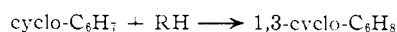
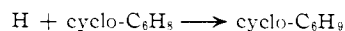
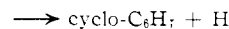
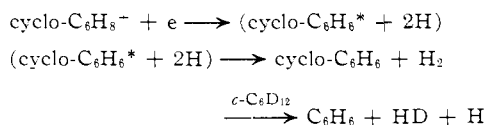


316 m μ which is attributed to cyclo-C₆H₇. This assignment rests upon the appearance of a very similar band when benzene in 3-MP was γ -irradiated at -196° . Its formation was suppressed by addition of MTHF, a scavenger for hydrogen atoms.⁴ The present results suggest that nascent, excited C₆H₆ and H from 1,4-cyclohexadiene undergo cage recombination promoted by the dense glassy state. The free radical C₆H₇ would have the lower energy 1,3-configuration and it could abstract a hydrogen from the solvent to give 1,3-cyclohexadiene. Finally, when 3-MP containing 0.5% 1,4-cyclohexadiene is γ -irradiated at -196° , an absorption band appears at λ_{\max} 770 m μ , quite similar to olefin cation bands observed previously,^{10,11} together with the electron band at λ_{\max} 1700 m μ . Optically bleaching the latter removes the cation band.

The summarized mechanism is



If this mechanism is to account for the results, it would be expected that cage effects will be more pronounced at low temperature than at room temperature. Parallel runs in 3-MP (Table IV), followed by thawing and chemical analysis, show that yields of benzene and of 1,3-cyclohexadiene are indeed much depressed at -196° . This is consistent with earlier measurements of the quantum yields of hydrogen from hydrogen iodide under the same experimental conditions.⁷

In summary, varied evidence supports the interpretation that the major part of the hydrogen yield from radiolysis of liquid cycloalkane, -alkene, and -alkadiene arises from charge neutralization of the respective molecular cations, producing C=C and two hot hydrogen atoms.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, NEW JERSEY 07971]

Rate and Mechanism of Proton Exchange in Aqueous Solutions of Phosphate Buffer

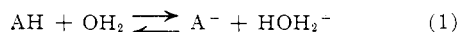
BY Z. LUZ AND S. MEIBOOM

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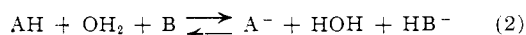
The proton transfer reaction between H₂PO₄⁻ and HPO₄⁻² in dilute aqueous solutions has been studied by n.m.r. line-broadening technique. The second-order rate constant is $k = 1.45 \times 10^9$ mole⁻¹ l. sec.⁻¹ at 25°. It is shown that this figure is consistent with a diffusion-controlled mechanism in which the proton transfer takes place *via* two solvent water molecules.

Introduction

The kinetics of the proton transfer between an acid and its conjugate base in solutions has been studied for a number of buffers.¹ In this paper we report such measurements in aqueous solutions of phosphate buffer. The n.m.r. technique used for measuring the exchange rates has been described previously.^{2,3} In the present case the rate of proton exchange between the various phosphate ions and water is very high, and only a single sharp proton line, resulting from the averaged-out proton lines of the phosphate buffer and solvent water, is observed. It is, however, possible to measure this rate indirectly, by measuring its contribution to the rate of proton exchange between solvent water molecules. The latter rate can be measured by using ¹⁷O-enriched water. References 2 and 3 present a detailed description of the method used. Only those reactions in which the solvent water participates in the exchange process can be measured by this method. Simple examples of such mechanisms are of the type



or



(1) For a review and references see the articles of H. Strehlow and of M. Eigen and L. De Maeyer, in "Technique of Organic Chemistry," Vol. VIII, Arnold Weissberger, Ed., 2nd Ed., Part II, Interscience Publishers, Inc., New York, N. Y., 1963.

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

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

where AH symbolizes an acid and B a base. AH and B are not necessarily neutral molecules and the charges in eq. 1 and 2 are meant to indicate differences only. Reactions of type 2, in which the proton transfer takes place through one or more water molecules (which may be thought of as belonging to the solvation shells of the buffer components) have been found to be important in many systems.¹

In reactions 1 and 2 the buffer can be looked upon as catalyzing the proton exchange between water molecules. The rate of the latter process is obtained from the broadening of the proton peak in ¹⁷O-enriched water. In principle very high rate constants for reactions 1 and 2 can be measured, since the rate of proton exchange in water can be kept within measurable limits by using sufficiently low buffer concentrations.³

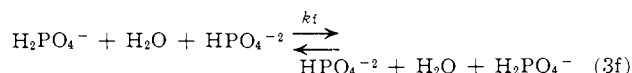
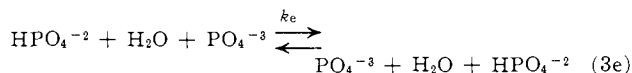
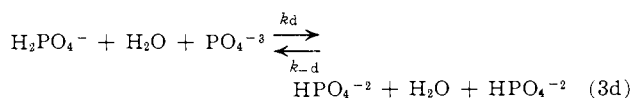
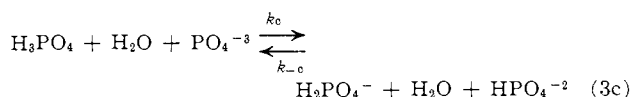
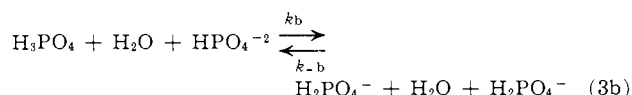
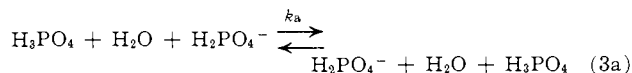
Results

A number of solutions of constant buffer ratio [NaH₂PO₄]/[Na₂HPO₄] = 1.70 and Na₂HPO₄ concentrations between about 0.008 and 0.03 M were made up. The solvent water was enriched to 0.33 atom % ¹⁷O. The proton relaxation times T_1 and T_2 of these solutions were measured by the spin-echo technique as described before.^{2,3} From these quantities the average lifetime between successive transfers of a proton in water, $1/\tau$, is calculated using eq. 3 of ref. 3. The result is plotted in Fig. 1 as a function of the square of the buffer concentration. All measurements relate to a temperature of

25°. It is seen that the points in Fig. 1 fall on a straight line, indicating that the reaction is indeed second order in buffer concentration. It follows that the dominant exchange reaction due to the buffer is of the type given in eq. 2. The slope of the curve in Fig. 1 measures the rate constant for the second-order reaction while the intercept is a measure of the exchange reaction due to H_3O^+ and OH^- ions (eq. 1 and 2 of ref. 3).

Discussion

Under the conditions of the experiment, the ions H_2PO_4^- and HPO_4^{2-} are the only buffer components which contribute significantly to the proton exchange reaction. This is seen as follows. The possible second order proton transfer reactions between the buffer components are



The rate of proton transfer in water induced by these reactions ($1/\tau'$) is given by^{2,3}

$$\frac{1}{\tau'} = \frac{1}{2[\text{H}_2\text{O}]} \frac{d[\text{H}_2\text{O}]}{dt} = \frac{C^2}{2[\text{H}_2\text{O}]} \left(k_a r^3 \frac{K_2}{K_1} + 2k_b r^2 \frac{K_2}{K_1} + 2k_c r \frac{K_3}{K_1} + 2k_d \frac{K_3}{K_2} + k_e \frac{1}{r} \frac{K_3}{K_2} + k_f r \right) \quad (4)$$

Here C is the molar concentration of HPO_4^{2-} , r the ratio $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}]$, and K_1 , K_2 , and K_3 , respectively, the first, second and third ionization constants of phosphoric acid. The slope of the curve in Fig. 1 gives $(1/\tau')/C^2 = 4.44 \times 10^7 \text{ mole}^{-2} \text{ l.}^2 \text{ sec.}^{-1}$. Substituting this value into eq. 4, as well as $r = 1.70$ and the ionization constants⁴ $K_1 = 7.1 \times 10^{-3} m$, $K_2 = 6.3 \times 10^{-8} m$, $K_3 \approx 5.8 \times 10^{-13} m$, we obtain

$$4.9 \times 10^9 = 4.4 \times 10^{-5} k_a + 5.1 \times 10^{-5} k_b + 2.3 \times 10^{-10} k_c + 1.5 \times 10^{-5} k_d + 4.5 \times 10^{-6} k_e + 1.7 k_f \quad (5)$$

The fastest reactions in solutions are diffusion controlled and have rates less than $5 \times 10^{11} \text{ mole}^{-1} \text{ l. sec.}^{-1}$.⁵ It is clear therefore that reactions 3a through 3e cannot appreciably contribute to the observed exchange rate, even if their rate were diffusion controlled. The

(4) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 497; "Handbook of Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(5) H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold Publishing Corp., New York, N. Y., 1963, Chapter 6.

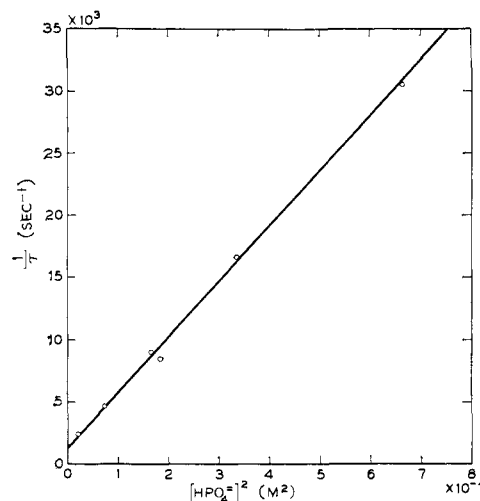


Fig. 1.—Specific rate of proton exchange in aqueous solutions of phosphate buffer, as a function of the square of Na_2HPO_4 concentration at 25°. The buffer ratio, $r = [\text{NaH}_2\text{PO}_4]/[\text{Na}_2\text{HPO}_4]$, was 1.70.

measured rate must, therefore, be ascribed to reaction 3f. Thus we find $k_f = 2.9 \times 10^9 \text{ mole}^{-1} \text{ l. sec.}^{-1}$. It should be pointed out that the value quoted is based on the assumption that only one water molecule is involved in reaction 3. It is, however, quite possible that the proton transfer takes place through a chain of n water molecules. In this case the induced rate of proton exchange in water will be n times the rate of reaction 3f and thus the observed rate must be interpreted as

$$k_f = (2.9 \times 10^9)/n \text{ mole}^{-1} \text{ l. sec.}^{-1} \quad (6)$$

It will be shown below that the observed rate suggests a value of $n = 2$ as the most probable.

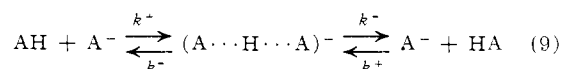
The most interesting aspect of the result is the high value of the rate constant for the reaction between similarly charged ions. In fact it will be shown that the observed rate is consistent with a diffusion-controlled mechanism. We use the Debye-Smoluchowski equation⁶ for the rate of encounter k_r

$$k_r = \frac{4\pi NZ_1 Z_2 e^2 (D_1 + D_2)}{10^3 \epsilon k T [e^{Z_1 Z_2 e^2 / \epsilon k T a} - 1]} \quad (7)$$

where Z_1 and Z_2 are charge numbers, e the electronic charge, ϵ the dielectric constant, and a the effective reaction distance. $D_1 + D_2$ is the sum of the diffusion coefficients of the reacting species and can be obtained from their equivalent conductivities (Λ) by⁵

$$D_1 + D_2 = \frac{kT}{Fe} \left(\frac{\Lambda_1}{|Z_1|} + \frac{\Lambda_2}{|Z_2|} \right) \quad (8)$$

where F is Faraday's constant. In applying (7) to the present case, we first note that for a symmetrical reaction of the form 3f one must compare k_f with $k_r/2$. This is seen as follows. We assume that the proton transfer reaction of type 2 takes place *via* a short-lived intermediate



For simplicity we have omitted the water molecules from eq. 9, as they are irrelevant for the present argument.

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

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

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

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 Maeyer⁶ 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 $Z_1 = -1$, $Z_2 = -2$, $\Lambda_1 = 33 \text{ cm}^2 \text{ sec}^{-1}$, $\Lambda_2 = 55 \text{ cm}^2 \text{ sec}^{-1}$ at 25° ,⁷ $\epsilon = 78.5$, we calculate from (7) and (8) for the effective reaction distance $a_1 = 10.4 \text{ \AA}$. 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 \AA . and two O-O distances of about 2.7 \AA .). 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 $a_2 = 7.4 \text{ \AA}$. 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 Maeyer⁶ 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 $a_3 = 6.2 \text{ \AA}$. 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 $k_f = 1.45 \times 10^9 \text{ mole}^{-1} \text{ l. sec}^{-1}$. 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.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, NEW JERSEY 07971]

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

BY Z. LUZ AND S. MEIBOOM

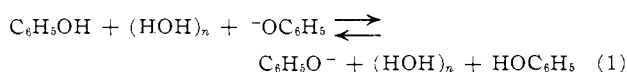
RECEIVED JUNE 15, 1964

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 $k = 7.1 \times 10^8 \text{ mole}^{-1} \text{ l. sec}^{-1}$ at 25° . The temperature dependence between 15 and 75° is described by $\Delta H^* = 4.2 \text{ cal. mole}^{-1}$ and $\Delta S^* = -5.0 \text{ e.u.}$ The rate constant k_2 for the proton transfer reaction between H_2O and OH^- has been remeasured with the result: $k_2 = 3.4 \times 10^9 \text{ mole}^{-1} \text{ l. sec}^{-1}$ 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



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 cases³ (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, $r \equiv [C_6H_5O^-]/[C_6H_5OH] = 0.0518; 0.01309; \text{ and } 0.00507$.

The results fit the rate law

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

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).