

INFLUENCE OF EXTERNAL ELECTRIC FIELD ON THE RATE OF HYDROGEN ISOTOPE EXCHANGE BETWEEN HYDROXYL-CONTAINING MOLECULES IN CCl_4

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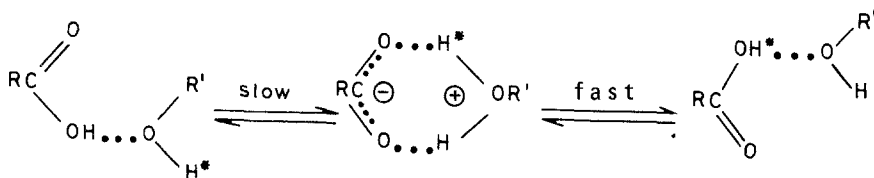
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Rates of the fast proton-deuteron exchange between CH_3OD and $\text{C}_6\text{H}_5\text{OH}$ (1), and CH_3OD and CH_3COOH (2) in dilute CCl_4 solutions have been measured by a kinetic IR spectroscopy technique. Under an imposed external electric field (10 V/m), the exchange rate in system (2) increases, which is not observed in (1). The effect is interpreted assuming that, in the second case, a cyclic ion pair with a high dipole moment is formed as a reaction intermediate.

Методом кинетической ИК-спектроскопии измерены скорости быстрого дейтериевого обмена между молекулами CH_3OD и $\text{C}_6\text{H}_5\text{OH}$ (1), CH_3OD и CH_3COOH (2) в разбавленных растворах в CCl_4 . При наложении внешнего электрического поля (10⁷ В/м) скорость обмена в системе (2) возрастает, чего не наблюдается для процесса (1). Эффект интерпретирован в предположении промежуточного образования в случае (2) циклической ионной пары, обладающей высоким дипольным моментом.

Depending on the properties of participating molecules, H-bonded complexes can be either molecular ($\text{AH} \dots \text{B}$), or ionic ($\text{A}^- \dots \text{HB}^+$), or an equilibrium can be observed with a reversible unimolecular proton transfer /1/: $\text{AH} \dots \text{B} \rightleftharpoons \text{A}^- \dots \text{HB}^+$. Sometimes on no reliable grounds whatsoever, the formation of an energetically unfavorable ion pair was postulated as the rate-determining step of some proton exchange reactions /2/. Apparently, it is sufficiently proved that most non-catalytic reactions of proton exchange between hydroxyl-containing molecules in non-polar aprotic solvents (CCl_4 , C_6H_{12}) follow a purely molecular mechanism, including a cooperative (synchronous) transfer of two protons in a cyclic H-bonded complex /3/. However, it has been shown recently /4/ that the proton exchange between the molecules of CD_3OH and CH_3COOH is sharply enhanced with increasing dielectric constant of solvents. This can hardly be interpreted in terms of the above mechanism since, during the formation of a molecular cyclic complex, the dipole moment must

slightly decrease. Actually, the rate of proton exchange between CD_3OH and $(\text{CH}_3)_3\text{COH}$ decreases with increasing ϵ of the solvent /4/. Therefore, it is natural to suppose that the exchange between alcohol and acid molecules includes, as the rate-determining step, an endothermic proton transfer in an H-bonded complex:



But the influence of solvents (even such as hydrocarbons and their halogenated derivatives) on the rate of chemical reactions consists not only in the effect of dielectric permeability. We believe it is expedient to measure the reaction rate variation under an imposed external electric field, determined entirely by the difference of the dipole moments of intermediate and initial reactants.

We have studied the $\text{CH}_3\text{OD}-\text{CH}_3\text{COOH}$ and $\text{CH}_3\text{OD}-\text{C}_6\text{H}_5\text{OH}$ exchange in CCl_4 solution by a kinetic IR spectroscopy technique. The kinetics of the proton exchange in the first system studied by a dynamic ^1H NMR method /4/, indicate that the exchange takes place in a bimolecular acid-alcohol complex. To study the kinetics of the process in a strong external electric field, a modified apparatus /5/ was used operating on the stopped-flow principle. The cell for recording the IR absorption of the solution after mixing was made of teflon. It had two stainless steel electrodes 2 mm apart along the optical path. The maximum electric field intensity, as the cell was loaded with CCl_4 , was 1.1×10^7 V/m. The dead time of our apparatus was 15 ms.

The method for calculating the parameters characterizing the exchange rates from the experimental kinetic curves was described elsewhere /5/. The maximum expected effect of the exchange rate variation in the field of the given intensity cannot be more than $\sim 10\%$, which corresponds to the average error of a single measurement. Therefore, we performed two series of numerous measurements, using the same samples of solutions both with and without the imposed external electric field. The data were processed by the least-squares method.

As is seen from Table 1, with a probability of $\alpha \leq 0.85$, one can state that, under the imposed electric field, the exchange process is enhanced in the $\text{CH}_3\text{OD}-\text{CH}_3\text{COOH}$ system. If the entire effect is attributed to the free energy variation of the intermediate, as compared to the initial molecules in the imposed electric field, then $-\Delta G = RT \ln k/k_0 = N\Delta\mu E$, where k/k_0 is the ratio of bimolecular rate constants with and without electric field, $\Delta\mu$ is the increase of

Table 1
Kinetic parameters of methanol exchange in CCl_4

	CH_3COOH		$\text{C}_6\text{H}_5\text{OH}$	
	$E = 10^7$ (V/m)	$E = 0$	$E = 10^7$ (V/m)	$E = 0$
n	62	59	66	70
$k^{293\text{ K}}$ (l/mol s)	1340	1260	381	395
S_n	201	183	84	81
$\Delta k, \alpha = \begin{cases} 0.68 \\ 0.8 \\ 0.9 \end{cases}$	25.5	23.8	10.4	9.7
	33	31	13.5	12.6
	43	41	17.7	16.5

dipole moment, E is the field intensity. The experimental ratio $k/k_0 = 1.064$ corresponds to $\Delta\mu \sim 7.5$ D. Thus, the intermediate must have a dipole moment of $\sim 8-9$ D, which is close to the values obtained for typical H-bonded ion pairs /6/. Bureiko et al. /7/ studied hydrogen exchange in the $\text{CH}_3\text{OD}-\text{C}_6\text{H}_5\text{OH}$ system in CCl_4 without external electric field, and made a conclusion on its cooperative mechanism. Our data (Table 1) indicate that the exchange rate in the external electric field does not, at least, increase (the conclusion on retardation can be drawn with a probability of $\alpha \leq 0.52$). Actually, if one assumes the molecular mechanism of exchange with the cooperative transfer of two protons, the decrease of the dipole moment of the cyclic intermediate in comparison with the initial molecules cannot be higher than ~ 1.5 D, which gives an effect of $\sim 1\%$. The results of studying the effect of a strong external electric field are in agreement with the data of Ref. /4/ on the mechanisms of rapid proton exchange in aprotic low-polar solvents. The possibility for proton exchange under similar conditions to follow the ion-pair mechanism can be considered as stated. The results confirm the conclusion drawn in Ref. /4/ on this mechanism of proton exchange between acetic acid and methanol in CCl_4 and in other non-polar solvents. It is highly probable that the potential surface of interaction in this system has two minima, the second (corresponding to the ionic pair) being higher.

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