

KINETICS OF PROTON EXCHANGE BETWEEN CD_3OH
AND $(\text{CD}_3)_2^{15}\text{NH}$ IN THE GAS PHASE AND IN SOLUTION
IN CYCLOHEXANE

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UDC 541.123.52

Data on the kinetics of proton exchange in the gas phase should be of great benefit for determination of the mechanism of proton exchange between molecules capable of forming hydrogen bonds both as proton donors and as proton acceptors and for elucidation of the role played by complexes with H bonding in this process. Thus far, significant information has been obtained on the kinetics of noncatalytic proton exchange in solutions in inert solvents (see [1]), showing that under these conditions the process proceeds with a very low activation energy (up to 1-3 kcal/mole), not exceeding, in a number of cases, the activation energy of diffusion in these solvents. On the other hand, gas-phase processes of proton exchange in systems with H bonding may be a class of reactions having great significance for reaction-rate theory because of symmetry of the reaction path (at least for exchange between identical molecules), because of the variety of systems with H bonding existing in the gas phase, because of the reality of nonempirical calculation of the potential surface of interaction of systems consisting of very simple molecules (hydrogen halides, water, ammonia, etc.), and, finally, because of the possibility of varying the conditions for carrying out the process (temperature, pressure, and content and type of buffer gas) in a wide range. These reactions may play a special role in comparisons of the kinetics in the gas phase and in solutions, supplementing the data obtained in the study of free-radical reactions.

Investigation of the kinetics of proton exchange in the gas phase involves significant experimental and often basic difficulties. Firstly, it is very difficult to eliminate the effect of catalytic heterogeneous processes which may significantly distort the results. Secondly, the use of dynamic NMR, which is the most suitable method for investigating such processes, is complicated by spin-rotational relaxation in the gas phase, something which requires the separation of the contributions of two mechanisms of line broadening.

In the present paper, dynamic NMR was used to study comparatively the kinetics of proton exchange in the $(\text{CD}_3)_2^{15}\text{NH}$ - $(\text{CD}_3)_2^{15}\text{NH}$ and $(\text{CD}_3)_2^{15}\text{NH}$ - CD_3OH systems in the gas phase and in solution in C_6D_{12} . These isotopic modifications were chosen in order to maximally simplify the proton-resonance spectra. Dimethylamine was obtained by the method of [2] from $^{15}\text{NH}_4\text{Cl}$ (of 98% isotopic purity) and deuterioformaldehyde D_2CO (of 98.5% isotopic purity). The gas was purified by fractional distillation in vacuo and dried with freshly prepared BaO . A commercial CD_3OH preparation (of 97% isotopic purity), dried with methyl methoxide and distilled in vacuo, was used. Subsequently, it was found that the ^1H line shapes in the gas phase and in inert solvents did not depend on the presence of water right up to stoichiometric amounts (~10% concentration of the investigated substances when exchange with H_2O molecules became significant). The gas mixtures and the samples were prepared in a glass vacuum unit with a VDG-1 manometer ensuring feeding of the gases with a precision of 5%. The range of the investigated pressures was 30-2400 torr for $(\text{CD}_3)_2^{15}\text{NH}$ and 20-500 torr with respect to the alcohol and 700-1600 torr with respect to the amine for the $(\text{CD}_3)_2^{15}\text{NH}$ - CD_3OH system. An ampul with the inserted external standard (a capillary with H_2O or D_2O) was connected to the unit, evacuated at 150°C for 1 h,

A. A. Zhdanov Leningrad State University. (Presented by Academician N. M. Émanuéil', July 1, 1980.)
Translated from *Doklady Akademii Nauk SSSR*, Vol. 256, No. 3, pp. 620-624, March, 1981. Original article submitted July 1, 1980.

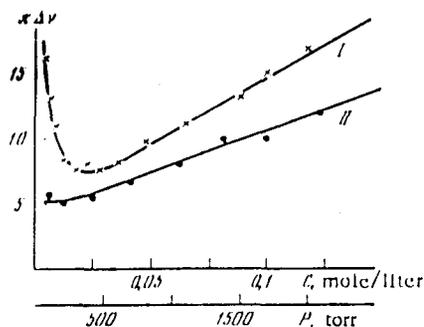


Fig. 1

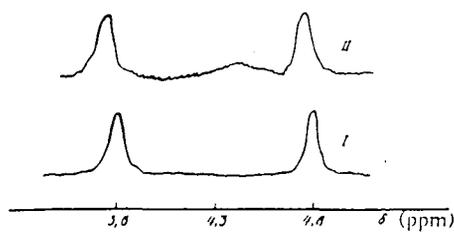


Fig. 2

Fig. 1. Relation of the half-width of the lines of $(\text{CD}_3)_2^{15}\text{NH}$ (in circular frequency units) to the concentration (pressure) in the gas phase (I) and in solution in C_6D_{12} (II).

Fig. 2. Spectra of samples containing 1500 torr $(\text{CD}_3)_2^{15}\text{NH}$ (I) and 1500 torr $(\text{CD}_3)_2^{15}\text{NH}$ + 400 torr CD_3OH (II); the chemical shifts δ were measured with respect to liquid H_2O (external standard).

and then the investigated substances were distilled into it until maximum filling of the ampul with liquid. After holding for 1 h, the ampul was again evacuated with heating, the gases were fed, and the ampul was cooled with liquid nitrogen and disconnected from the unit. The purpose of these two operations was to bring the walls of the ampul into equilibrium with the sample and to eliminate the effect of the previous history of the walls on the characteristics of the process being measured. This ensured reproducibility of the ^1H NMR absorption line shapes with a precision of 5–10% (depending on the concentrations). When the ampul was filled with glass spirals ensuring a 20-fold surface increase, the width of the lines in the spectra did not change, indicating the negligible rate of heterogeneous processes. The spectra were recorded with Jeol C60 HL (60 MHz) and Varian-CFT-20 (80 MHz) instruments in the temperature range of 40–180°C at 10° increments. Since in the studied systems the frequencies of proton exchange were small in comparison with the frequency difference of the signals ($\tau_1^{-1} \ll 2\pi J_{15}\text{NH}$ and $\tau_2^{-1} \ll 2\pi(\delta_{\text{OH}} - \delta_{\text{NH}})$, where τ_1^{-1} and τ_2^{-1} are the frequencies of homo- and heteromolecular exchange processes), in the determination of the lifetimes of states it was possible to restrict ourselves to the approximation of slow exchange.

Exchange between $(\text{CD}_3)_2^{15}\text{NH}$ Molecules. The relation of the half-width $\pi\Delta\nu$ of the doublet lines of the amine to the pressure of the pure gas at 40°C is shown in Fig. 1. As the pressure was increased from 30 to 300 torr, the half-width decreased to a value of 8 Hz. In this concentration range, the addition of several atmospheres of a foreign gas (argon) caused the doublet lines to narrow. Such a situation is characteristic of the spin-rotational mechanism of broadening of lines in a gas [3]; the rate of proton exchange in the low-pressure region was too low to measure. With increasing temperature, the lines narrowed somewhat, something which is also characteristic of shapes due to spin-rotational relaxation. In the region of 700–2400 torr, the widths of the signals increased practically linearly with pressure; in this case, a temperature increase caused the lines to broaden. It can be considered that at high pressures, spin-rotational relaxation did not make a significant contribution to the shape, which was determined by homomolecular exchange. In this case, in the absence of exchange, the half-width of the lines which was due to inhomogeneity of the field and unresolved D-H spin-spin coupling could be determined approximately from the spectra of solutions of $(\text{CD}_3)_2^{15}\text{NH}$ in C_6H_{12} at low concentrations; this evaluation gave $T_2^{-1} \cong 5 \text{ sec}^{-1}$. The linear change of the half-width $\pi\Delta\nu = T_2^{-1} + \tau_1^{-1}$ with pressure means that the rate of exchange had a second order: $V_1 = k_1[\text{XH}]^2$. Figure 1 also shows the relation of the half-width of the line of $(\text{CD}_3)_2^{15}\text{NH}$ dissolved in deuterocyclohexane C_6H_{12} to the concentration. It is evident that at identical concentrations the width of the lines in the gas was somewhat higher than in solution, and, therefore, the rate of exchange in the solution was less than in the gas.

Exchange between CD_3OH and $(\text{CD}_3)_2^{15}\text{NH}$ Molecules. For the light CD_3OH molecule in the gas phase, the spin-rotational relaxation process was very efficient, and the width of the proton resonance line at pressures of 20–150 torr was several tens of hertz. In the presence of $(\text{CD}_3)_2^{15}\text{NH}$, the width changed in a complex manner, and it did not seem possible to determine the part of the broadening due to proton exchange. Therefore, only the amine doublet was used to measure the rate of the heteromolecular reaction. The inverse lifetime of the proton in this molecule was composed additively of the probabilities of homo- and heteromolecular exchanges, with the probability of the first process being known from the results of the experiment in the ab-

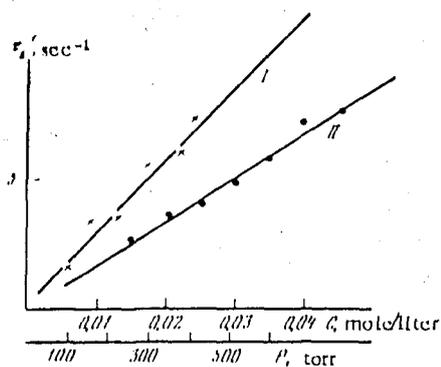


Fig. 3

Fig. 3. Relation of the frequency of exchange at 50°C between CD_3OH and $(\text{CD}_3)_2^{15}\text{NH}$ molecules to the concentration (pressure) of CD_3OH in the gas phase (I) and in solution in C_6H_{12} (II).

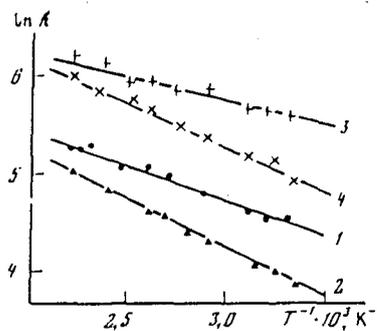
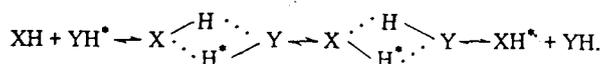


Fig. 4

Fig. 4. Temperature dependence of the bimolecular rate constant of proton exchange. Systems: 1) dimethylamine, gas; 2) dimethylamine, solution in C_6D_{12} ; 3) dimethylamine-methanol, gas; 4) dimethylamine-methanol, solution in C_6D_{12} .

sence of the alcohol: $W_2 = T_2^{-1} + \tau_1^{-1} + \tau_2^{-1} = T_2^{-1} + [\text{XH}]^{-1}(V_1 + V_2)$. Figure 2 shows spectra of the amine as a pure gas and with addition of CD_3OH at 50°C. The difference in the widths was the result of exchange with alcohol molecules. The relation of the value of τ_2^{-1} to the concentration (pressure) of the alcohol at a fixed concentration of the amine (Fig. 3) was found to be close to linear. When the content of the alcohol was fixed, the value of τ_2^{-1} practically did not change as the amount of the amine changed, although the overall width of the lines changed because of the homomolecular process. This proves that the heteromolecular-exchange reaction was also bimolecular: $V_2 = k_2[\text{XH}][\text{YH}]$.

The final experimental results, namely, the reaction orders with respect to the amine α and the alcohol β , the bimolecular rate constant k , and the activation energy E_a , the Arrhenius dependences for whose determination are shown in Fig. 4, are given in Table 1. The main conclusion which can be drawn from these data consists in the fact that during transition from the gas phase to solution in an inert solvent no sharp change occurred in the parameters of the reaction (its orders and free energies and entropies of activation). From this, it follows, firstly, that the mechanisms of proton exchange between the studied molecules in the gas and in solution were most likely identical. Secondly, the process did not require the participation or intermediate formation of ionic pairs (otherwise, exchange in the gas would be greatly retarded) and proceeded by a purely molecular mechanism characterized, apparently, by cooperative transition of protons along the H bonds in the cyclic complex [4]:



In this case, it is natural to explain the retardation of the process during transition from the gas to the liquid by the stronger solvation of the starting molecules in comparison with the cyclic transition state having a smaller dipole moment (for homomolecular exchange, the dipole moment is equal to zero). One more argument in favor of such a mechanism is the data of [4] concerning the effect of the solvent on the kinetics of proton exchange of alcohols.

TABLE 1. Kinetic Parameters of Homo- (NH-NH) and Heteromolecular (NH-OH) Proton Exchange in the Gas Phase and in Solution in C_6D_{12}

Quantity	NH-NH		NH-OH	
	gas	solution	gas	solution
α	$1,9 \pm 0,1$	$2,0 \pm 0,1$	$1,0 \pm 0,3$	$1,0 \pm 0,1$
β			$1,1 \pm 0,2$	$1,1 \pm 0,1$
$k^{30^\circ\text{C}}$ (liters/mole/sec)	87 ± 7	47 ± 6	260 ± 30	140 ± 20
E_a (kcal/mole/sec)	$1,4 \pm 0,4$	$2,0 \pm 0,4$	$1,0 \pm 0,3$	$1,8 \pm 0,4$

It seems obvious that it is precisely the possibility of formation of H bonds which determines all the special characteristics of the observed kinetics. However, we should note the following. The energy of the cyclic bimolecular complex is not more than 2-3 kcal/mole (e.g., for water dimers the calculations of [5] and [6] give a value of 2.1 kcal/mole), experimental values are lacking because these complexes are less favorable energetically than linear ones and were not recorded reliably spectroscopically, the H bonds in such a complex are highly nonlinear, and the complex can be classified quite well as a Van der Waals one. Therefore, it seems very nontrivial that the process of rearrangement of bonds with strengths of the order of 100 kcal/mole is characterized by an activation energy of the order of 1-9 kcal/mole. This may be, for example, because of strong stabilization of the activated state by two central H bonds, a stabilization which compensates practically completely the energy of the breaking X-H bonds. Another possibly explanation may be the fact that the measured values of E_a are some effective values not related directly to the event of proton transfer in the intermediate complex (if, for example, the limiting step of the reaction is the formation of cyclic complexes or effective tunneling occurs in them). It is clear that a problem of primary importance is the further experimental investigation of such processes in the gas phase, in particular the effect of pressure and the type of the foreign gas on their kinetic parameters, and also the calculation of the potential surface of the system and the profile of the reaction path, which could give convincing arguments in favor (or against) the proposed mechanism.

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