made up by mixing stock solutions of buffer with pure water. The ^{17}O concentration in the water was adjusted to match the one in the stock solutions. The specifications of the three series so obtained were: buffer ratio, ^{17}O atom %: 0.0518, 0.618; 0.01309, 0.290; and 0.00507, 0.531.

The phenol used was of C.P. grade and was distilled at 181°. The middle fraction was used in the experiments.

Nuclear relaxation times were measured by the spin-echo method. Details of the technique and the interpretation procedure were the same as described previously.[1,2]

The Activation Energies of Proton Transfer Reactions in Water
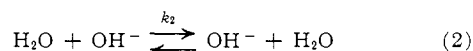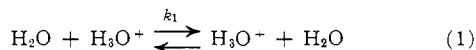
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The rate constants for the proton transfer reactions in water, $H_2O + H_3O^+ \xrightarrow{k_1} H_3O^+ + H_2O$ and $H_2O + OH^- \xrightarrow{k_2} OH^- + H_2O$, have been measured between 15 and 75° using n.m.r. line-broadening technique The results can be represented by the Arrhenius equations $k_1 = 6.0 \times 10^{11}e^{-2.4/RT}$ mole^{-1} l. sec.$^{-1}$ and $k_2 = 1.0 \times 10^{11}e^{-2.1/RT}$ mole^{-1} l. sec.$^{-1}$. The activation energies are compared with those calculated from the temperature dependence of the abnormal conductances of the H^+ and OH^- ions.

Introduction

In this paper we report measurements of the temperature dependence between 15 and 75° of the rates of the proton transfer reactions in water.

$$H_2O + H_3O^+ \underset{}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + H_2O \tag{1}$$

$$H_2O + OH^- \underset{}{\overset{k_2}{\rightleftharpoons}} OH^- + H_2O \tag{2}$$

The rates were obtained from proton magnetic relaxation measurements in ^{17}O-enriched water.[1,2] The activation energy for reactions 1 and 2 has been studied previously by Loewenstein and Szöke[3] by a similar technique. In view of the basic importance of the above reactions, we deemed it worthwhile to repeat these measurements.

Experimental

The exchange broadening of the water proton resonance was obtained from T_1 and T_2 measurements at 60 Mc. sec.$^{-1}$ using a modified Carr-Purcell spin-echo technique.[4] The pulse repetition rate used was 5 to 10 sec.$^{-1}$, low enough for pulse rate effects[2] to be absent. The rate of exchange, $1/\tau$, of the water protons was calculated using the equation[1,2]

$$(1/T_2) - (1/T_0) = \tau \sum_i [p_i \delta_i^2/(1 + \tau^2 \delta_i^2)] \tag{3}$$

where τ is the average lifetime of water protons between successive exchanges; the summation is over the ^{17}O satellite lines which have frequencies δ_i and relative amplitudes p_i; T_0 is the relaxation rate in the absence of exchange broadening and was measured on samples to which enough acid or base was added to make the exchange broadening negligible. The spin–spin interaction between hydrogen and oxygen in water was taken[2] as 713 radians sec.$^{-1}$. A correction for quadrupole relaxation of ^{17}O was applied, using eq. 54 of ref. 1. The longitudinal relaxation time of ^{17}O was taken as 0.063 sec. at 25° in making this correction.[2] The temperature dependence of this quantity was assumed to be the same as for the protons, which, in the temperature range studied, are characterized by an activation energy of 3.0 kcal. mole^{-1}.

The rate of reactions 1 and 2 becomes sufficiently low for the n.m.r. method to be applicable only in the pH range between 5 and 9. In order to get accurate rate constants for reactions 1 and 2 the ion concentration has to be known accurately. In the pH range used this necessitated the use of buffered solutions. By the nature of the buffering action the presence of buffers will

contribute to the exchange rate in water.[2,5–7] For this reason a number of solutions with constant buffer ratio (i.e., the ratio of acid to conjugate base), but with varying buffer concentration were measured and the results extrapolated to zero buffer concentration. The buffers chosen in the present work were acetic acid–sodium acetate (pK_A about 5) for measurements in the acidic range, and phenol–sodium phenolate (pK_A about 10) for measurements in the basic range. This choice was made because the rate law for proton exchange between buffer and water is known for both buffers.[5,7]

Three solutions of acetic acid–sodium acetate, with buffer ratio $r = [AcOH]/[AcONa] = 0.1087$ and sodium acetate concentrations of $[AcONa] = 0.00511$, 0.0259, and 0.0671 mole l.$^{-1}$, were made up. The solvent water contained 0.672 atom % ^{17}O and was normalized to natural abundance of hydrogen isotopes. Details of the preparation procedure are described in ref. 5. The extrapolation of the rates to zero buffer concentration was done as follows. The measured rate of proton exchange, $1/\tau$, is given by

$$1/\tau = 0.33k_1[H^+] + 0.5k_2[OH^-] +$$
$$k_3[AcOH]/2[H_2O] = 0.33rk_1K_A +$$
$$0.5k_2K_w/(rK_A) + k_3[AcOH]/2[H_2O] \tag{4}$$

where k_1 and k_2 are the rate constants for reactions 1 and 2, K_A the acid dissociation constant of the buffer, r the buffer ratio, and k_3 the rate constant for the proton exchange between buffer and water.[8] The term with k_2 in eq. 4 can be neglected completely relative to the term in k_1, as one can easily see by inserting the applicable quantities. In the extrapolation procedure it is assumed that k_1 and k_3 are independent of buffer concentration, but a small correction of interionic effects on K_A was made. The effect of sodium acetate on the K_A of acetic acid is not known but is expected to be similar to that of sodium chloride. Values of K_A of acetic acid between 0 and 40° in the presence of sodium chloride, measured by Harned and Hickey,[9] have therefore been used here (with some extrapolation to higher temperatures). For each temperature k_1 and k_3 were calculated from a least-squares fit of the experimental $1/\tau$ to eq. 4.

Three solutions of phenol–sodium phenolate buffer with ratio[10] $r = [C_6H_5OH]/[C_6H_5ONa] = 203$ and phenol concentrations of 0.0515, 0.202, and 0.358 mole l.$^{-1}$ were used. The concentration of ^{17}O was 0.351 atom %. The preparation procedure was as described in ref. 7. In the present case the exchange due to

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(2) Z. Luz and S. Meiboom, ibid., 39, 366 (1963).

(3) A. Loewenstein and A. Szöke, J. Am. Chem. Soc., 84, 1151 (1962).

(4) S. Meiboom and D. Gill, Rev. Sci. Instr., 29, 688 (1958).

(5) Z. Luz and S. Meiboom, J. Am. Chem. Soc., 85, 3923 (1963).

(6) Z. Luz and S. Meiboom, ibid., 86, 4764 (1964).

(7) Z. Luz and S. Meiboom, ibid., 86, 4766 (1964).

(8) The k_3 defined here actually corresponds to the product nk_3 of ref. 5. Since k_3 will be taken as a free parameter, the actual value of n is irrelevant here.

(9) H. S. Harned and F. C. Hickey, J. Am. Chem. Soc., 59, 1284 (1937); 59, 2303 (1937).

(10) Note that r defined here is the reciprocal of the buffer ratio used in ref. 7.
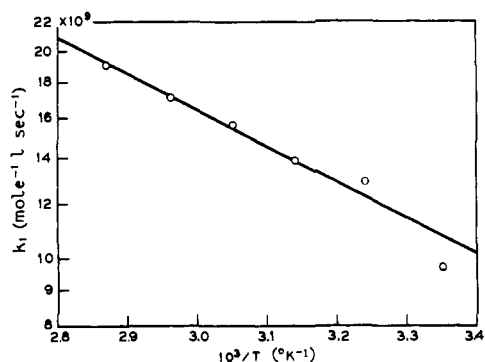
Fig. 1.—Rate constant of the proton transfer reaction between hydronium ion and water (reaction 1) as a function of reciprocal temperature.

the buffer is second order in buffer concentration, and the measured rate is given by[6]

$$1/\tau = 0.33 r k_1 K_A + 0.5 k_2 K_w/[r K_A] +$$
$$k_3 [C_6H_5OH]^2/2r[H_2O] \quad (5)$$

where K_A and k_3 now apply to the phenol–phenolate buffer. The k_1 term in eq. 5 amounts to a few per cent of the k_2 term in the solutions used. In the calculations it was subtracted from the measured $1/\tau$, using the k_1 values obtained from the acetic acid–acetate buffer. The ionization constant of water, K_w, as a function of temperature was taken from Harned and Robinson,[11] and the acid dissociation constant, K_A, of phenol was taken from Chen and Laidler.[12] No correction for interionic effects on K_w and K_A was considered necessary as the sodium phenolate concentration was at most 0.002 M. For each temperature, k_2 and k_3 were calculated from a least-squares fit to eq. 5.

Results and Discussion

Semilog plots of k_1 and k_2 as functions of reciprocal temperature are given in Fig. 1 and 2. The curves are described by the Arrhenius equations

$$k_1 = 6.0 \times 10^{11} e^{-2.4/RT} \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

$$k_2 = 1.0 \times 10^{11} e^{-2.1/RT} \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

where R is to be taken in kcal. mole^{-1} °K^{-1}. The above activation energy of reaction 1, $\Delta E_{H^+} = 2.4$ kcal. mole^{-1}, agrees well with the value quoted by Loewenstein and Szöke,[3] 2.6 kcal. mole^{-1}. However, for reaction 2 our figure is $\Delta E_{OH^-} = 2.1$ kcal. mole^{-1} while Loewenstein and Szöke give 4.8 kcal. mole^{-1}. The difference seems to be well outside the experimental error.

It is natural to compare the above activation energies with those describing the abnormal part of the H$^+$ and OH$^-$ electrical mobilities in water, as the latter are a consequence of the proton transfer processes (1 and 2).[13] The connection between rate, $1/\tau$, and

(11) H. S. Harned and R. A. Robinson, Trans. Faraday Soc., **36**, 977 (1940).

(12) D. T. Y. Chen and K. J. Laidler, ibid., **58**, 480 (1962).

(13) The values for the activation energy calculated by Bjerrum[14] and quoted by Loewenstein and Szöke[3] are not comparable with the values determined here. Bjerrum calculated an activation energy for the proton jump in a hydrogen bond, under the assumption that this process is rate determining in water. The very high proton mobility in ice, which was
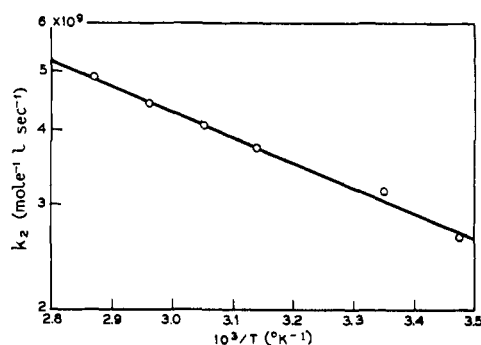
Fig. 2.—Rate constant of the proton transfer reaction between hydroxyl ion and water (reaction 2) as a function of reciprocal temperature.

mobility, μ, is given by the well-known equations

$$\mu = eD/kT \text{ (Nernst)} \quad (6)$$

$$D = \langle x^2 \rangle/6\tau_D \text{ (Einstein)} \quad (7)$$

where τ_D is the average lifetime of a hydronium (or hydroxyl) ion between successive proton transfers. It is related to k_1 and k_2 by $1/\tau_D = k_{1,2}[H_2O]$. In eq. 6 and 7, e is the electron charge, D a diffusion coefficient describing electrical charge transport due to proton transfers, and $\langle x^2 \rangle$ the average of the square of the charge displacement accompanying a proton transfer. From (6) and (7)

$$1/\tau_D = C\mu T \quad (8)$$

where C is a temperature-independent constant. One has, therefore, to compare the apparent activation energy of the proton transfer rate, $1/\tau$, to that of the quantity, μT, rather than just μ. Using the regular procedure of estimating the abnormal mobilities of H$^+$ and OH$^-$ as the difference of the mobilities of, respectively, H$^+$ and Na$^+$ and of OH$^-$ and Cl$^-$, we obtain for the apparent average activation energies between 15 and 75°[16]: for $T\mu_{H^+}$, $\Delta E_{H^+} = 2.4$ kcal. mole^{-1}; and for $T\mu_{OH^-}$, $\Delta E_{OH^-} = 2.9$ kcal. mole^{-1}. This value for ΔE_{H^+} agrees with the value of 2.4 kcal. mole^{-1} from the proton transfer measurements, and confirms the expectation that both effects are controlled by the same mechanism. The agreement is somewhat less satisfactory for ΔE_{OH^-}, the value of 2.9 from the abnormal mobility being between our value of 2.1 and that of Loewenstein and Szöke[3] of 4.8. The cause for this range of values remains an open question.

measured[15] subsequent to Bjerrum's work, makes this assumption highly improbable. But even if Bjerrum's model should hold, the apparent activation energy for proton transfer should be compared with that for the abnormal conductance, rather than with that for the proton jump in a hydrogen bond. (The two differ because of the variation of the fraction of hydrogen-bonded molecules with temperature.)

(14) N. Bjerrum, Dan. Mat. Fys. Medd., **27**, No. 1 (1951).

(15) M. Eigen and L. De Maeyer, Proc. Roy. Soc. (London), **A247**, 505 (1958).

(16) The mobilities as functions of temperature were taken from J. Johnston, J. Am. Chem. Soc., **31**, 1010 (1909); A. Gierer and K. Wirtz, Ann. Physik [6] **6**, 257 (1949).