SPECTROSCOPIC INVESTIGATION OF THE KINETICS OF HYDROGEN EXCHANGE BETWEEN AMINO AND SULFHYDRYL GROUPS IN THE GAS PHASE. DIMETHYLAMINE – METHYL MERCAPTAN

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The exchange of hydrogen between dimethylamine and deuteromethyl mercaptan in the gas phase was studied using IR absorption methods. Values of the rate constant were obtained at temperatures in the range 10-80°C. The results were interpreted assuming a stepwise reaction mechanism: formation of a bimolecular complex with hydrogen bonding, and proton transfer within the complex during interaction with a third molecule. It was found that the value of the rate constant is determined by the same features of the electronic structure of the XH groups as control the ability of these groups to form hydrogen bonds.

In studies of the kinetics of hydrogen exchange in groups able to form hydrogen bonds both as proton donors and acceptors it has been shown [1-3] that the rate constant k for isotopic hydrogen exchange in such systems is determined by those features of the electronic structure of the XH group which determine the ability of these groups to form hydrogen bonds. In [3] it was found that the increase in the proton donor ability of the XH groups in a series of alcohols and secondary amines leads to an increase in the value of k. However, almost all the investigations of hydrogen exchange have been carried out in liquids or solutions. There is a particular interest in examining the kinetics on intermolecular hydrogen exchange in the gas phase, where the process occurs under conditions of minimal interaction between a component and its environment. Thus, infra-red absorption measurements have shown [4] that the exchange mechanism is appreciably different in the gas and liquid phases.

In the present work IR spectroscopy has been used to study the kinetics of hydrogen exchange between the NH group in dimethylamine and the SD group in deuteromethyl mercaptan in the gas phase and at various temperatures and reagent pressures. During the experiments the intensities of the absorption bands ν_{NH}, ν_{ND}, ν_{SH} were recorded as a function of time. The spectrometer was tuned onto the maxima of the appropriate absorption bands; for the amine recording was carried out at the frequencies 3348 cm^{-1} (P-branch) or 3366 cm^{-1} (R-branch) of ν_{NH} and 2517 cm^{-1} of ν_{ND}, and for the mercaptan at 2622 cm^{-1} (R-branch of ν_{SH}); these frequencies are in good agreement with literature values [5, 6]. As an example a spectrogram obtained after an exchange reaction is shown in Fig. 1. The maximum scatter in the kinetic characteristics obtained for the various absorption bands was 15%, the error being defined as the average deviation from the measured value for a large number of experiments (16-25 at each temperature).

The work was carried out on a modified IKS-11 spectrometer with a LiF prism and a PbTe detector cooled with liquid oxygen. The time for half exchange in the amine-mercaptan system at CH_3SD pressures of 40-120 mm Hg ($[CH_3SD] = 1.8 \cdot 10^{-3}$-$6.8 \cdot 10^{-3}$ mole/liter) and $(CH_3)_2NH$ pressures of 80-160 mm Hg ($[(CH_3)_2NH] = 3.6 \cdot 10^{-3}$-$9.1 \cdot 10^{-3}$ mole/liter), in the temperature range 10-80°C, was at least an order of magnitude greater than the time constant of the detector-recorder system. The reaction $(CH_3)_2NH + CH_3SD \rightleftharpoons (CH_3)_2ND + CH_3SH$ was carried out in a thermostatted glass vessel 35 cm long, fitted with CaF_2 windows; before each experiment the vessel was pumped out to a pressure of the order of 10^{-4}-10^{-5} mm Hg. The main body of the vessel was connected through a stopcock to a small glass bulb in which a measured amount

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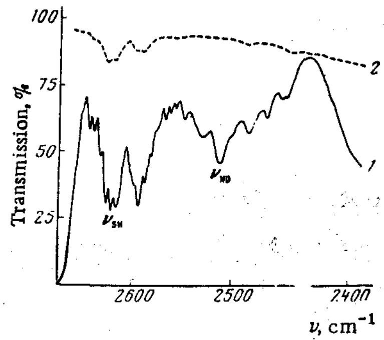

Fig. 1

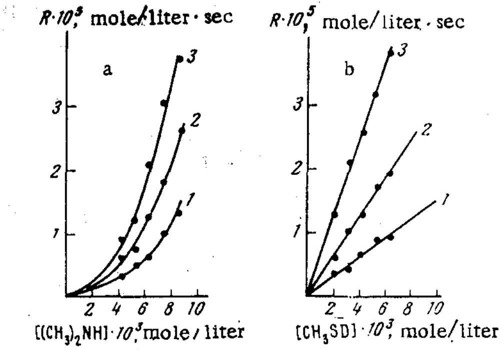

Fig. 2

Fig. 1. 1) Spectrum after exchange in the system 120 mm Hg $(CH_3)_2NH$ + 100 mm Hg CH_2SD; 2) spectrum of 100 mm Hg CH_3SD.

Fig. 2. Dependence of the reaction rate on concentration: a) amine [1) $2.25\cdot10^{-3}$, 2) $4.3\cdot10^{-3}$, 3) $6.4\cdot10^{-3}$ mole/liter CH_3SD]; b) mercaptan [1) $4.3\cdot10^{-3}$, 2) $7.5\cdot10^{-3}$, 3) $8.6\cdot10^{-3}$ mole/liter $(CH_3)_2NH$].

of CH_3SD was frozen out (spectroscopic measurements showed a deuterium content of ~80%). After filling the main section with amine the mercaptan was admitted from the small bulb; the mixing time did not exceed 0.1 sec. Since the optical density of the ν_{XH} absorption band did not exceed 0.3 under the experimental conditions, the scale of the recording on the transmission coordinate was increased by expanding the scale of the recording potentiometer (so-called "extended zero" method).

The hydrogen exchange rate was calculated from the equation [7]:

$$R=\frac{r}{p_1+p_2}p_1p_2\frac{1}{R_0T}, \tag{1}$$

where p_1 and p_2 are the amine and mercaptan pressures, respectively; r is the experimentally determined rate of approach of the system to equilibrium; R_0 is the gas constant; R is the time-independent exchange rate, R being related to the true exchange rate Q by the relationship

$$R=Q/g, \tag{2}$$

where g is a parameter characterizing the isotope effect associated with the nonideality of the label.

The dependence of the rate of the process on the component pressures at 25°C is shown in Fig. 2. Similar behavior was observed at all temperatures. It is evident that the exchange rate increases with amine concentration much faster than with an increase in the mercaptan concentration. From the experimental results values were calculated for α and β in the expression

$$R = k_{exp}\,[(CH_3)_2NH]^{\alpha}\,[CH_3SD]^{\beta}, \tag{3}$$

these having the meaning of reaction orders for each component. Taking logarithms of (3) and using equation (1) the following equation was obtained:

$$\lg r(p_1+p_2)=(\alpha-1)\lg p_1+(\beta-1)\lg p_2+\text{const.} \tag{4}$$

The quantities $(\alpha-1)$ and $(\beta-1)$ were determined from the slopes of straight line plots of $\log(r/(p_1+p_2))$ versus the partial pressure of one of the reagents, the pressure of the other being constant. The value of k_{exp} was then determined using equation (3). These calculations were carried out at all the temperatures investigated, giving the root-mean-square values of k_{exp}, α and β which are shown in Table 1.

At 25°C values of k_{exp}, α and β were determined by the least squares method from the system of 25 equations

$$\ln R_i=\ln k_{exp}+\alpha\ln C_{1i}+\beta\ln C_{2i},$$

where R_i is the experimentally measured rate at amine and mercaptan concentrations C_{1i} and C_{2i}, respectively. The values obtained were $\alpha = 1.93 \pm 0.07$; $\beta = 1.11 \pm 0.05$; $k_{exp} = 78 \pm 4$, in good agreement with the results given in Table 1. It follows from Table 1 that the reaction is close to trimolecular, with

TABLE 1. Kinetic Characteristics for the Hydrogen Exchange Reaction $(CH_3)_2NH + CH_3SD \rightleftharpoons (CH_3)_2ND + CH_3SH$ in the Gas Phase

T, °C	α	β	k_{exp}	k, liter^2/mole^2 · sec
10	2,5 ±0,3	0,9 ±0,2	130 ±20	84 ±20
18	2,1 ±0,1	1,0 ±0,1	90 ±10	84 ±8
25	2,1 ±0,2	0,9 ±0,2	77 ±10	81 ±20
34	1,9 ±0,2	1,0 ±0,1	70 ±8	83 ±7
45	2,0 ±0.2	1,1 ±0,1	91 ±10	84 ±8
60	1,7 ±0,2	1,0 ±0,2	78 ±10	96 ±10
80	1,6 ±0,3	1,1 ±0,2	73 ±8	118 ±20

orders approximately second with respect to amine and first with respect to mercaptan. Values of rate constant k calculated on the trimolecular basis are also shown. However, if it is assumed that the order in mercaptan β is constant, within experimental error, over the temperature range, then for the order in amine α there is an observable tendency for it to decrease with increasing temperature: from 2.5 ± 0.3 at 10° to 1.6 ± 0.3 at 80°.

The temperature dependence of reaction rate R for fixed reagent concentrations is illustrated in Fig. 3. In most cases R has a minimum value at about 40°, while the character of the dependence is closely associated with the relative concentrations of the reagents: the higher the relative concentration of amine the more clearly marked is the minimum on the low-temperature side. The rise in R with increasing temperature here becomes less important or does not appear at all.

It is evident that the temperature dependence of the reaction rate is not exponential and the process does not obey the Arrhenius equation. We should emphasize the fact that the reagent vapor pressures never exceeded 0.2 p_s (p_s is the saturated vapor pressure) so that microcondensation of the gas on the walls [8] should not have an appreciable effect on the kinetics of the process.

In order to investigate the possible effect of chemisorption the exchange of CH_3SD and $(CH_3)_2NH$ was carried out in the vessel after packing with glass to increase the surface — volume ratio by a factor of four. Measurements made at the same gas pressures and over the whole temperature range revealed no systematic changes in the kinetic characteristics; within experimental error (10-15%) the rates were the same in the packed and unpacked vessel.

In discussing these results we will start from the assumption that the elementary act of hydrogen exchange is a cooperative transfer of protons in a cyclic complex formed by hydrogen bonds. Unlike the exchange between amines and mercaptans in solution, where the process is bimolecular and the Arrhenius equation is obeyed, in the gas phase the mechanism is more complex. The observed third order kinetics and nonexponential temperature dependence can be interpreted on the assumption that the process occurs in two stages: formation of a bimolecular complex with hydrogen bonding, and proton transfer within the complex during interaction with a third molecule.* Such a mechanism leads [9] to the following expression for the reaction rate:

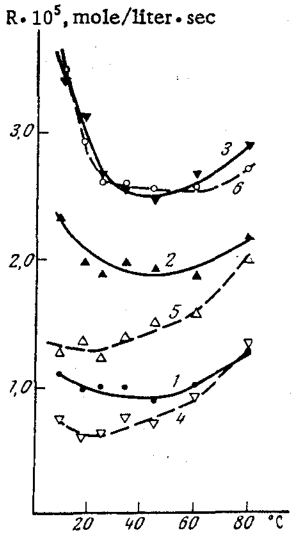

Fig. 3. Temperature dependence of the exchange reaction rate: 1) $2.15 \cdot 10^{-3}$; 2) $4.3 \cdot 10^{-3}$; 3) $5.35 \cdot 10^{-3}$ mole/liter CH_3SD with $[(CH_3)_2NH]$ = const = $7.5 \cdot 10^{-3}$ mole/liter: 4) $4.3 \cdot 10^{-3}$; 5) $6.4 \cdot 10^{-3}$; 6) $8.6 \cdot 10^{-3}$ mole/liter $(CH_3)_2NH$ with $[CH_3SD]$ = const = $4.3 \cdot 10^{-3}$ mole/liter.

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*The use of the term "proton transfer" implies the use of a label (deuterium) for spectroscopic observations and takes into account its nonideality.

$$R = \frac{k_1}{k_2} k_3 [C_1]^2 [C_2] \left(1 + \frac{k_5}{k_3} \cdot \frac{C_2}{C_1}\right), \tag{5}$$

where C_1 and C_2 are the overall reagent concentrations; k_1 and k_2 are rate constants for the forward and reverse reactions for formation of the hydrogen-bonded complex; k_3 and k_5 are rate constants for activation of hydrogen exchange in the complex by molecules of the first and second reagents, respectively. From (5) it is evident that the reaction order in each of the components can change, depending on the value of the ratio k_3/k_5. In addition it must also depend on their relative concentrations. Since in our case the concentrations of amine and mercaptan are of the same order of magnitude, while the experimentally determined reaction order in $(CH_3)_2NH$ is close to two, it can be concluded that $k_3 \gg k_5$ and the second term in (5) is small. From the inequality $k_3 > k_5$ it follows that $\Delta E_5 > \Delta E_3$ and the contribution of the second term should increase with increasing temperature. This also leads to a change in the nature of the dependence of k_{exp} on temperature, changes the experimental reaction orders, and in addition determines the dependence of the rate on the ratio of the amine and mercaptan concentrations. Thus from the assumption that hydrogen exchange in the gaseous system $(CH_3)_2NH + CH_3SD \rightleftharpoons (CH_3)_2ND + CH_3SH$ occurs in two stages there follow those principal behavioral characteristics which we have observed experimentally.

It is of interest to compare our value of the rate constant in the trimolecular approximation with the data in [4, 9]. The following values of the rate constant were found for isotopic hydrogen exchange with methyl mercaptan in the gas phase: k = 13000 ± 3000, 3300 ± 500, and 220 ± 20 liter^2/mole$^2\cdot$sec for reactions with formic acid, acetic acid, and methanol, respectively, at 25°; k = 80 ± 20 liter^2/mole$^2\cdot$sec for reaction with dimethylamine (cf. Table 1). The decrease in the value of the rate constant in this series is in accord with the reduced capabilities of these compounds in forming hydrogen bonds through proton donation. Thus in the gas phase there is the same correspondence between the rate of hydrogen exchange and the ability to form hydrogen bonds as is observed in liquid systems.

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