KINETICS OF HYDROGEN EXCHANGE BETWEEN THE CARBONYL GROUP OF AN ACID AND THE THIOHYDRYL GROUP OF A MERCAPTAN IN THE GAS PHASE

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The results obtained from measurements of the kinetics of hydrogen exchange are of great value in studies of intermolecular proton transfer in systems where the partners may act as proton donors as well as proton acceptors in the formation of the hydrogen bond. The exchange obviously involves cooperative transfer of protons in a cyclic complex with hydrogen bonds [1, 2], and in constructing a model for this elementary act it is expedient to make use of kinetic data obtained in the gas phase. The present paper investigates the kinetics of the reaction

$$RCOOD + CH_3SH \rightleftharpoons RCOOH + CH_3SD$$

for formic and acetic acids in the gas phase by the method of IR spectroscopy. The reaction was carried out in a gas cell made of glass 20 cm long with CaF_2 windows. The change in intensity with time of the ν(OH) and ν(OD) bands of the isotopic forms of the acid gave the rate of establishment of the equilibrium isotopic distribution between the OH and SH groups. In the concentration and temperature range investigated, the half-period of the reaction varied between 10 sec and 30 min. The velocity of hydrogen exchange, independent of time, $R \equiv Q/g$ (g, the isotope correction), was calculated as in [3]. For each system the value of R was determined as a function of the concentration of one component for a constant amount of the other component. In determining the reaction orders α and β from the experimental rate values

$$R = k[OD]^{\alpha}[SH]^{\beta}$$

the question arises of allowing for dimerization of the acid in the gas phase. If for [OD] we use only the concentration of the monomeric acid, which may be found with the aid of known values of the monomer–dimer equilibrium constant, the value of α for acetic acid at 25° is found to be 3.7, and for formic acid 3.4. If we use the concentrations determined by the total number of acid molecules in unit volume, we obtain for α a value ~2. The order of the reaction with respect to mercaptan, β, is close to unity. We assume that at the present time it is expedient to use total acid concentrations, since this is done when evaluating liquid phase data obtained by the NMR method [4]. In the first place, studies of similar exchange reactions in the gas phase between methylmercaptan and very weakly associated methanol gave the value 2 for α [5]. Also, in CCl_4 solutions, when the methanol concentration was varied over wide limits, considerable changes of the proportions of monomers and dimers had no effect on the velocity constant or on the reaction orders, calculated on the total alcohol concentrations [3]. In the second place, experiments in the present work showed no systematic change of the velocity constant when the concentration was varied over a fairly wide range. Finally, an attempt to discriminate kinetically between monomers and dimers in the hydrogen exchange of amides with water in solution was also unsuccessful [6]. Over the investigated range of total reactant concentrations for the system formic acid–mercaptan $(0.27\text{-}1.8)\cdot 10^{-3}$ and $(0.27\text{-}3.2)\cdot 10^{-3}$ mole/liter respectively, and for the system acetic acid–mercaptan $(0.11\text{-}0.97)\cdot 10^{-3}$ and $(0.27\text{-}3.2)\cdot 10^{-3}$ mole/liter, the following values were obtained for the reaction orders:

$$HCOOD + CH_3SH, \quad \alpha = 2.1 \pm 0.2 \quad \beta = 0.8 \pm 0.2; \tag{I}$$

$$CH_3COOD + CH_3SH, \quad \alpha = 1.9 \pm 0.1, \quad \beta = 0.8 \pm 0.1. \tag{II}$$

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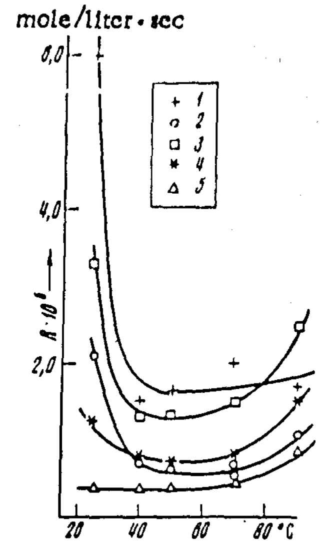

Fig. 1. Dependence of the velocity of the process $CH_3SH + CH_3COOD \rightleftharpoons CH_3SD + CH_3COOH$ on temperature. Concentrations of acid and mercaptan (mole/liter): 1) (0.97 and 2.16)·10^{-3}; 2) (0.97 and 0.54)·10^{-3}; 3) (0.97 and 1.08)·10^{-3}; 4) (0.47 and 1.08)·10^{-3}; 5) (0.23 and 1.08)·10^{-3}.

As in the system alcohol – mercaptan [5], the reaction velocity increases quadratically with the concentration of the hydroxyl-containing component, and linearly with the mercaptan concentration. In this case, it may be assumed that we are concerned with a trimolecular reaction, if the process takes place homogeneously. At 25° the kinetics of the exchange reaction of methylmercaptan with formic acid showed no systematic variation when the walls and windows of the cell were coated with a polyvinyl chloride film, when the surface of the CaF_2 windows was increased threefold, or finally when the S/V ratio was increased by factors of 2.3 and 4.8 by packing with glass tubes. It may therefore be assumed that in our experiments the process is in fact mainly homogeneous. The values of the velocity constant calculated for $\alpha = 2$, $\beta = 1$ are equal to $(1.3 \pm 0.3) \cdot 10^4$ and $(0.33 \pm 0.05) \cdot 10^4$ liter^2/mole·sec for systems (I) and (II), respectively. The velocity constant of proton exchange increases with increasing tendency for the parrners to form H bonds as proton donors from acetic acid to formic acid. The values of k obtained for acids are more than 10 times greater than the values of the exchange velocity constant in the gas-phase system methanol – methylmercaptan $(0.022 \pm 0.002) \cdot 10^4$ liter^2/mole^2·sec [5], corresponding to a considerable increase in the proton donor property of the OH group. *A similar increase in the exchange velocity with increased proton donor property of the alcohols and secondary amines is also observed in* CCl_4 *solution, where, in contrast to the gas phase, the kinetics obey a bimolecular law.*

The velocity of hydrogen exchange was measured at different temperatures from 5 to 90°. The results obtained are shown in Figs. 1 and 2, in which it is particularly evident that the reaction velocity decreases with temperature. The nature of the temperature behavior depends on the relative reactant concentrations. At low acid concentrations a temperature rise from 50 to 90° even gives a slight increase in the exchange velocity. An examination of the concentration dependence of the exchange velocity at different temperatures shows for the system: $HCOOD + CH_3SH$ that the reaction order does not remain constant: the value of α decreases from 2.1 ± 0.2 at 10° to 1.8 ± 0.2 at 50° and then to 1.3 ± 0.2 at 90°; the value of β remains close to unity.

The main results of the work may be interpreted on the basis that the hydrogen exchange reaction involves two stages, the formation of a bimolecular complex with hydrogen bonds, and proton transfers within this complex when it is activated by a third molecule or in a trimolecular complex formed by interaction with a third molecule:

$$AH^* + BH + N \underset{2}{\overset{1}{\rightleftarrows}} C + N, \qquad (1) \qquad\qquad C + B \underset{6}{\overset{5}{\rightleftarrows}} D + B, \qquad (3)$$

$$C + A \underset{4}{\overset{3}{\rightleftarrows}} D + A, \qquad (2) \qquad\qquad D + N \underset{8}{\overset{7}{\rightleftarrows}} AH + BH^* + N. \qquad (4)$$

Here $A \equiv AH^* + AH$; $B \equiv BH^* + BH$; $N \equiv A + B$; C and D are complexes with hydrogen bonding before and after the exchange act. For ideal labeling, $k_1 = k_8$, $k_2 = k_7$, $k_3 = k_4$, $k_5 = k_6$. Taking $d[C]/dt = 0$, $d[D]/dt = 0$, which is strictly true for the hydrogen exchange reaction, we have for the change of concentration of BH^* with time:

$$d[BH^*]/dt = k_1[N]([AH^*][BH] - [AH][BH^*]) \cdot \cdot (k_3[A] + k_5[B]) / (2k_3[A] + 2k_5[B] + k_2[N]). \qquad (5)$$

It is known [7] that the change in concentration of the labelled compounds with time, resulting from the reaction $AH^* + BH \rightarrow AH + BH^*$, is described by the equation $d[BH^*]/dt = R([AH^*][BH] - [AH][BH^*])/[A][B]$. Therefore, from (5),

$$R = k_1[A][B][N](k_3[A] + k_5[B]) / (2k_3[A] + 2k_5[B] + k_2[N]). \qquad (6)$$

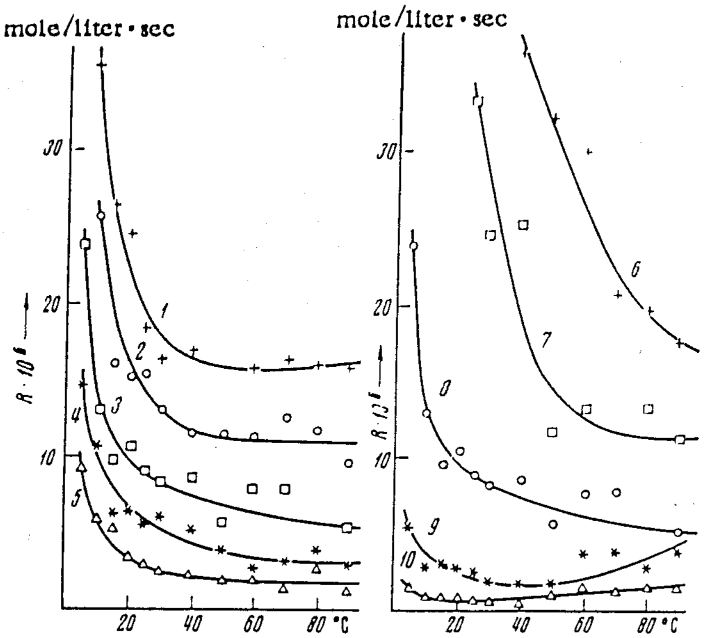

Fig. 2. Dependence of the velocity of the process $CH_3SH + DCOOD \rightleftharpoons CH_3SD + DCOOH$ on temperature and on concentrations of acid and mercaptan (mole/liter):

Curves No.	Conc. of acid $\times 10^3$	Conc. of mercaptan $\times 10^3$	Curves No.	Conc. of acid $\times 10^3$	Conc. of mercaptan $\times 10^3$
1	0,87	3,24	6	1,83	1,08
2	0,87	2,16	7	1,35	1,08
3	0,87	1,08	8	0,87	1,08
4	0,87	0,54	9	0,41	1,08
5	0,87	0,27	10	0,21	1,08

Since the processes of formation and dissociation of the complexes with hydrogen bonding proceed much more rapidly than proton exchange processes inside the molecular complexes [1], we may assume that in the denominator of (6) $2k_3[A] + 2k_5[B] \ll k_2[N]$, and hence

$$R = \frac{k_1}{k_2}[A][B]\{k_3[A] + k_5[B]\}. \tag{7}$$

If formation and dissociation of the bimolecular complexes of (1) and (4) proceed without the participation of a third molecule, then the approximation gives $2k_3[A] + 2k_5[B] \ll k'_2$.

It is seen from (7) that, according to the magnitude of the ratio k_5/k_3, the observed reaction is of second order with respect to A and B, or else there is an intermediate case. It is not likely that participation of the molecules A and B in processes (2) and (3) leads only to transfer of energy of the complex. In the interaction processes there is the possibility of forming a trimolecular complex with hydrogen bonding, where, as noted in [8], synchronous transfer of protons occurs with lower activation energies than in the bimolecular complex. Obviously the OH group of molecule A forms stronger bonds with the complex AB than the group SH of molecule B, which leads to $k_3 > k_5$ and $\Delta E_3 < \Delta E_5$. At 25° the velocity of the exchange reaction depends quadratically on the concentration of the acid AH, and hence (7) may conveniently be expressed in the form

$$R = \frac{k_1}{k_2} k_3 [A]^2 [B] \left\{1 + \frac{k_5}{k_3} \frac{[B]}{[A]}\right\}, \tag{8}$$

where the second term in the brackets must be small compared with unity, and since in our conditions the concentrations [A] and [B] are not very different, we may in fact assume that $k_3 > k_5$.

The temperature variation of the reaction velocity also confirms the assumption of a stage mechanism. If the second term in (8) is small, the observed velocity constant

$$k_e = \frac{k_1}{k_2} k_3 = k_0 \exp\left(-\frac{\Delta H + \Delta E_3}{RT}\right), \qquad (9)$$

where ΔH is the energy of the complex with hydrogen bonding ($\Delta H < 0$), and ΔE_3 is the energy of the trimolecular process (2). In those cases in which $|\Delta H| > \Delta E_3$, the velocity of the process decreases with rising temperature. It is seen from (8) that as the temperature rises, the contribution of the second term in brackets must increase for $\Delta E_5 > \Delta E_3$. This leads to a perturbation of the simple exponential function $k_e(t)$. The measured velocity constant decreases more slowly than according to an exponential law, and after passing through a minimum, begins to increase slowly at high temperatures. The contribution of the second term depends on the ratio B/A, and the experimentally determined orders will vary with temperature. Thus the experimentally determined temperature dependence of the exchange velocity may be due to the fact that the reaction proceeds along two parallel paths after formation of the bimolecular complex. Recording the temperature dependence of the pre-exponential factor in the form $k_0 = k_0' T^n$ (the value of n for the trimolecular reaction, calculated for different models of the activated complex, lies between −3 and −5) also fails to describe the experimental data by an Arrhenius type equation. Of course the temperature dependence of the pre-exponential multiplier may make an appreciable contribution to the observed temperature behavior of the velocity of the exchange reaction, if the energy in the exponential index is not very great.

It is not out of the question that exchange is also occurring in the reaction system by some other mechanism not allowed for in our suggested scheme and that the kinetic parameters obtained here are to some extent effective values.

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