significantly to the initiation of isotopic labeling in various tritium and light hydrocarbon systems.[5-8] The average β-energy for tritium decay is 5.67 ke.v. and so the maximum contribution from $^3HeT^+$ initiation would lead to G for tritium incorporation of 0.018. More than 90% of labeling in the tritium–polystyrene fluff system must be accounted by β-radiation processes.

A mechanism for tritium incorporation by radiation-induced intermediates from the tritium molecule has been proposed by Yang and Gant.[6,7] The importance of such processes is apparently magnified in the heterogeneous tritium–polystyrene fluff system. Radiolytic intermediates from polystyrene lead primarily to cross linking of the polymer. The enhancement and reduction in tritium incorporation due, respectively, to the presence of xenon and nitric oxide together with the lack of effect on the polymer cross linking clearly indicate that two independent series of reactions are involved.

Our findings in tritium incorporation are consistent with a mechanism involving both ionic and radical intermediates in a series of well-characterized reactions.

$$T_2 \xrightarrow{\beta} T_2^+ + e^- \tag{1}$$

$$T_2^+ + T_2 \longrightarrow T_3^+ + T \tag{1a}$$

$$T_2 \xrightarrow{\beta} T^+ + T + e^- \tag{2}$$
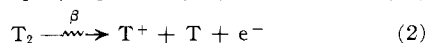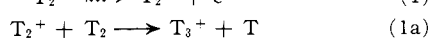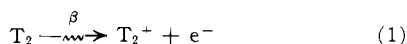
In the presence of an inert gas, the following initiating reaction[22-25] becomes important.

(22) D. P. Stevenson and D. O. Schissler, J. Chem. Phys., 23, 1353 (1955).

$$X^+ + T_2 \longrightarrow XT^+ + T \tag{3}$$
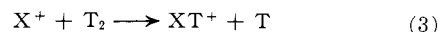
The presence of ionic intermediates is supported by our observed enhancement in tritium incorporation with xenon as additive. The high efficiency for xenon sensitization in reaction 3 has been demonstrated by Lampe.[26] The XeT^+ ion is subsequently neutralized,[27] and tritium incorporation proceeds via radical intermediates. Both our electron spin resonance observations[28] and the product tritium distribution data indicate that the intermediate radicals are of the cyclohexadienyl type resulting from tritium atom addition to the aromatic ring. Since about 90% of the tritium activity appears as styrene in the depolymerized sample, the preferred termination must take place via ring hydrogen atom abstraction by another radical, analogous to the sequence of reactions proposed for hydrogen formation in the radiolysis of toluene.[29]

(23) D. O. Schissler and D. P. Stevenson, ibid., 24, 926 (1956).
(24) D. P. Stevenson, J. Phys. Chem., 61, 1453 (1957).
(25) F. W. Lampe, F. H. Fields, and J. L. Franklin, J. Am. Chem. Soc., 79, 6132 (1957).
(26) F. W. Lampe, ibid., 82, 1551 (1960).
(27) A. Mascke and F. W. Lampe, ibid., 84, 4602 (1962).
(28) R. B. Ingalls and D. Kivelson, J. Chem. Phys., 38, 1907 (1963).
(29) R. B. Ingalls, J. Phys. Chem., 65, 1605 (1961).

Kinetics of Proton Exchange in Aqueous Solutions of Acetate Buffer

By Z. Luz and S. Meiboom

Rates of proton exchange between the carboxyl group of acetic acid and water are reported. The rates were determined from the broadening of the proton magnetic resonance line of water enriched in O^{17}. The observed kinetics are interpreted in terms of proton transfer within a hydrogen-bonded complex consisting of one acetic acid molecule and two water molecules. On the basis of this mechanism a rate constant for the reaction of 4.8×10^7 sec.$^{-1}$ at 25° is calculated.

Introduction

In this paper we report n.m.r. measurements of the rate of proton exchange between the carboxyl group of acetic acid and water. This rate is too high for direct measurement by the n.m.r. technique. In the n.m.r. spectrum of aqueous solutions of acetate buffer the carboxyl protons and the water protons give a single averaged line; careful measurements of the width of this line over a wide range of buffer ratios did not yield a measurable exchange broadening. However, it proved possible to measure the exchange rate by a somewhat indirect way. The method is based on the fact that proton exchange between acetate buffer and water necessarily results in the transfer of protons between water molecules. The contribution of the acetate buffer to the rate of proton exchange in water can be kept in the experimentally accessible range by suitable choice of the buffer concentration and the buffer ratio.

The rate of proton exchange between water molecules can be measured by n.m.r. in water enriched in O^{17}. The latter nucleus has a spin of $^5/_2$ and provides the spin–spin splitting of the proton resonance necessary for exchange broadening of the resonance line. The details of the method have been described previously.[1] The results show that under our experimental conditions (acid/base ratios between 0.1 and 0.01 and

(1) Z. Luz and S. Meiboom, J. Chem. Phys., 39, 366 (1963).

NaOAc concentrations up to 0.1 M) there is one dominant exchange reaction between the buffer and the water. The rate of this reaction is proportional to the concentration of acetic acid molecules and is much higher than that of the acid dissociation of acetic acid. In analogy with recent findings[2] for benzoic acid–benzoate buffers in methanol, a cyclic proton-transfer mechanism is suggested.

Rate Measurements.—In the present system, proton exchange between water molecules is due to reactions[3] with H^+ and OH^-

$$H_3O^+ + H_2O \longrightarrow H_2O + H_3O^+ \tag{1}$$

$$OH^- + H_2O \longrightarrow H_2O + OH^- \tag{2}$$
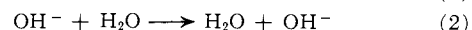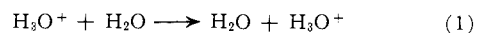
and to reactions between water and either or both of the buffer components, acetic acid and sodium acetate. Since we are interested in the reactions due to the buffer components, we want their contribution to the exchange rate to be dominant or at least comparable to that of reactions 1 and 2. This can be achieved by choosing a buffer ratio such that the pH of the solutions is near 7, where the combined rate of 1 and 2 is a minimum.[3]

The transverse and longitudinal relaxation times of the water protons were measured by the spin echo

(2) E. Grunwald, C. F. Jumper, and S. Meiboom, J. Am. Chem. Soc., 85, 522 (1963).
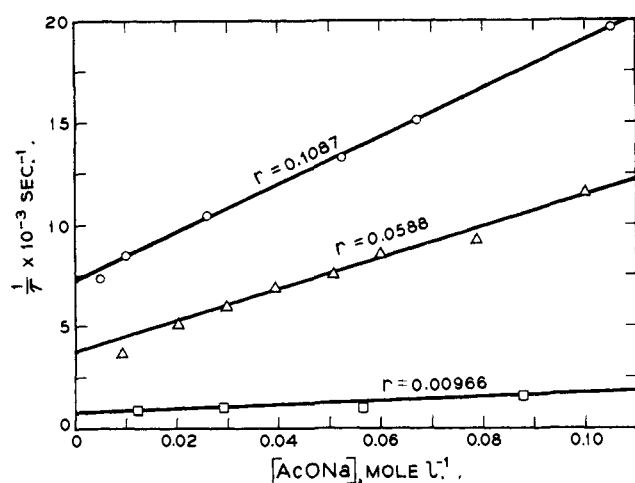(3) S. Meiboom, J. Chem. Phys., 34, 375 (1961).

Fig. 1.—Specific rate of proton exchange in aqueous solutions of acetate buffer as a function of sodium acetate concentration for three different buffer ratios, r = [AcOH]/[AcONa].

technique, as described in reference 1. Solutions with water containing 0.3 to 0.7 atom $\%$ O^{17} were measured, as well as solutions with natural O^{17} abundance (0.037 $\%$).

The lifetime, τ, of a proton on a specific water molecule is obtained from the equation[1,3]

$$\frac{1}{T_2} - \frac{1}{T_0} = \tau \sum_i \frac{p_i \delta_i^2}{1 + \tau^2 \delta_i^2} \qquad (3)$$

where T_2 is the observed transverse relaxation time of the water protons in water with an O^{17} atom fraction of P, T_0 the same quantity in O^{17}-free water, $p_i = P/6$ the relative intensity of the i-th line of the proton multiplet due to spin–spin interaction with O^{17}, and δ_i the frequency difference of the i-th component of the multiplet and the central (H_2O^{16}) line. The spin–spin coupling constant between H and O^{17} was taken as 713 rad./sec. For the final computation of τ a correction was applied[3] for the quadrupole relaxation of the O^{17} nuclei. The longitudinal relaxation time of O^{17} at 25° was taken[1] as 0.0063 sec.

Results

The specific rate, $1/\tau$, of proton exchange at 25° is plotted in Fig. 1 as a function of the buffer concentration for three series of different buffer ratios, r = [AcOH]/[AcONa]. The buffer ratios were: I, 0.1087; II, 0.0588; and III, 0.00966. In each series the rate of exchange increases linearly with the buffer concentration, the slope being proportional to the buffer ratio. This indicates that the proton exchange between water and buffer molecules is first order with respect to buffer, and also that the exchange involves acetic acid molecules rather than acetate ions. We thus conclude that the total rate, $1/\tau$, of proton exchange can be represented by

$$\frac{1}{\tau} = \frac{1}{3}k_1[H^+] + \frac{1}{2}k_2[OH^-] + nk_3 \frac{[AcOH]}{2[H_2O]} \qquad (4)$$

where k_1 and k_2 are the second-order rate constants for reactions 1 and 2, and k_3 is the pseudo-first-order rate constant for the reaction with acetic acid. The stoichiometric coefficient n is equal to the number of water molecules participating in that reaction.

Equation 4 contains three rate constants. However, the pH in these experiments was in the acidic range, and the term $(1/2)k_2[OH^-]$ was at most barely significant. In the actual calculation this term was subtracted from $1/\tau$, using 4.8×10^9 mole^{-1} l. sec.$^{-1}$ for k_2 at 25°.[1] The differences were then used to calculate the parameters, k_1 and nk_3, for each series. The re-

sults are shown in the second and third columns of Table I. In calculating k_1 we used [H$^+$] = rK_A, where K_A, the acid dissociation constant of acetic acid, was taken as 1.754×10^{-5} at 25°.[4]

TABLE I

RESULTS FOR k_1 AND nk_3 AT 25°, OBTAINED FROM AQUEOUS SOLUTIONS OF ACETATE BUFFER

r	k_1, mole^{-1} l. sec.$^{-1}$ $\times 10^{-9}$	nk_3, sec.$^{-1}$ $\times 10^{-8}$	k_1 cor., mole^{-1} l. sec.$^{-1}$	nk_3 cor., sec.$^{-1}$ $\times 10^{-8}$
0.1087	11.4	1.2		0.87
.0588	11.2	1.4		1.05
.00966	11.0	1.1		0.93
			Av. 9.8 $\times 10^9$	.95

In the preceding treatment we have neglected interionic effects on K_A and on the rate constants. For the final calculation we again neglect interionic effects on k_1 and nk_3, but correct for the interionic effects on K_A since we expect these to be larger. The effect of sodium acetate on K_A for acetic acid is not known. However, it is reasonable to assume that the effect is similar to that of sodium chloride, for which data do exist.[4] With the help of these data, and using a single best fit value for k_1, the results given in Table I under k_1 cor. and nk_3 cor. were obtained. The value for k_1 is in good agreement with previously reported values[3,5] of 10.6×10^9 and 11.0×10^9 mole^{-1} l. sec.$^{-1}$.

Some additional measurements were made on a series of buffer solutions with constant acid concentration (0.0057 M) and varying amounts of sodium acetate. The results for 25° are summarized in Table II.

TABLE II

PROTON EXCHANGE IN AQUEOUS SOLUTIONS CONTAINING 0.0057 M ACETIC ACID AND VARYING AMOUNTS OF SODIUM ACETATE AT 25°

[NaOAc], M	$1/\tau$, sec.$^{-1}$ $\times 10^{-3}$	$\Delta(1/\tau)$,[a] sec.$^{-1}$ $\times 10^{-3}$	$\Delta(1/\tau)/[NaOAc]^2$, mole^{-2} l.^{2} sec.$^{-1}$ $\times 10^{-4}$
0.053	13.3	−0.4	
.092	10.4	0.2	7.3[b]
.097	11.0	1.1	
.189	10.3	2.9	8.1
.354	13.7	7.4	5.9

[a] $\Delta\left(\dfrac{1}{\tau}\right) = \dfrac{1}{\tau} - \dfrac{1}{3}k_1[H^+] - \dfrac{1}{2}k_2[OH^-] - nk_3([AcOH]/2[H_2O])$.
[b] Average of second and third lines.

We have seen that in series I–III, in which [NaOAc] ranged up to 0.1 M, there is no evidence for a kinetic term involving [NaOAc]. The purpose of the data in Table II is to explore the kinetics under conditions where reactions involving NaOAc might be more readily apparent. As can be seen in column 3 of Table II, the extra rate $\Delta(1/\tau)$ is small up to 0.1 M sodium acetate, being within the experimental error in that range. At higher concentrations, $\Delta(1/\tau)$ becomes significant and appears to be proportional to the square of [NaOAc], as shown in the last column of Table II.

In connection with an investigation of the temperature dependence of k_1 and k_2, we also obtained data for the temperature dependence of nk_3. The results are: temp. (°C.), $10^{-8}nk_3$ (sec.$^{-1}$); 35, 1.11; 45, 1.30; 55, 1.23; 65, 1.99; 75, 1.60; $\langle\Delta H^{\ddagger}\rangle$ = 3.1 kcal./mole; $\langle\Delta S^{\ddagger}\rangle$ = −11.6 − R ln n, e.u.

Discussion

Reaction of Acetic Acid.—The dominant proton exchange reaction between acetate buffer and water was found to be first order in acetic acid concentration.

(4) H. S. Harned and R. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284 (1937).
(5) A. Loewenstein and A. Szöke, *ibid.*, **84**, 1151 (1962).

The pseudo-first-order rate constant was found to be $k_3 = (9.5/n)\ 10^7$ sec.$^{-1}$, where n is the number of water molecules involved in the proton transfer.

It is highly improbable that k_3 can be identified with the acid dissociation rate constant of acetic acid (5)

$$\text{AcOH} + \text{H}_2\text{O} \longrightarrow \text{AcO}^- + \text{H}_3\text{O}^+ \qquad (5)$$

The rate constant for this reaction has been measured by Eigen and Schoen, using the dissociation field method, and is 8×10^5 sec.$^{-1}$ at 20°.[6] The highly improbable value of $n \approx 100$ would be necessary to obtain the required value of k_3.

A much more probable mechanism for the exchange reaction is a cyclic proton transfer within a hydrogen-bonded complex, which does not involve dissociation to free ions. Such reactions have been found for benzoic acid in methanol,[2] where it could be shown that two methanol molecules are involved in the proton transfer. The analogous mechanism for the present case is described by the scheme

The second step is a proton transfer within a hydrogen-bonded complex, and the final step a dissociation of the complex, with the result that two water molecules have each exchanged one proton. Detailed analysis of the possible mechanisms is given in reference 7. For mechanism 6 we have $n = 2$ and thus $k_3 = 4.8 \times 10^7$ sec.$^{-1}$, $\langle \Delta H^{\pm} \rangle = 3.1$ kcal./mole, and $\langle \Delta S^{\pm} \rangle = -13.0$ e.u. For comparison, the entropy of activation in the supposedly analogous reaction of benzoic acid in methanol is -14.4 e.u.[2]

Effect of Sodium Acetate.—As seen in Table II, at sodium acetate concentrations above $\sim 0.1\ M$, the rate of proton exchange increases significantly with the sodium acetate concentration. The kinetics of this reaction is probably second order in sodium acetate, but owing to experimental uncertainty a first-order dependence cannot be ruled out completely. A possible reaction that is second order in sodium acetate would be the transfer of a proton from the hydration shell of Na^+ to AcO^-.

$$\text{Na}^+\cdot(\text{OH}_2) + \text{AcO}^- \longrightarrow \text{Na}^+\text{OH}^- + \text{HOAc} \qquad (7)$$

Reaction 7 would be facilitated by the acid-strengthening effect of the sodium ion on the adjacent water molecule.

(6) M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955).

(7) E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 2047 (1963).

Other Exchange Reactions.—One could expect the hydrolysis reaction of acetate ion (8) to contribute to the proton exchange

$$\text{AcO}^- + \text{H}_2\text{O} \underset{k^-}{\overset{k^-}{\rightleftarrows}} \text{AcOH} + \text{OH}^- \qquad (8)$$

However, following Grunwald and Jumper,[8] it can be shown that this process is too slow to be detected. The maximum possible rate of the return reaction (k^-) can be obtained from the assumption that it is diffusion controlled: $k^- \approx 10^{11}$ mole^{-1} l. sec.$^{-1}$. The maximum rate of the forward reaction is then $k^+ = Kk^- = 1$ mole^{-1} l. sec.$^{-1}$ where K is the equilibrium constant, $K = K_w/(K_A[\text{H}_2\text{O}]) \approx 10^{-11}$. Furthermore, a cyclic mechanism similar to that suggested for acetic acid is inapplicable to acetate ion because there is no acidic proton to initiate this process.

In many systems proton transfer between acid and conjugate base *via* solvent has been observed.[8] In the present case such a reaction is given by (9).

$$\text{AcOH} + \text{OH}_2 + \text{AcO}^- \longrightarrow \text{AcO}^- + \text{HOH} + \text{AcOH} \qquad (9)$$

Our data do not exclude the possibility that the rate constant of reaction 9 might be as high as 1×10^8 mole^{-1} l. sec.$^{-1}$, although this is an upper limit, since still higher values would result in upward curvature in Fig. 1. On the other hand, with a rate constant of 1×10^8 mole^{-1} l. sec.$^{-1}$, reaction 9 would contribute only 2.0×10^3 sec.$^{-1}$ to $\Delta(1/\tau)$ at the highest acetate concentration in Table II.

Finally, it should be mentioned that in principle another protolysis reaction may occur which involves only acetic acid and acetate ion.

$$\text{AcOH} + \text{AcO}^- \longrightarrow \text{AcO}^- + \text{AcOH} \qquad (10)$$

This reaction does not involve water and can therefore not be detected by the present technique. In some cases (for instance, in ammonia buffer solutions[9]) proton transfer proceeds predominantly by such a reaction.

Experimental

(8) E. Grunwald and C. F. Jumper, *ibid.*, **85**, 2051 (1963).

(9) S. Meiboom, A. Loewenstein, and S. Alexander, *J. Chem. Phys.*, **29**, 969 (1958).