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KINETIC ISOTOPE EFFECT IN PROTON EXCHANGE PROCESSES BETWEEN METHANOL AND WATER IN INERT SOLVENTS

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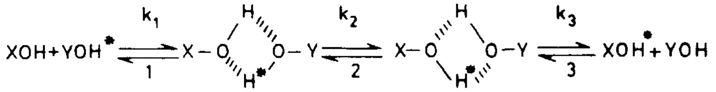
The kinetic isotope effect in proton exchange between methanol and water in CCl_4 solution was studied by ^1H and ^2H NMR and kinetic IR spectroscopy. The exchange rate increases in the series $CD_3OH + H_2O < CD_3OD + H_2O < CD_3OD + D_2O$. It has been concluded that the limiting step of the reaction involves the formation of an H-bonded cyclic intermediate.

Методами ^1H и ^2H ЯМР и кинетической ИК-спектроскопии исследован кинетический изотопный эффект в протонном обмене между метанолом и водой в растворах в CCl_4. Показано, что скорость реакции увеличивается в ряду
$CD_3OH + H_2O < CD_3OD + H_2O < CD_3OD + D_2O$.
Сделан вывод, что лимитирующей стадией процесса является образование циклического промежуточного комплекса с Н-связями.

The kinetics of proton exchange (H-exchange) between OH (OD) groups of different molecules has been investigated in dilute CCl_4 solutions by kinetic IR spectroscopy /1–3/. The exchange in these solutions was shown to proceed much more rapidly than in binary mixtures of these substances studied mainly by NMR spectroscopy /4, 5/. The results obtained permit to conclude that in this case the exchange follows a molecular mechanism via a cyclic complex with H-bonds:



(1)

At the same time, in binary systems (as well as in concentrated solutions) every molecule forms several H-bonds, being both a proton donor and a proton acceptor. The formation of the intermediate in reaction (1) requires two molecules to be released from a net of H-bonds, which is extremely disadvantageous as regards energy and entropy. Hence, the exchange in alcohol-water binary systems is likely to follow other (in particular, ionic) mechanisms, induced by acidic or basic impurities. Recently this has been supported /6/: the rate of H-exchange between carefully purified ethanol and water at any concentration is unmeasurably slow on the NMR time scale; the molecular mechanism in solutions diluted with an inert solvent is supported by the reproducibility of results obtained with substances of different purity.

The rate of reaction (1) may be limited either by the formation of the cyclic complex or by cooperative proton transfer in it. The two mechanisms are in accordance with the experimental dependence of the rate on the H-bond forming ability of the reagents, since the strengthening of the complex may result in an increase of k_1 and k_2. The latter is possible due to an increased probability of proton tunnelling for shorter H-bonds between the functional groups and to a decrease in the barrier height. If proton transfer is the limiting step, then in the case of a deuteron one should expect the reaction rate to be considerably lower (see, e.g. /7/).

The investigation of the kinetic isotope effect in H-exchange processes was undertaken for the $CD_3OH + H_2O$ (I), $CD_3OD + H_2O$ (II), $CD_3OD + D_2O$ (III) systems in CCl_4 solutions. Systems I and III were studied by means of dynamic ^1H and ^2H NMR spectroscopy, respectively, system II was examined by kinetic IR spectroscopy. To simplify the computation of NMR spectra, CD_3OH was taken instead of CH_3OH (spin-spin coupling of the mobile proton signal may be neglected). The reactions were studied at $(1-8) \times 10^{-3}$ mol/l water and 2×10^{-3} -3×10^{-2} mol/l alcohol concentrations; under these conditions the molecules of alcohol and water are present in the solution mainly as monomers. The measurements were made over the temperature range of 5–70°C.

To study the exchange kinetics in system II, an apparatus based on the stopped-flow principle was used /8/ (3 msec resolution). The process was followed by measuring the time dependence of the intensity at the absorption maxima of the alcoholic

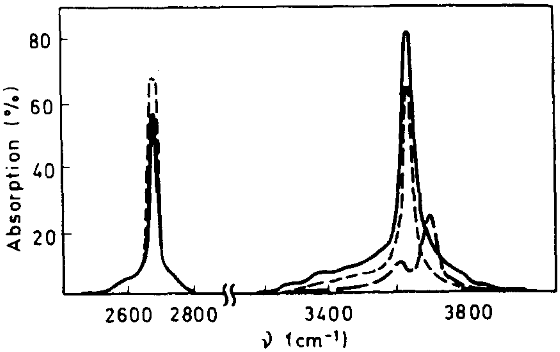


Fig. 1. Changes in the νOD and νOH bands after H-exchange in the system 1.5 x 10^{-2} mol/l CD_3OD + 2 x 10^{-3} mol/l H_2O at 20°C, optical path 20 mm, solid line – after the end of the process

νOH (3645 cm^{-1}) or νOD (2691 cm^{-1}) stretching vibrations (Fig. 1). The kinetic parameters obtained from different bands agree within the experimental error (10–15 %). The kinetic curves were photographed from the oscillograph screen at 10–30 msec time base. The pulse ^1H and ^2H NMR spectra with accumulation and Fourier transformation were obtained using Bruker HX-90 and Varian CFT-20 instruments. The internal capillaries of C_6D_6 and C_6H_6 served to lock the field for ^1H and ^2H spectra, respectively. The NMR spectra are illustrated in Fig. 2.

A complete analysis of the line shape of the OH (OD) signals in the NMR spectra was performed according to the method described in Ref. /9/, on a M-222 computer. Here, in the absence of exchange, the lineshape was determined from the spectra of

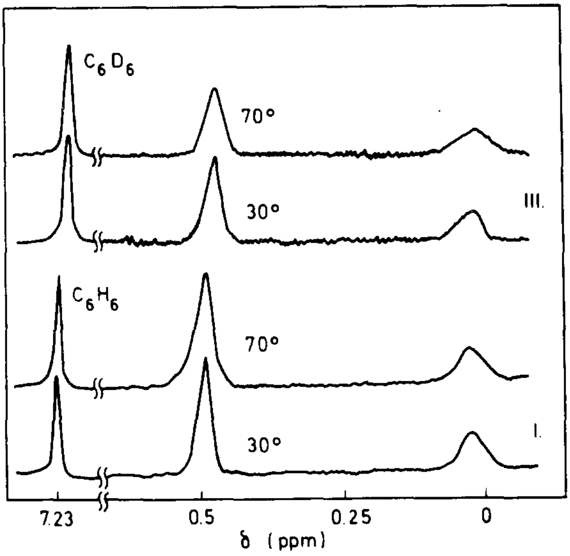


Fig. 2. NMR spectra of systems I (^{1}H, 250 scans) and III (^{2}H, 15 000 scans) at various temperatures. $c_{alc.} = 3 \times 10^{-2}$ mol/l, $c_{water} = 7 \times 10^{-3}$ mol/l

the solutions containing only one component. The reaction orders were obtained from the slopes of the straight lines according to the equations

$$\ln \tau_A/C_A = C - \alpha \ln C_B,$$
$$\ln \tau_B/C_B = C' - \beta \ln C_A, \tag{2}$$

and the rate constant was derived from

$$k = -\frac{1}{\tau_A}\frac{1}{C_A^{\alpha-1}C_B^{\beta}} \tag{3}$$

When using the IR kinetic curves, the rate constant of the reaction was calculated from the equation

$$R = k\, C_A^{\alpha}\ C_B^{\beta} \tag{4}$$

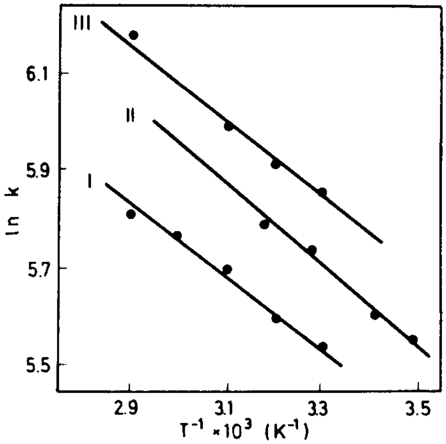


Fig. 3. Determination of the activation energies in systems I, II and III

where the value of the specific rate R was determined from the experimentally measured rate (r) of approach to the equilibrium isotope distribution /8/, with regard to the presence of two equivalent protons in a water molecule (so-called "complicated exchange") /10/:

$$R = r\,\frac{2C_A C_B}{C_A + 2\,C_B} \qquad (5)$$

(C_A and C_B are the concentrations of alcohol and water, α and β are the orders with respect of components A and B, respectively).

The results obtained show that the kinetics of H-exchange obey an exponential law. The reaction orders towards methanol and water are close to unity, e.g. for system II at 20°C, the values found from the abundant system of equations (4) by the least-squares method are $\alpha_a = 0.9 \pm 0.2$; $\beta_w = 1.2 \pm 0.3$. Hence, bimolecular constants were calculated and the activation energies were defined from their temperature dependence (Fig. 3).

When hydrogen is successively substituted by deuterium the rate of H-exchange somewhat increases, the rate constant being 250, 300 and 360 l/mol sec at 30°C foi processes I, II, III, respectively. Though the effect is not great, it exceeds the experimental error. The activation energies are the same within the experimental error (for I, II, III they are 1.5 ± 0.3; 1.7 ± 0.2; 1.5 ± 0.5 kcal/mol, respectively), and apparently, they are determined by the temperature coefficient of diffusion.

The value and sign of the isotope effect for the exchange rate constant is at variance with the assumption that proton transfer (proton tunnelling) is the rate-limiting step. Assuming that the formation of the cyclic intermediate is the slowest step, the effect observed may be easily explained. Indeed, upon substitution of the deuteron for a proton, the stability of the intermediate increases /11/, which may result in the acceleration of H-exchange. But it is the considerable decrease in entropy accompanying the formation of the four-membered cyclic complex that mainly reduces the rate of step 1 in eq. (1) as compared with that of step 2 (the approximate ΔS for the cyclic dimer of water is about 25–30 e.u.).

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