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An NMR Study of Proton Exchange in Alcohols. II.[*1] Proton Transfer in the Water-Isopropanol System

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Proton exchange has been investigated in the system of water and isopropanol by means of high-resolution nuclear magnetic resonance. The rates of proton transfer have been obtained at different hydrogen ion concentrations and at different ratios of water and isopropanol. It has been shown that the exchange reaction is of higher order with respect to water and isopropanol concentrations. Possible mechanisms of proton transfer have been discussed, and values for their respective rate constants given.

Proton transfer in systems of water and simple aliphatic alcohols has been studied by several workers.[1-3] In these studies the exchange reaction has been assumed to be of first order with respect to water and alcohol concentrations. However, this assumption has not been verified in all the cases which have been reported so far. In this note, we attempted to check the validity of this assumption using a water-isopropanol system. Several types of exchange reaction will be proposed to explain the rate of proton transfer obtained experimentally, and values for their respective rate constants will be given. For this purpose, the water-isopropanol system has the following advantages: (i) spectral analysis can always be done to a good approximation using first-order perturbation theory, and (ii) since the proton exchange is much slower than in the cases of methanol-water and ethanol-water systems, the proton transfer can be studied over a wide range of molar ratios of water and isopropanol, thus making it possible to determine the order of the exchange reactions in some cases.

Experimental

Commercial reagent-grade isopropanol was dried by treatment with magnesium and a trace of iodine,[4] and was then distilled several times at ordinary pressure. Water was deionized by passing it through a

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[*1] Part I, S. Fujiwara, Y. Fujiwara and M. Nagai, This Bulletin, **39**, 2356 (1966).

1) E. Grunwald, C. F. Jumper and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).

2) Z. Luz, D. Gill and S. Meiboom, *J. Chem. Phys.*, **30**, 1540 (1959).

3) W. G. Paterson, *Can. J. Chem.*, **41**, 2472 (1963).

4) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

column packed with a cation exchange resin, and was boiled just before use. In the following, the readings of a Toa Dempa Model HM-5A pH meter with micro glass and calomel electrodes will be cited as *h*.

A Varian HA-100 high-resolution NMR spectrometer operating at 100 Mc/sec was employed at 28°C under the condition of slow passage and negligible saturation. Several examples of the spectra are shown in Fig. 1. Chemical shift data for the protons of water and isopropanol are summarized in Fig. 2.

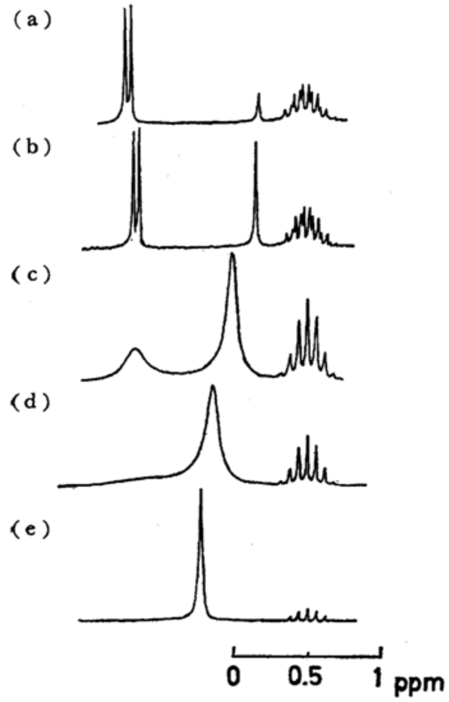

Fig. 1. NMR spectra of isopropanol containing water at various concentrations, [H_2O] being (a) 2.78 M, (b) 5.56 M, (c) 11.1 M, (d) 22.2 M, and (e) 33.4 M.

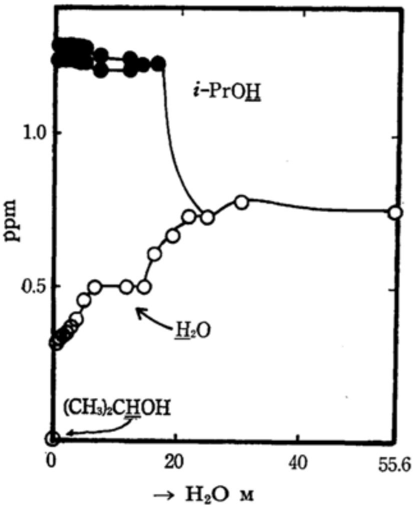

Fig. 2. The change in the chemical shifts of the OH protons of water and isopropanol in the water-isopropanol system. The CH proton signal of isopropanol is tentatively taken as a reference of the chemical shifts.

The average times a proton is bonded to a specific oxygen atom of isopropanol, and water are designated as τ_A, and τ_W, respectively. τ_A^{-1} may be expressed as:

$$\tau_A^{-1} = \tau_{AA}^{-1} + \tau_{AW}^{-1} \tag{1}$$

where τ_{AA}^{-1}, and τ_{AW}^{-1} refer to the proton transfer rate between isopropanol and isopropanol, and that between water and isopropanol, respectively. When the OH signals of water and isopropanol are observed separately, the full widths of the resonance line at half height (in cycles per second), Δ_A and Δ_W, are measured to obtain the specific rate of exchange. τ_A and τ_W are given by the relations:

$$\begin{aligned} \tau_W^{-1} &= \pi\Delta_W - \pi\Delta_W^0 \\ \tau_A^{-1} &= \pi\Delta_A - \pi\Delta_A^0 \end{aligned} \tag{2}$$

where Δ_W^0, and Δ_A^0 are full widths at half height for the OH protons of water, and isopropanol in the absence of exchange. When the two OH signals collapse into a singlet, the line-width, Δ, is given by[5]:

$$\begin{aligned} \Delta &= p_A\Delta_A^0 + p_W\Delta_W^0 \\ &\quad + \pi^{-1}p_A^2p_W^2(2\pi\delta)^2(\tau_{AW}+\tau_W) \end{aligned} \tag{3}$$

where p_A, and p_W, are the fractional populations for the OH protons of isopropanol, and water, respectively, and δ is the chemical shift difference (in cycles per second) between the OH protons of water and isopropanol, which is dependent on the ratio of water and isopropanol. From Eq. (3), the sum $(\tau_{AW}+\tau_W)$ can be obtained, and using the relation

$$\frac{[i\text{-PrOH}]}{\tau_{AW}} = \frac{2[H_2O]}{\tau_W}, \tag{4}$$

which is valid for equilibrium, τ_{AW}, and τ_W can be obtained separately.

Results and Discussion

In Fig. 3, the line-widths for the OH protons of water and isopropanol at $h=6.5$ are plotted as a function of the molar concentration of water, [H_2O]. The line-widths, and therefore the exchange rates, are strongly dependent on *h*. For [H_2O]= 2.78 M, the exchange is shown to be of first order with respect to *h*. In Figs. 4 and 5 $(\tau_Wh)^{-1}$, $(\tau_{AW}h)^{-1}$, and $(\tau_{AA}h)^{-1}$ are plotted as a function of [H_2O].

For the proton exchange between water and isopropanol, the following reaction schemes are assumed:

$$a\,i\text{-PrOH} + b\,H_2O + H_3O^+ \xrightarrow{k_1} \tag{I}$$

$$c\,i\text{-PrOH} + d\,H_2O + i\text{-PrOH}_2{}^+ \xrightarrow{k_2} \tag{II}$$

For these reactions, the following relation holds:

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[5] See *e. g.*, J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959), p. 222.

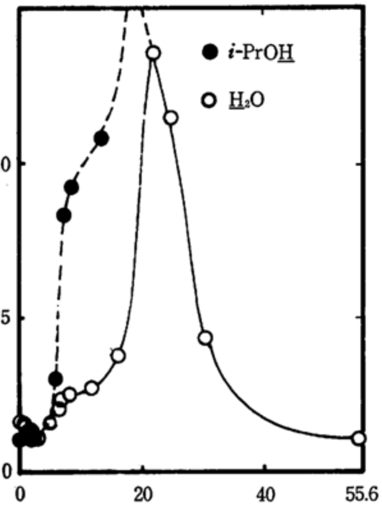


Fig. 3. The change in the line-widths of the OH protons of water and isopropanol in the water-isopropanol system.

$$\begin{aligned}-\frac{d}{dt}[H_2O] &= \frac{2}{\tau_W}[H_2O]\\ &= k_1[i\text{-PrOH}]^a[H_2O]^b[H_3O^+]\\ &\quad + k_2[i\text{-PrOH}]^c[H_2O]^d[i\text{-PrOH}_2{}^+] \qquad (5)\end{aligned}$$

It is assumed that the following equilibrium exists in the solution:

$$i\text{-PrOH} + H_3O^+ \overset{K}{\rightleftarrows} i\text{-PrOH}_2{}^+ + H_2O$$

and that h is equal to $-\log([H_3O^+]+[i\text{-PrOH}_2{}^+])$.

$$\begin{aligned}(\tau_W\ h)^{-1} &= \frac{1}{2}(k_1[i\text{-PrOH}]^a[H_2O]^{b-1}\\ &\quad + k_2K[i\text{-PrOH}]^{c+1}[H_2O]^{d-2})\\ &\quad \times(1+K[i\text{-PrOH}][H_2O]^{-1})^{-1} \qquad (6)\end{aligned}$$

For $[H_2O] \lesssim 0.3$ M, $(\tau_W h)^{-1}$ decreases with increasing $[H_2O]$, as shown in Fig. 4. In this case, Eq. (6) can be approximated as:

$$\begin{aligned}(\tau_W h)^{-1} &= \frac{1}{2}k_2K[i\text{-PrOH}]^{c+1}[H_2O]^{d-2}\\ &\quad \times(1+K[i\text{-PrOH}][H_2O]^{-1})^{-1} \qquad (7)\end{aligned}$$

For $[H_2O] > 0.3$ M, $(\tau_W h)^{-1}$ increases with increasing $[H_2O]$. In this case, Eq. (6) can be approximated as:

$$(\tau_W\ h)^{-1} = \frac{1}{2}k_1[i\text{-PrOH}]^a[H_2O]^{b-1} \qquad (8)$$

From Eqs. (7) and (8) and Fig. 4, it is found that $a=1$, $b=2$, and $d=1$. When $[H_2O]$ is small, $(\tau_W h)^{-1}$ changes greatly with a small change in $[H_2O]$. Since $[i\text{-PrOH}]$ changes only a little in this region of low concentration, c cannot be determined from this experiment. In the proton transfer reactions (I) and (II), the roles of water and isopropanol molecules are interchanged, so that it is assumed that $c=2$. From these results, the constants k_1, k_2, and K can be determined. These constants can also be determined from the change in $(\tau_{AW}h)^{-1}$ in a similar way. The results are as follows:

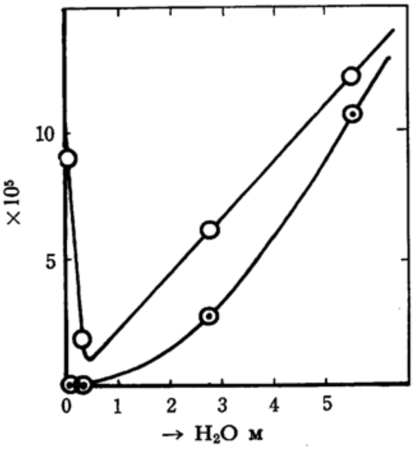


Fig. 4. The change in $(\tau_W\ h)^{-1}$ and $(\tau_{AW}\ h)^{-1}$ with the concentration of water in the water-isopropanol system. ○ and ⊙ refer to $(\tau_W\ h)^{-1}$ and $(\tau_{AW}\ h)^{-1}$, respectively.

$k_1 = 2 \times 10^4$ $l^3\,\text{mol}^{-3}\,\text{sec}^{-1}$

$k_2 = 5 \times 10^3$ $l^3\,\text{mol}^{-3}\,\text{sec}^{-1}$

$K = 2 \times 10^{-4}$

In order to explain the change in $(\tau_{AA}h)^{-1}$, the following reaction schemes are assumed:

$$e\, i\text{-PrOH} + f\, H_2O + H_3O^+ \xrightarrow{k_3} \qquad \text{(III)}$$

$$g\, i\text{-PrOH} + i\text{-PrOH}_2{}^+ \xrightarrow{k_4} \qquad \text{(IV)}$$

From Fig. 5, it is found that $f=1$. However, e and g cannot be determined for a reason similar

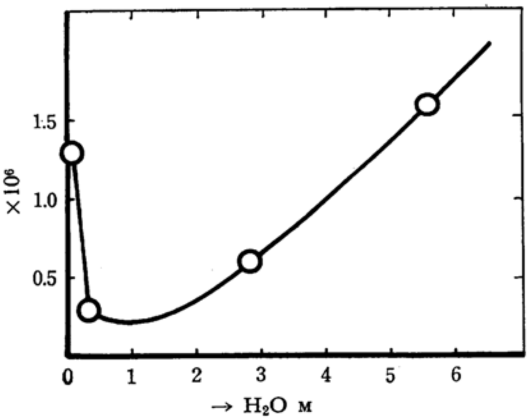


Fig. 5. The change in $(\tau_{AA}\ h)^{-1}$ with the concentration of water in the water-isopropanol system.

to that mentioned above for c in reaction (II). If both e and g are tentatively assumed to be unity, the constants k_3 and k_4 become:

$$k_3 = 2 \times 10^6 \quad l^2\,\mathrm{mol}^{-2}\,\mathrm{sec}^{-1}$$

$$k_4 = 3 \times 10^6 \quad l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$$

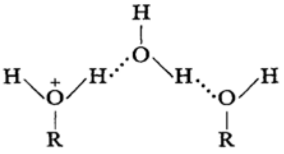
Another possible reaction for proton exchange between water and isopropanol is the following one, which is not catalyzed by acid:

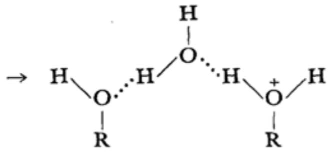
$$i\text{-PrOH} + H_2O \xrightarrow{k_5} \qquad \text{(V)}$$

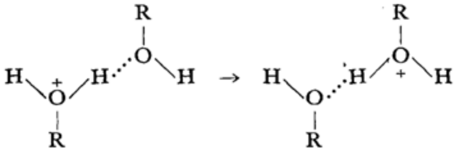
From the values for $\tau_W{}^{-1}$ and $\tau_{AW}{}^{-1}$ obtained for the sample with no acid added externally, k_5 is found to be $2\ l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$.

From the above results, it is clear that in the water-isopropanol system, proton exchange reactions are not of first order with respect to water and isopropanol concentrations, as has been assumed in previous works. Possible mechanisms for proton transfer will be discussed in the following.

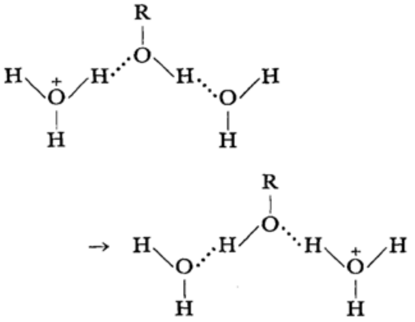
Possible Mechanisms for Proton Transfer. At low water concentrations, the isopropyloxonium ion plays a majar role in proton transfer. Possible models for proton transfer are shown in the following:







At higher water concentrations, a possible model for proton exchange is:



The above mechanisms can be responsible for the proton transfer between water and isopropanol, and for that between isopropanol and isopropanol.