

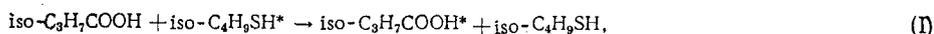
KINETICS OF HYDROGEN EXCHANGE BETWEEN  
ISOBUTYRIC ACID AND ISOBUTYLTHIOL IN  
VARIOUS SOLVENTS

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The kinetics of hydrogen exchange between isobutyric acid and isobutylthiol in nonpolar solvents, as well as in  $C_2Cl_4$  in the presence of pyridine, was investigated by the method of IR spectroscopy. The rate constant and activation energy of the process were determined.

According to the NMR data [1-4], the rate of proton exchange in the OH group of water and alcohols decreases appreciably in solvents, the molecules of which are capable of the formation of a hydrogen bond as proton acceptors. This communication presents the results of an investigation of the influence of the solvent on the kinetics of the reaction



previously studied in  $CCl_4$  [5]. We used tetrachloroethylene, the molecules of which practically do not differ from  $CCl_4$  in the nature of the interaction with the active groups XH of the dissolved molecules, according to the spectroscopic criteria; cyclohexane, one of the most inert solvents; benzene, a weak electron donor [6]; tetrachloroethylene with additions of various amounts of pyridine, an active proton acceptor [7, 8].

The rate of establishment of an equilibrium distribution of isotopes in the system isobutyric acid -d-isobutylthiol-solvent was measured according to the IR absorption spectra. The process was conducted in a glass cuvette 1, 2, or 5 cm thick with fluorite windows. The monochromator of the IKS-12 instrument (LiF prism) was tuned to one of the maxima of the compound band  $\nu_{OD}$  of dimers of d-isobutyric acid, 2260 or 2080  $\text{cm}^{-1}$ , the cuvette with the solution of acid was set up in the spectrometer beam, and after the spraying of a measured amount of d-thiol into it, the decrease in the transmission at the given frequency with time on account of an increase in the concentration of the d-acid, was recorded. Identical results were obtained at both frequencies. To avoid distortions on account of the inertia of the recording device, the results of the experiments at concentrations and temperatures at which the period of half-exchange  $\tau_{1/2}$  was no less than 10 sec were subjected to quantitative treatment. The cuvette was thermostatically controlled with an accuracy within 0.5°. The rate of hydrogen exchange, independent of the time,  $Q/g$  ( $g$  is the isotopic correction), was calculated according to the formula

$$\frac{Q}{g} = \frac{\ln 2}{\tau_{1/2}} \cdot \frac{[A][B]}{[A] + [B]} \quad (1)$$

([A], [B] are the concentrations of the acid and thiol;  $\tau_{1/2}$  is the period of half exchange, determined experimentally). The use of this formula for systems in which the distribution coefficient of the isotopes differs from one may lead to appreciable systematic errors [9]; therefore, the distribution coefficient  $K$  was measured under equilibrium conditions:

$$K = \frac{[OD]_{\infty}[SH]_{\infty}}{[OH]_{\infty}[SD]_{\infty}}$$

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TABLE 1

Solvent	T, °C	Number of experiments	Interval of concentrations · 10 <sup>3</sup> , M		α	β	k, liters/mole · sec (at α = β = 1)
			acids	thiol			
C <sub>2</sub> Cl <sub>4</sub>	20	15	1-17	1-20	0,9 ± 0,1	0,8 ± 0,1	4,2 ± 0,5
	12	16	2-20	1-20	1,1 ± 0,1	1,0 ± 0,1	2,0 ± 0,2
	7	18	5-25	2-25	0,8 ± 0,1	1,0 ± 0,1	1,4 ± 0,2
	1	16	5-25	2-30	0,9 ± 0,1	1,0 ± 0,1	0,9 ± 0,1
	-4	12	5-25	4-40	0,6 ± 0,1	0,9 ± 0,1	0,55 ± 0,06
	-8,5	23	5-50	4-60	0,9 ± 0,1	1,0 ± 0,1	0,22 ± 0,06
C <sub>6</sub> H <sub>6</sub>	20	20	7-35	4-30	0,7 ± 0,1	1,1 ± 0,1	2,3 ± 0,2
	12	18	7-25	4-30	1,1 ± 0,1	0,9 ± 0,1	1,7 ± 0,2
	7	20	5-25	4-30	0,9 ± 0,1	0,9 ± 0,1	1,2 ± 0,1
C <sub>6</sub> H <sub>12</sub>	20	16	2-35	3-25	0,9 ± 0,1	0,8 ± 0,1	2,6 ± 0,2
	13	17	2-25	2-25	1,0 ± 0,1	1,2 ± 0,1	1,6 ± 0,1
	7	20	2-25	2-20	1,0 ± 0,1	0,8 ± 0,1	1,0 ± 0,1
C <sub>2</sub> Cl <sub>4</sub> + 0,2% C <sub>6</sub> H <sub>5</sub> N	16	12	7-50	6-40	1,0 ± 0,1	0,9 ± 0,1	1,5 ± 0,1
	-4	11	10-40	5-25	0,8 ± 0,1	0,9 ± 0,1	0,36 ± 0,04
C <sub>2</sub> Cl <sub>4</sub> + 0,42% C <sub>6</sub> H <sub>5</sub> N	20	10	14-50	12-40	0,6 ± 0,1	0,8 ± 0,1	1,2 ± 0,2
	0	9	10-40	5-25	0,9 ± 0,1	1,2 ± 0,1	0,35 ± 0,04
C <sub>2</sub> Cl <sub>4</sub> + 0,94% C <sub>6</sub> H <sub>5</sub> N	21	10	10-70	6-30	0,7 ± 0,1	1,3 ± 0,1	0,63 ± 0,06
	-0,5	8	10-40	10-50	0,9 ± 0,1	1,1 ± 0,1	0,20 ± 0,02
C <sub>2</sub> Cl <sub>4</sub> + 2,8% C <sub>6</sub> H <sub>5</sub> N	22	10	10-70	10-50	1,4 ± 0,1	1,2 ± 0,1	0,49 ± 0,07
	0	9	10-40	10-40	0,8 ± 0,2	0,9 ± 0,1	0,16 ± 0,02
C <sub>2</sub> Cl <sub>4</sub> + 5% C <sub>6</sub> H <sub>5</sub> N	22,5	11	15-70	10-70	1,0 ± 0,3	1,1 ± 0,2	0,44 ± 0,04
	-2,5	8	10-40	10-40	1,4 ± 0,3	1,1 ± 0,2	0,14 ± 0,02

The equilibrium concentration  $[OH]_{\infty}$  was determined according to the band  $\nu$  OH 3540  $\text{cm}^{-1}$ , the remaining concentrations from the initial conditions and equations of the balance. We found  $K = 1.1 \pm 0.1$ , i.e., the use of the formula is justified. Just as in [5], we investigated the dependence of the reaction rate on the concentration of the components, and to determine the orders of the reaction with respect to the acid  $\alpha$  and with respect to the thiol  $\beta$  we solved the surplus system of equations

$$\lg \{r/([A] + [B])\} = \lg k + (\alpha - 1) \lg A + (\beta - 1) \lg B \quad (r = \ln 2/\tau_{1/2})$$

The calculations were performed on a MIR-1 electronic computer by the method of least squares. The results obtained are presented in Table 1. It is evident that the values of  $\alpha$  and  $\beta$  in all the solvents at each temperature are close to one, so that the reaction of isotopic exchange proceeds according to a bimolecular mechanism, regardless of the nature of the nonpolar solvent, and also in the case of a mixed solvent, tetrachloroethylene-pyridine. The last column of the table presents the average values of the bimolecular rate constant, calculated for  $\alpha = \beta = 1$ . In a plot of  $\log k$  vs  $1/T$ , the points for all nonpolar solvents are situated around one straight line (Fig. 1), which was constructed by the method of least squares, considering the weight of each point. The activation energy  $E$ , calculated from the slope of this straight line, is equal to  $12.6 \pm 0.8$  kcal/mole, so that the rate of the reaction of hydrogen exchange (I) in nonpolar solvents is expressed by the formula

$$Q/g = 6.8 \cdot 10^9 \exp(-12600/RT)[A][B]$$

It can be concluded that differences in the intermolecular interaction of active proton donors with hydrocarbon, chlorocarbon, and aromatic solvents have no appreciable effect on the kinetics of the exchange reaction. According to [5], the elementary events of this reaction consists of a synchronous transfer of protons to the cyclic complex from hydrogen bonds:



The activation energy of this reaction is significantly higher than the activation energy of the exchange of thiol with alcohols and amines [10]. The rate constant of reaction (I) at room temperature is two orders of magnitude greater than the rate constants of the exchange reactions of butylthiol with alcohols and amines. Thus, the predominant influence on the rate of exchange is exerted not by the height of the activation barrier, but by the concentration of cyclic complexes with two hydrogen bonds, in which the elementary event of exchange occurs. The concentration of such complexes in the case of the acid should be greater, in the first place, on account of its greater proton donor capacity in comparison with the alcohol or amine, and in the second place, in view of the closer to optimum orientation of the hydrogen bonds in the complexes (II) and in the four-membered mercaptan-alcohol or -amine complex.

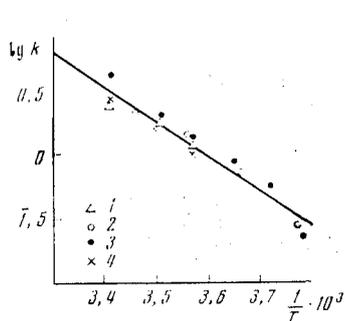


Fig. 1

Fig. 1. Dependence of  $\log k$  on  $1/T$  for the exchange reaction in nonpolar solvents: 1) benzene; 2)  $\text{CCl}_4$  (according to the data of [5]); 3)  $\text{C}_2\text{Cl}_4$ ; 4) cyclohexane.

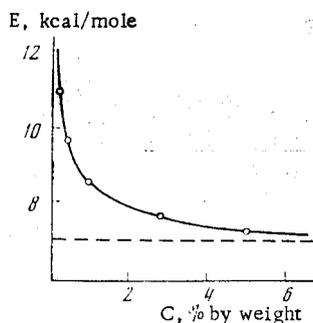


Fig. 2

Fig. 2. Dependence of the activation energy of exchange in a tetrachloroethylene-pyridine mixture on the pyridine concentration.

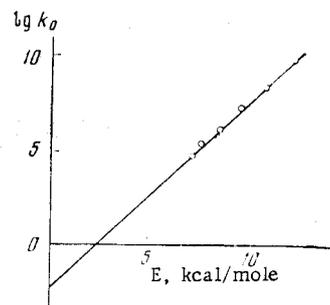


Fig. 3

Fig. 3. Relationship between  $\log k_0$  and  $E$  for the reaction of isotopic exchange in the presence of pyridine.

The rate constants of the exchange reaction between iso- $\text{C}_3\text{H}_7\text{COOH}$  and iso- $\text{C}_4\text{H}_9\text{SH}$  in  $\text{C}_2\text{Cl}_4$  in the presence of various amounts of pyridine were determined at two values of the temperature and used to calculate the activation energy, which was calculated according to the formula

$$E = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{k_1}{k_2}$$

The dependence of the value of  $E$  on the content of pyridine in  $\text{C}_2\text{Cl}_4$  is presented in Fig. 2. From the figure it is evident that  $E$  decreases with increasing pyridine concentrations, approaching a value of 7 kcal/mole. At the same time, the preexponential factor  $k_0$  in the Arrhenius equation  $k = k_0 \exp(-E/RT)$  decreases. There is a linear relationship between the quantities  $\log k_0$  and  $E$  (Fig. 3) expressing the so-called compensation effect (see, for example, [11]). Taking into account the considerations expressed in [12], the existence of a compensation effect was also verified by a comparison of the rate constants of the exchange reaction at 0 and 20°C for various concentrations of pyridine in solution. It was found that in a plot of  $\log k_{0^\circ}$  vs  $\log k_{20^\circ}$ , the points also fit well on a straight line, which confirms the existence of a correlation between  $\log k_0$  and  $E$ . The straight line of Fig. 3 is described by the equation

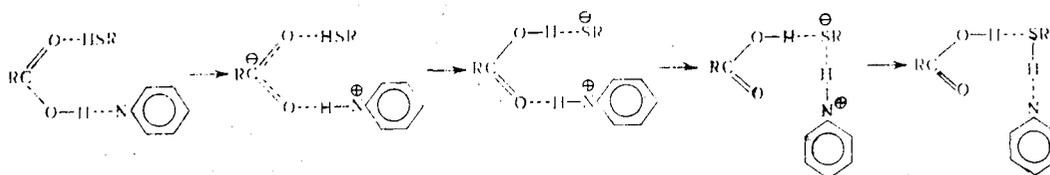
$$\lg k_0 = \lg k_{0i} + \frac{E}{2.3RT_i} \quad (2)$$

where  $T_i$  is the temperature of inversion (isokinetic temperature), equal to 230°K. At this temperature the rate constant  $k = k_{0i} = 0.01$  liter/mole·sec, regardless of the pyridine concentration in solution. Considering (2), the Arrhenius equation takes the form

$$k = 0.01 \cdot \exp \frac{E}{R} \left( \frac{1}{230} - \frac{1}{T} \right),$$

where  $E$  can be determined from the graph of Fig. 2.

As was shown in [7], isobutyric acid forms a strong molecular complex with pyridine, with an OH . . . N hydrogen bond. The addition of a third molecule to this complex – the proton donor  $\text{RXH}$  – through a hydrogen bridge  $\text{XH} \dots \text{O}=\text{C}$ , leads to an increase in the strength of the OH . . . N bond, and in a number of cases to the appearance of a minimum on the potential energy surface of the system, corresponding to the ion pair. Therefore, the first step in the reaction of hydrogen exchange between acid and thiol with the participation of pyridine may be considered to be the transfer of a proton in the trimolecular complex from the acid to pyridine. The proton donor capacity of the oxygen atom is greatly increased as a result of the formation of the carboxylate ion; the hydrogen bond  $\text{SH} \dots \text{O}$  is strengthened, which facilitates the transfer of a proton from the SH group. The event of exchange ends in the recombination of the mercaptide ion and the pyridinium cation, with the formation of neutral molecules:



With increasing pyridine concentration in solution, this mechanism evidently becomes dominant, since in the presence of a 10-fold excess of pyridine, more than 90% of the acid molecules in solution are already in the form of a complex with pyridine [7].

#### LITERATURE CITED

1. J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Amer. Chem. Soc.*, **84**, 4677 (1962).
2. O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).
3. K. C. Tewari and N. C. Li, *Canad. J. Chem.*, **48**, 1616 (1970).
4. P. A. Clarke and N. F. Hepfinger, *J. Organ. Chem.*, **35**, 3249 (1970).
5. G. S. Denisov and A. L. Smolyanskii, *Kinetika i Kataliz*, **9**, 902 (1968).
6. A. L. Smolyanskii, *Optics and Spectroscopy* [in Russian], *Collection II* (1963), p. 254.
7. G. V. Gusakova, G. S. Denisov, and A. L. Smolyanskii, *Zh. Prikl. Spekr.*, **14**, 860 (1971).
8. S. E. Odinokov, A. V. Iogansen, and A. K. Dzizenko, *Zh. Prikl. Spekr.*, **14**, 418 (1971).
9. G. S. Denisov, B. M. Kuznetsov, and K. G. Tokhadze, *Kinetika i Kataliz*, **12**, 1555 (1971).
10. S. F. Bureiko, G. S. Denisov, and K. G. Tokhadze, *Kinetika i Kataliz*, **12**, 62 (1971).
11. A. A. Balandin, *The Multiplet Theory of Catalysis* [in Russian], Part 11, *Izd. MGU* (1964).
12. O. Exner, *Coll. Czech. Chem. Comm.*, **29**, 1094 (1964).