The rate constant for proton exchange is given by $k_f = k^+k^-/2k^- = k^+/2$. For a diffusion-controlled reaction the rate constant k_r of eq. 7 can be identified with k^+; therefore

$$k_f = k_r/2 \qquad (10)$$

We have assumed that the steric factor is one. This is probably a fair assumption for proton transfer between the two solvated phosphate ions because of the presumably very high proton mobility within the solvation shells. The arguments are the same as those advanced by Eigen and De Maeyer[6] for the neutralization reaction between H^+ and OH^-.

In comparing the experimental results with eq. 7 and 8, we shall first tentatively assume that only one water molecule is involved in reaction 3f; i.e., $n = 1$. We have then from (6) and (10) $k_r = 2k_f = 2 \times 2.9 \times 10^9$. Taking $Z_1 = -1$, $Z_2 = -2$, $\Lambda_1 = 33$ cm.^{2} sec.$^{-1}$, $\Lambda_2 = 55$ cm.^{2} sec.$^{-1}$ at $25°$,[7] $\epsilon = 78.5$, we calculate from (7) and (8) for the effective reaction distance $a_1 = 10.4$ Å. This value is larger than the largest possible P–P distance with one intervening water molecule be-

(7) "Landolt-Bornstein," Vol. II, 6th Ed., Springer-Verlag, Berlin, 1963, Part 7, p. 259.

tween $H_2PO_4^-$ and HPO_4^{-2} (two P–O distances of about 1.54 Å. and two O–O distances of about 2.7 Å.). In other words, the observed exchange rate is higher than can be accounted for by this model.

It is natural to consider that the proton transfer takes place through two water molecules. The same calculation as above for $n = 2$ gives $a_2 = 7.4$ Å. This value seems quite reasonable for the P–P distance with two intervening water molecules between the phosphate ions. It is worth noting that this estimate is very nearly the same as the one obtained by Eigen and De Maeyer[6] for the neutralization reaction $H_3O^+ + OH^- \rightarrow (H_2O)_2$. The assumption that more than two water molecules are involved in the reaction will result in shorter reaction distances, $n = 3$ giving $a_3 = 6.2$ Å. This seems improbable considering the long transfer chain involved.

In conclusion, there seems to be good evidence that the exchange reaction 3f is diffusion controlled and has a rate of $k_f = 1.45 \times 10^9$ mole^{-1} l. sec.$^{-1}$. The proton exchange takes place via two water molecules, and it seems natural to suppose that these belong to the hydration shells of the reacting phosphate ions, proton transfer being rapid whenever the hydration shells of the ions come into contact.

Rate and Mechanism of Proton Exchange in Aqueous Solutions of Phenol–Sodium Phenolate Buffer

By Z. Luz and S. Meiboom

The proton transfer reaction between phenol and phenolate ion in dilute aqueous solutions has been studied by n.m.r. line-broadening technique. It is probable that the transfer reaction involves one water molecule. Under this assumption, the second-order rate constant is $k = 7.1 \times 10^8$ mole^{-1} l. sec.$^{-1}$ at $25°$. The temperature dependence between 15 and $75°$ is described by $\Delta H^* = 4.2$ cal. mole^{-1} and $\Delta S^* = -5.0$ e.u. The rate constant k_2 for the proton transfer reaction between H_2O and OH^- has been remeasured with the result: $k_2 = 3.4 \times 10^9$ mole^{-1} l. sec.$^{-1}$ at $25°$

Introduction

In this paper, we report measurements of the rate of proton transfer in aqueous solutions of phenol–sodium phenolate buffer. Rate measurements were made by the n.m.r. line-broadening technique. The rate of proton exchange between buffer and solvent water is too high to be measurable directly, i.e., the water protons and the hydroxyl protons of the phenol give a single sharp n.m.r. peak with no appreciable excess width due to exchange. For this reason, the exchange reaction was studied indirectly through the measurement of its contribution to the proton transfer rate in water. The latter rate can be measured if the water is enriched in ^{17}O. We refer to earlier papers[1,2] for a detailed description of this method, as well as experimental details.

It will be shown that the kinetic data fit a reaction of the form

$C_6H_5OH + (HOH)_n + {}^-OC_6H_5 \rightleftharpoons$
$\qquad\qquad C_6H_5O^- + (HOH)_n + HOC_6H_5 \quad (1)$
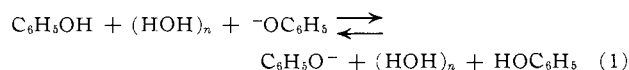
Equation 1 has been written for the case of proton transfer taking place through a chain of n water mole-

cules. Actually, the number of water molecules involved in reaction 1 cannot be obtained from the present experiments. From analogy with previously studied systems, it is believed that one water molecule is involved in the reaction.

Direct proton transfer reactions, i.e., without intervening water molecules, have been observed in a number of cases[3] (for example, ammonium–ammonia buffer in water). Such a reaction may very well occur in the present case also. As it does not catalyze proton exchange between water molecules, it would not be detected by the technique used here.

Results and Discussion

In Fig. 1, the specific rate of proton exchange at $25°$, $1/\tau$, is plotted against the square of the buffer concentration for three different buffer ratios, $r \equiv [C_6H_5O^-]/[C_6H_5OH] = 0.0518$; 0.01309; and 0.00507.

The results fit the rate law

$1/\tau = 0.33k_1[H^+] + 0.5k_2[OH^-] +$
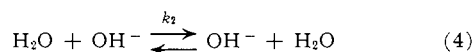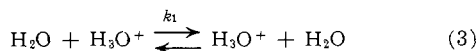$\qquad\qquad k_3[C_6H_5OH][C_6H_5O^-]/2[H_2O] \quad (2)$

The first two terms in eq. 2 describe the proton ex-

(1) Z. Luz and S. Meiboom, J. Am. Chem. Soc., 85, 3923 (1963).
(2) Z. Luz and S. Meiboom, J. Chem. Phys., 39, 366 (1963).

(3) E. Grunwald, P. J. Karabatsos, R. A. Kromhout, and E. L. Purlee, ibid., 33, 556 (1960).

change in water catalyzed by H^+ and OH^- ions.[4]

$$H_2O + H_3O^+ \underset{\longleftarrow}{\overset{k_1}{\longrightarrow}} H_3O^+ + H_2O \qquad (3)$$

$$H_2O + OH^- \underset{\longleftarrow}{\overset{k_2}{\longrightarrow}} OH^- + H_2O \qquad (4)$$

The third term in eq. 2 describes the exchange with the buffer (eq. 1). Introducing the acid-dissociation constant, K_A, of phenol, and the ionization constant, K_w, of water, eq. 2 can be written

$$1/\tau = 0.33k_1 \frac{K_A}{r} + 0.5k_2r\frac{K_w}{K_A} + k_3r\frac{[C_6H_5OH]^2}{2[H_2O]} \qquad (5)$$

It is the last term in eq. 2 and 5 which is our main interest here. It describes the proton transfer from an acid (phenol) to its conjugate base *via* one or more solvent molecules, as indicated in eq. 1.

The slope of the curves in Fig. 1 equals n times the rate constant for reaction 1.[1,2] The intercepts in the figure measure the sum of the exchange rates due to reactions 3 and 4. The actual buffer ratios chosen were such that the pH of the solutions was in the basic range and the term $0.33k_1[H^+]$ accounted for at most a few per cent of the measured $1/\tau$. It was thus possible to obtain a fairly accurate determination of k_2 from the intercepts. In the calculations the value[5] $K_A = 0.955 \times 10^{-10}$ mole l.$^{-1}$ at 25° was used. A small correction for the k_1 term was made using $k_1 = 9.8 \times 10^9$ mole^{-1} l. sec.$^{-1}$. Table I gives the values of k_2 and k_3 obtained, the latter calculated on the assumption that the number of water molecules in reaction 1, n, is 1. If this assumption does not hold, the values in the last column of the table must be interpreted as giving nk_3, rather than k_3.

Table I

Proton Exchange Rate Constants k_2 and k_3 for Aqueous Solutions of Phenol–Sodium Phenolate Buffer

r	$k_2 \times 10^{-9}$, mole^{-1} l. sec.$^{-1}$	$k_3 \times 10^{-8}$, mole^{-1} l. sec.$^{-1}$
0.0518	3.5	7.5
0.01309	3.5	7.1
0.00507	3.0	6.8
Av.	3.4	Av. 7.1

The temperature dependence of k_3 was studied in the range from 15 to 75°. The results are: temperature (°C.), $10^{-8} \times k_3$; 15, 4.9; 45, 10.6; 55, 13.5; 65, 16.7; 75, 20.2; $\langle \Delta H^* \rangle = 4.2$ cal. mole^{-1} and $\langle \Delta S^* \rangle = -5.0$ e.u.

In the following discussion, we shall assume that $n = 1$. This assumption is supported by the findings for the analogous reactions between trimethylammonium ion and trimethylamine in aqueous solution,[2] and between benzoic acid and benzoate ion in methanol.[6] In these two cases the value of $n = 1$ could be confirmed experimentally because the rate could be obtained from the buffer n.m.r. peaks as well as from the solvent peaks. The results suggest that one water, or methanol, molecule is involved when the proton transfer takes place between an ion and a neutral molecule,
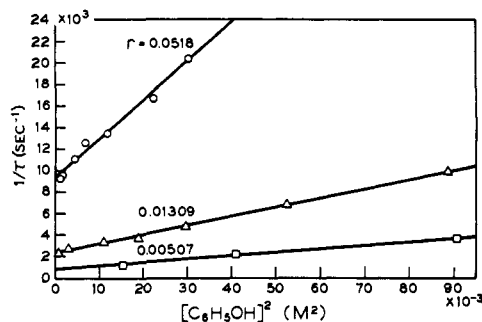
(4) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).
(5) D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58**, 480 (1962).
(6) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

Fig. 1.—Specific rate of proton exchange in aqueous solutions of phenol–sodium phenolate buffer as a function of the square of the phenol concentration. The buffer ratio, $r = [C_6H_5ONa]/[C_6H_5OH]$, is indicated in the figure.

the solvent molecule probably belonging to the solvation shell of the ion. In fact, for the proton transfer between the two ions $H_2PO_4^-$ and HPO_4^{-2}, the experimental evidence[7] indicates that two water molecules are involved.

It is instructive to compare the observed rate constant k_3 with values calculated on the assumption of a diffusion-controlled reaction. The Smoluchowski equation[8] gives for the encounter rate $k_s = 4\pi(D_1 + D_2)aN/1000 = 10.9 \times 10^9$ mole^{-1} l. sec.$^{-1}$. In this calculation, we have taken for the diffusion coefficients: $D_1 = D_2 = 0.96 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for both phenol and phenolate ion.[9]

The reaction distance was taken as $a = 7.5$ Å. (estimated using molecular models). In order to compare k_s with the observed rate constant k_3, it must be multiplied with the following factors: (i) a factor 0.5, which is the probability that an encounter does not result in a proton transfer[7]; and (ii) a steric factor, which in the present case is estimated at 0.25. We thus obtain $^1/_8 k_s = 1.36 \times 10^9$ mole^{-1} sec.$^{-1}$, which is about twice the observed value: $k_3 = 0.71 \times 10^9$ mole^{-1} l. sec.$^{-1}$. Whether this difference is due to the crudeness of the estimates made or whether the reaction is not completely diffusion controlled remains an open question.

The observed value $k_2 = 3.4 \times 10^9$ mole^{-1} l. sec.$^{-1}$ at 25° for reaction 4 is comparable to previously reported values[10] for this reaction: 3.8×10^9, 5.5×10^9, and 4.8×10^9 mole^{-1} l. sec.$^{-1}$. It is felt that the value reported here might be somewhat more accurate than the previous ones, mainly because the procedure of extrapolating to zero buffer concentration is considered more reliable.

Experimental

The buffer solutions were prepared from anhydrous phenol and a solution of NaOH in normal water and water enriched in ^{17}O. The latter had been normalized to the natural abundance of hydrogen isotopes. The buffer ratio was calculated from the amounts of phenol and NaOH used. Three series, each of constant buffer ratio but variable buffer concentration, were

(7) Z. Luz and S. Meiboom, *ibid.*, **86**, 4764, 4768 (1964).
(8) M. V. Smoluchowski, *Physik. Z.*, **17**, 557, 585 (1916).
(9) The diffusion coefficient of phenol was extrapolated to 25° from data between 12 and 20° quoted in "The International Critical Tables," Vol. 5, McGraw–Hill Book Co., New York, N. Y., 1929, p. 73. The diffusion coefficient of phenolate ion has been assumed to be equal to that of phenol.
(10) The quoted values are from, respectively, ref. 4, 11, and 2.
(11) A. Loewenstein and A. Szöke, *J. Am. Chem. Soc.*, **84**, 1151 (1962).

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]
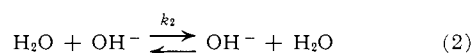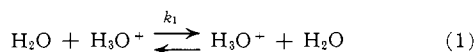

The Activation Energies of Proton Transfer Reactions in Water

By Z. Luz and S. Meiboom

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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.

$$H_2O + H_3O^+ \underset{k_1}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + H_2O \qquad (1)$$

$$H_2O + OH^- \underset{k_2}{\overset{k_2}{\rightleftharpoons}} OH^- + H_2O \qquad (2)$$

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]

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

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

$$1/\tau = 0.33k_1[H^+] + 0.5k_2[OH^-] +$$
$$k_3[AcOH]/2[H_2O] = 0.33rk_1K_A +$$
$$0.5k_2K_W/(rK_A) + k_3[AcOH]/2[H_2O] \qquad (4)$$

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

(1) S. Meiboom, J. Chem. Phys., 34, 375 (1961).
(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.