KINETICS OF THE FAST PROTON EXCHANGE
BETWEEN ETHANOL AND WATER IN AN
INERT SOLVENT

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The kinetics of intermolecular proton exchange between deuteroethanol and water has been studied in dilute CCl_4 solutions. The rate constants at 8-50° and the activation energy of the process have been determined. Comparison has been made of the parameters of the exchange reaction obtained in an inert solvent and in a binary mixture.

Among systems studied with respect to the kinetics of the fast proton exchange (proceeding according to a molecular mechanism) the most complete data have been reported for binary alcohol—water mixtures. The NMR measurements of the rate constants of the proton exchange between water and aliphatic alcohols [1-4] are in reasonable agreement and lie between 0.2-2 liters/mole · sec, with activation energies ranging from 7 to 10 kcal/mole. We have attempted to measure the rate of the process
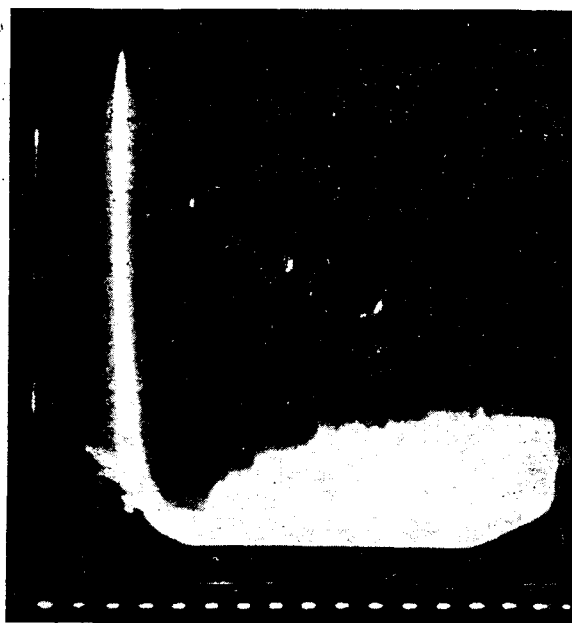
Fig. 1. The oscillogram of the deuteroethanol—water exchange in CCl_4 (time scale unit 200 msec).

$$ROH^* + HOH \rightleftarrows ROH + HOH^*$$
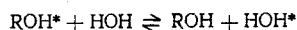
(where H^* denotes deuterium-labeled hydrogen) in CCl_4 solution by means of the infrared absorption spectra using a standard apparatus and method described in [5]. The exchange half-time (measured for reactant concentrations of the order of 10^{-3} mole/liter) was less than 1 sec. Consequently, the rate constant k calculated for the bimolecular approximation would have to be larger than 100 liter/mole · sec.

Therefore, our study of the ethanol—water system in an inert CCl_4 solution has been carried out using a stopped-flow method described in [6]. It allows the kinetic study in a liquid phase to be performed within a milisecond by measurements of the intensity of IR absorption bands of the reactants and/or products. The apparatus included an IKS-11 monochromator, a liquid-mixing device with 4-msec time resolution, and a light detector — a PbTe photoresistance ($\tau \sim$ 20-30 sec) cooled with liquid nitrogen. The optical path length in the cuvette was 20 mm. The number of experiments varied for various reactant concentrations from 15 to 19 at each of the five temperature settings studied.

Experimental work with water is difficult owing to its low solubility in CCl_4 (0.0086 mole/liter [7]) and to the presence of two equivalent protons in the water molecule. The problems connected with kinetic measurements of such complex exchange reactions have been discussed in [8]. Relationships derived in [8] were used by us to calculate the time-independent rate of the proton exchange. Water solutions were prepared using carefully dried CCl_4 (over P_2O_5 and NaA zeolite) and an MShM microsyringe with $3 \cdot 10^{-5}$-ml scale division. The accuracy of solution preparation was checked spectroscopically by measurements of the band intensity of the symmetric and antisymmetric OH vibrations ν_s and ν_{as}. The total integral absorption coefficient of these bands was found to the $(7 \pm 0.7) \cdot 10^3$ liter/mole · cm^2 in agreement with the literature value [9]. In kinetic experiments water concentration was varied from $(1-4) \cdot 10^{-3}$ mole/liter; deuteroethanol from $(5-30) \cdot 10^{-3}$ 34 mole/liter.

The deuterium exchange was monitored spectroscopically by measurements of the changes in time of the intensity at the maximum of the absorption bands of the alcohol νOD (2684 cm^{-1}) and νOH (3632 cm^{-1}). The νOH and νOD bands of water lie sufficiently far in the spectrum from those of ethanol and do not interfere with the recording. Kinetic curves were photographed from the oscillograph screen. The oscillogram recorded at 18° for the 0.01 M C_2H_5OD + 0.002 M H_2O system is shown in Fig. 1.

Experimental results show that under the conditions studied the exchange half-time between the hydroxyl groups of ethanol and water is 0.1-0.7 sec. The kinetics of the process obey an exponential law (cf. Fig. 2), and the reaction orders with respect to all reactants are close to unity (e.g., at 18°C α_C = 0.94 ± 0.08, β_B = 0.9 ±0.2).

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TABLE 1. Rate Constants of the Proton Exchange in the C_2H_5OD + H_2O System in CCl_4

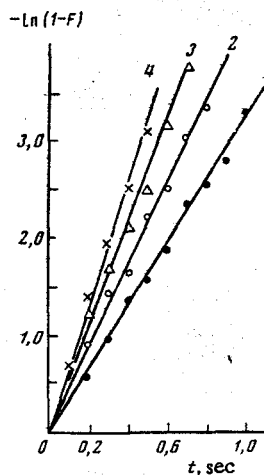| T, °C	Number of experiments	k, liters/ mole·sec	T, °C	Number of experiments	k, liters/ mole·sec
8	16	215±20	40	16	315±10
18	19	240±20	50	15	325±20
30	19	280±10			

Fig. 2. Determination of the rate of attaining the equilibrium distribution in the 0.03 mole/liter C_2H_5OD + 0.004 mole/liter H_2O at 8° (1), 18° (2) 30° (3), and 40°C (4).

The results are shown in Table 1. The activation energy of the exchange reaction calculated from these data is 1.9 ± 0.2 kcal/mole. The entropy change ΔS (17±2 cal/mole·degree) and the preexponential factor k_0 in the Arrhenius equation were calculated from well-known equations. Thus, the rate constant of the proton exchange between alcohol and water in a dilute neutral solution is given by

$$k = (6.5\pm0.1)\cdot10^3 \exp[-(1900\pm200)/R_0T] \text{ liter} \,|\text{mole}\cdot\text{sec}.$$

It can be seen that the rate constant of the proton exchange reaction studied is close to those reported for alcohol—amine and alcohol—phenol systems in CCl_4 [6, 10, 11] and exceeds by two orders of magnitude the value determined by NMR (2.7 liters/mole·sec at 42° [1]). The obtained value of the activation energy, 1.9 kcal/mole, is also considerably lower than that obtained by NMR (10 kcal/mole). This deviation, which is far out of the range of experimental errors, can be due to the fact that our experiments were carried out in CCl_4, whereas the NMR studies were carried out in binary alcohol—water mixtures. The different rates of the exchange reaction may be explained as follows. In the CCl_4 solution, water and alcohol molecules are predominantly monomers weakly interacting with the medium. In the binary alcohol—water system each molecule forms a few hydrogen bonds, acting both as a proton donor and acceptor. Therefore, the probability of formation of an intermediate cyclic complex between water and alcohol molecules is strongly diminished in the binary mixture as compared to the inert CCl_4 solution [12].

The experimental data indicate a direct correlation between the rate of intermolecular proton exchange and the tendency to form hydrogen bonds between the exchanging molecules. In our case, k is approximately two times larger than that for an ethanol—secondary amine system [10]. This parallels the hydrogen bond strength higher in the intermediate complex formed by water than in that formed by an amine molecule. For this kind of mechanism, a considerable part of the activation energy is contributed by the energy necessary to break the hydrogen bonds of the molecules undergoing exchange. It has been often stated (e.g., in [13, 14]) that the rate of the proton exchange is lower in solvents whose molecules can act as proton acceptors.

The present results confirm once more the molecular mechanism of the exchange reaction (it should be noted that ionic processes should proceed faster in the water—alcohol mixture of high dielectric permeability, than in CCl_4). They also are the first example of a quantitative comparison of parameters obtained for this type of exchange reaction in a binary mixture and in an inert solvent.

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