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MECHANISM OF NON-CATALYTIC PROTON EXCHANGE IN APROTIC LOW-POLAR SOLVENTS

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The kinetics of proton exchange for the CD_3OH-$(CH_3)_3COH$ and CD_3OH-CH_3COOH systems in various solvents have been studied by dynamic ^1H and ^2H NMR. The mechanism of the process is discussed.

Методом динамического ^1H и ^2H ЯМР изучена кинетика протонного обмена в системах CD_3OH–$(CH_3)_3COH$ и CD_3OH–CH_3COOH в различных растворителях. Обсуждён механизм исследованного процесса.

The mechanism of fast proton exchange between OH groups in solvents such as hydrocarbons and their halogenated derivatives will be considered. The kinetics of proton exchange between the CD_3OH-$(CH_3)_3COH$ and CD_3OH-CH_3COOH molecules, and between their d_1-derivatives, have been studied by dynamic ^1H and ^2H NMR in several aprotic low-polar solvents (ε = 2–10) incapable of strong specific solvation. The concentrations did not exceed 10^{-2} mol/l. Spectra were recorded on Jeol C-60 HL, Varian CFT-20 and Bruker XH-90 spectrometers in the temperature range from solvent freezing to 40 °C. The full lineshape analysis was made as described in Ref. /1/; the linewidths and chemical shifts at a given concentration and temperature without exchange were determined from the spectra of solutions containing only one component. Typical spectra for the lifetime calculations are shown in Fig. 1. Kinetic parameters were calculated from the lifetimes as described in Ref. /1/[x]. For two solvents with strongly different ε (CCl_4 and

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[x] Erratum: in Ref. /1/ it is necessary to interchange the positions of α and β in eq. (2), and to remove the minus from eq. (3).

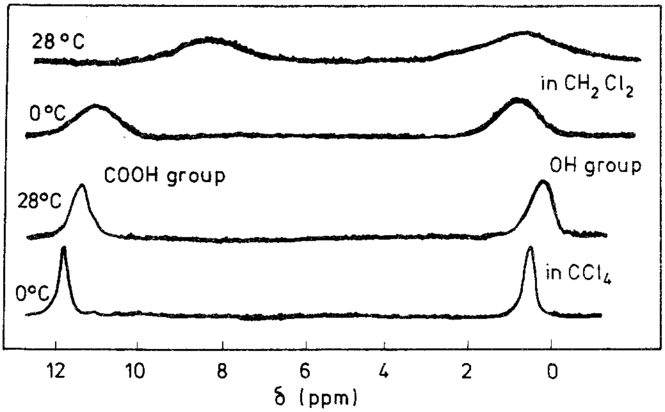


Fig. 1. ^{1}H NMR spectra of solutions containing 0.01 mol/l CD_3OH and 0.01 mol/l CH_3COOH

CH_2Cl_2), the kinetic orders with respect to both components as well as the rate constants (k) and activation energies (ΔE) were determined. The proton lifetime in the XH molecule is independent of the XH concentration and inversely proportional to the YH concentration. Therefore, the exchange is of the first order with respect to both components. This indicates that the elementary act of exchange proceeds in a binary (1:1) complex. Assuming the same kinetic orders, the bimolecular rate constants were calculated for other solvents.

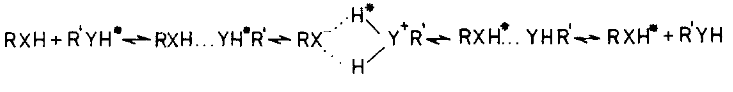
The kinetic parameters of the exchange are given in Table 1. Increasing of the solvent decreases the rate of exchange between two alcohol molecules and increases the rate of exchange between alcohol and acid molecules. On passing from CCl_4 to CH_2Cl_2, the activation energy of the exchange between CD_3OH and $(CH_3)_3COH$ remains practically unchanged, probably owing to the temperature coefficient of the diffusion rate. The activation energy of exchange between CD_3OH and CH_3COOH, which is significantly larger than that of diffusion in CCl_4, is 2.5 times lower in the more polar CH_2Cl_2. This points to different mechanisms of exchange in these two cases.

Table 1

Solvent effects on proton exchange with the participation of methanol

Solvent	$\varepsilon_{solv.}$	$(CH_3)_3COH$		CH_3COOH	
		k (l/mol s)	ΔE (kcal/mol)	k (l/mol s)	ΔE (kcal/mol)
C_6H_{12}	2.02	960	-	-	-
CCl_4	2.28	850	1.8	4 800	5.6
C_6H_6	2.28	480	-	-	-
$CHCl_3$	4.70	420	-	-	-
C_6H_5Cl	5.62	80	-	11 000	-
CH_2Cl_2	8.90	150	2.1	65 000	2.2
$C_6H_4Cl_2$	9.93	120	-	90 000	-

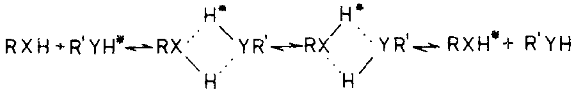
The strong increase of the exchange rate with ε in the CD_3OH-CH_3COOH system points to a considerable increase in the dipole moment upon going to the transition state. Exchange probably occurs through consecutive steps of linear H-bonded complex formation, proton transfer within it, reverse proton transfer within the cyclic ion pair with two equivalent H-bonds, and the dissociation of the complex:



$$RXH + R'YH^{*} \rightleftharpoons RXH\ldots YH^{*}R' \rightleftharpoons RX^{-}\overset{H^{*}}{\underset{H}{\rangle}}Y^{+}R' \rightleftharpoons RXH^{*}\ldots YHR' \rightleftharpoons RXH^{*} + R'YH \qquad (1)$$

This process does not require ion separation (electrolytic dissociation) and, therefore, may take place even in the most inert solvents. Most probably the endothermic proton transfer limits the rate of exchange as confirmed by the strong kinetic isotope effect ($k_H/k_D = 8$ in CCl_4).

The retardation of the exchange between two alcohol molecules with increasing ε points to an increase in the dipole moment upon going to the transition state. In this case the exchange seems to occur via the intermediate formation of a molecular cyclic complex, followed by the cooperative transfer of two protons



(2)

Indeed, the dipole moment of this complex must be close to zero. Increasing solvent polarity leads to stronger solvation of the free molecules, compared with the cyclic complex, and, hence, to a decrease in their concentration. It is not clear what step of process (2) is rate-determining. The very small activation energy as well as the small kinetic isotope effect (k_H/k_D = 1.3 in CCl_4) may imply that cyclic complex formation is the slowest step /1/. It is also possible that the formation of this complex and the cooperative proton transfer have similar rates. It should be emphasized, however, that the observed dependence of the proton exchange rates, between the alcohol molecules on the solvent polarity excludes the participation of any ionic complexes in the rate-determining step.

REFERENCES

1. S.F. Bureiko, N.S. Golubev, G.S. Denisov, I.Ya. Lange: React. Kinet. Catal. Lett., 7, 139 (1977).