33 percent.

Table 1

Velocity of Atomic Exchange
$CH_3I^* + I_2$

Time of illumination in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % hour
	x	c		
1	18	60000	0,03	0,02
3	38	60000	0,06	
8	90	60000	0,15	

Table 2

Velocity of Atomic Exchange
$CH_3CH_2I^* + I_2$

Time in illumination in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % hour
	x	c		
1	60	120000	0,05	0,04
4	200	120000	0,17	
8	400	120000	0,33	

Isotope Exchange $CH_3CH_2CH_2I^* + I_2$. The results of our experiments on the study of the isotope exchange of a normal propyl iodide (0.01 equiv/l) with elementary iodine (0.005 equiv/l) in cyclohexane solution are represented in Table 3.

The Effect of the Replacement of Hydrogen Atoms in CH_3I by Methyl Radicals on the Velocity of Atomic Exchange

We studied the effect of the replacement of hydrogen atoms in the mocecule of CH_3I by the methyl radical on the velocity of atomic exchange in the following alkyl iodides: CH_3I, CH_3CH_2I and $CH(CH_3)_2I$. The results of the experiments on the exchange of the first two compounds are described in the preceding section. Experimental data on the study of the reaction of the isotope exchange of isopropyl iodide with atoms of iodine are given below.

Isotope Exchange $CH_3CHI^*CH_3 + I_2$. Data an the reaction of isopropyl iodide with molecules of iodine in cyclohexane solution are given in Table 4.

Table 3

Velocity of Atomic Exchange
$CH_3CH_2CH_2I^* + I_2$

Illumination time in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % in an hour
	x	c		
2	180	162000	0,11	0.056
4	390	162000	0,24	
6	540	162000	0,33	

Table 4

Velocity of Atomic Exchange
$CH_3CHI^*CH_3 - I_2$

Illumination time in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % in an hour
	x	c		
2	120	3250	3,7	1,6
4	170	3250	5,2	
5	260	3250	8	

The ratios of concentration of reagents were the same in these experiments as in the preceding ones; therefore, the equilibrium distribution of activity will also be achieved when x/c reaches 33 percent.

The results of the study of the effect of the replacement of hydrogen in the molecule of CH_3I by methyl radicals on the velocity of the atomic exchange are represented in Fig. 2. As we see in this figure, the replacement of hydrogen atoms in the molecule of CH_3I by methyl radicals increases the velocity of atomic isotope exchange, and it is particularly noticeable during the transition from CH_3CH_2I to $CH(CH_3)_2I$.

The Effect of Isomerization of Alkyl Radical and of the Substitution of Hydrogen in the Molecule of CH_3I by Atoms of Iodine on the Velocity of the Atomic Isotope Exchange

We can get an idea of the effect of the isomerization of the alkyl radical on the velocity of isotope exchange if we compare the relative magnitudes of the velocities of exchange of normal propyl iodide and isopropyl iodide with atoms of iodine.

Data resulting from experiments on the study of atomic isotope exchange of propyl iodide and isopropyl iodide are given in Tables 3 and 4. Straight lines are traced on Fig. 3 through the experimental points. Their inclination allows us to evaluate the velocity of the atomic isotope exchange of propyl iodide 2 and of isopropyl iodide 1.

It is seen from the figure that isopropyl iodide exchanges are approximately 25 times faster than those of normal propyl iodide.

We carried out experiments on the study of exchange reactions of methylene iodide and iodoform in order to examine the effects of replacements of atoms of hydrogen in the molecule CH_3I by atoms of iodine, on the velocity of the atomic isotope exchange. The exchange of methyl iodide with elementary iodine was studied earlier (Table 1)

Isotope Exchange $CHI^*_3 + I_2$. The time of illumination of cyclohexane solutions of methylene iodide and iodine varied between six to 30 minutes. The results of the study of the velocity of the atomic exchange $CH_2I^*_2 + I_2$ are given in Table 5.

The concentrations of exchanging substances were $|CH_2I^*_2| = 0.01$ equiv/1 and $|I_2| = 0.005$ equiv/1. In this case, the ratio x/c tends towards its limiting value

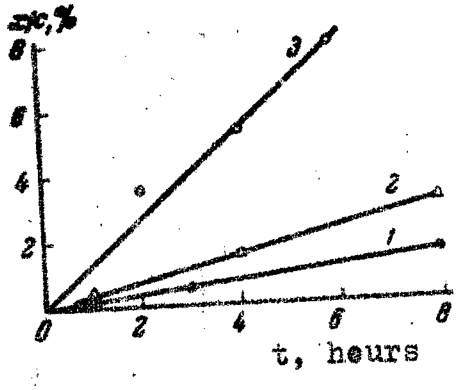


Fig. 2. Velocities of atomic reactions of isotope exchange for: 1 - CH_3I, 2 - CH_3CH_2I, 3 - $CH(CH_3)_2I$ depending on the length of illumination of the solutions.

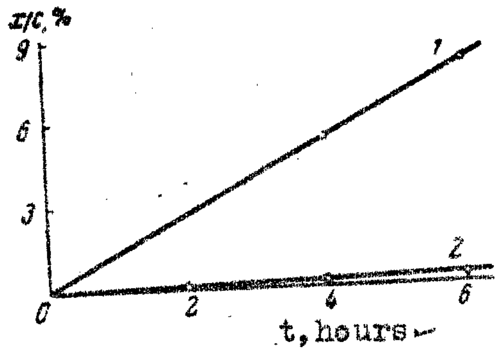


Fig. 3. Velocities of atomic isotope exchange in percentages for: 1 - isopropyl iodide; 2 - propyl iodide, depending on the length of illumination of the solutions.

Table 5

Velocity of the Atomic Exchange.

Time of illumination in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % in an hour
	x	c		
0,1	500	10000	5	34
0,17	574	10000	5,7	
0,34	900	10000	9	
0,5	1200	10000	12	

Table 6

Velocity of Atomic Exchange $CHI_3^* + I2$

Time of illumination in hours	Activity in imp/min		$\frac{x}{c}$, %	Average velocity in % in 1 hour
	x	c		
0,17	730	260000	0,28	114
0,5	2600	260000	1,0	
1,0	5000	260000	1,9	

of 33 percent. The average exchange velocity is about 34 percent an hour.

Isotope Exchange $CHI_3^* + I_2$. The time of illumination of cyclohexane solutions of iodoform with iodine did not exceed one minute. The results of experiments on the study of atomic exchange $CHI_3^* + I_2$ are given in Table 6.

The concentration of substances was: $|CHI_3^*| = 0.001$ equiv/l and $|I_2| = 0.005$ equiv/l. The concentration of iodoform decreased 10 times as much in comparison with the alkyl iodides in prior experiments, because otherwise the exchange takes place so rapidly that it becomes difficult to measure. In this case, the ratio x/c tends towards 83 percent as the length of time is increased. The average exchange velocity is 114 percent an hour. If we evaluate again the exchanve velocity, according to equation (10), for a concentration equal to the one of the alkyl iodides in the previous experiments, we obtain an average exchange velocity equal to 1140 percent an hour.

We related the data collected in our experiments on the effect of the accumulation of atoms of iodine in the molecule $CH_{4-n}I_n$ to the velocity of atomic isotope exchange. The results of our study are represented in Fig. 4. According to that figure, the velocity of atomic exchange rapidly increases in proportion to the increase in thenumber of atoms of iodine in the molecule of methane, in which hydrogen is replaced by iodine.

Discussion of Results

The data which we obtained show that identical variations of molecular structure have a different effect on the velocity of the ionic and atomic reactions of the isotope exchange. The results of the study of velocities of ionic reactions of isotope exchanges are shown in our papers [8-11]. Some data on the velocity of ionic reactions of isotope exchanges taken from these papers are compared in Table 7 wih velocities of atomic reactions of isotope exchange studied in this paper.

We see from this table that, in the cases which we studied, the velocity of the atomic isotope exchange increases in the following series: methyl iodide, ethyl iodide, propyl and isopropyl iodides. The increase in the number of atoms of iodine in the molecule of methane, in which hydrogen is replaced by iodine, also causes an increase in the velocity of the atomic isotope exchange. At the same time, a reverse dependence takes place in bimolecular

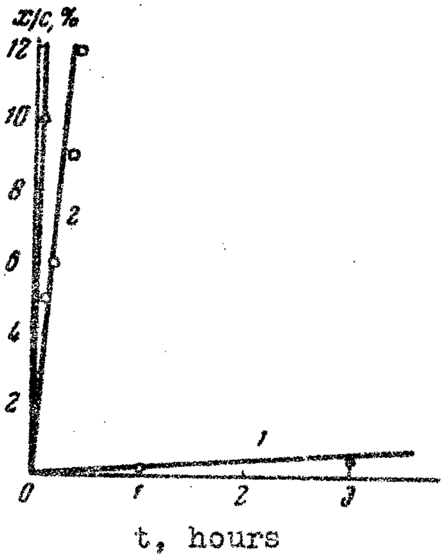
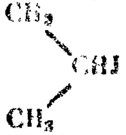


Fig. 4. The velocity of the atomic exchange in percentages for methane replaced by iodine depending on the time of illumination of reagents:
1 - CH_3I;
2 - CH_2I_2;
Δ - CHI_3
(The scale in axes is increased ten times).

Table 7

Comparison Between the Velocities of Ionic and Atomic Reactions in Isotope Exchange

RJ	Atomic exchange	Ionic exchange
	w, % per hour	$k_{100^\circ} \cdot 10^6$ 1 mol^{-1} sec^{-1}
CH_3J	0,02	1200
CH_3CH_2J	0,04	175
$CH_3CH_2CH_2J$	0,056	100
	1,6	10
CH_2J_2	34	2,3
CHJ_3	1140	1,2

ionic exchange, related to the inversion of configuration (15]. Delamare, England, Fowden, Hughes and Ingold [16], who studied the kinetics of isotope exchanges of a series of alkyl bromides, RBr, with Br* ions in acetone solutions found that the reaction slows down and the activation energy increases when hydrogen in the molecule CH_3Br is replaced by methyl radicals.

It was shown in our papers on the study of the kinetics of ionic isotope exchanges of alkyl iodides with atoms of iodine in 90 percent solutins of ethyl alcohol, cited above, that the velocity of the reaction diminishes when the carbon chán of the alkyl radical in transition from a normal propyl to its isomer is lengthened, and when the atoms of iodine accumulatein the molecule of methane, in which hydrogen is replaced by iodine.

The reason for such a difference between ionic and atomic reaction undoubtedly lies in the difference of energy barriers, which are to be surmounted in reactions of the types mentinned above.

It is possible that the activation energy of the process, in cases of inversion of the configuration, is determined by the barrier which the atom of carbon has to overcome when passing between three substitutes.

It is very possible that the substitution of atoms of hydrogen by alkyl radicals increases this barrier. The activation energy therefore increases during the transition from CH_3I to CH_3CH_2I and CH_3CHICH_3. This explains why the isotope exchange goes faster in the case of CH_3CH_2I than in the case of CH_3CHICH_3.

Dostrovsky, Hughes and Ingold [17, 18] express a point of view close to ours concerning the reason for the delay in ionic exchange reactions, when atoms of hydrogen are substituted by methyl radicals in molecules of CH_3Br and CH_3CH_2Br. These authors consider that the delay of reactions in the above mentioned cases is related to the appearance of steric hindrances. The above mentioned authors consider however that the effect of "steric compression" does not lower the entropy but increases the activation energy. In this manner, both points of view virtually coincide. It seems to us that our point of view permits one to give a better explanation of the effect of the substitution of atoms of hydrogen by atoms of halogen in the molecule of methyl halides, than the hypothesis of steric hindrances.

Atomic exchanges take place according to the radical-chain mechanism. The activation energy in this case depends directly on the strength of the bond between halogens and the atom of carbon. According to kinetic data, the energy of this bond is equal to 50 kcal in case of normal C_3H_7I. In iso-C_3H_7I, it is equal to 46 kcal [19]. Data based on the spectra of combination dispersion [20] gives approximately the same ratio of energies for these bonds. It was shown in a similar manner that the energy of bonds C - Br and C - I for the same atom of carbon gradually diminishes [21] with the accumulation of atoms of bromine and iodine in the molecule.

It is clear, therefore, that the velocity of the atomic exchange must increase with the accumulation of atoms of halogen in the molecule, with the transition from normal radicals to the iso structure, and with the substitution of hydrogen in CH_3I by the methyl radical.

Thus, data which we obtained confirm the hypothesis concerning various effects of structural changes on the velocity of reactims proceeding according to ionic or radical-chain mechanisms.

The rules, which we discovered in the current study, have created a new criterion for the establishment of the mechanism of reactions which take place in solutims.

Results

1. It is shown in the case of iodine-substituted hydrocarbons that the isomerization of alkyl radicals, as well as the substitution of hydrogen atoms in the molecule of CH_3I by atoms of iodine or by hydrocarbon radicals, accelerates the atomic reactions of isotope exchange.

2. The velocity of the process changes in atomic reactions of isotope exchange in proportion to the variation of the strength of the bond of carbon with halogen.

3. It is shown that equal changes of molecular structure influence the velocity of ionic and atomic reactions of isotope exchange differently. Structural changes in the molecule of alkyl halogen which cause a delay of ionic reactions, accelerate the reactions, which proceed according to radical-chain mechanism.

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