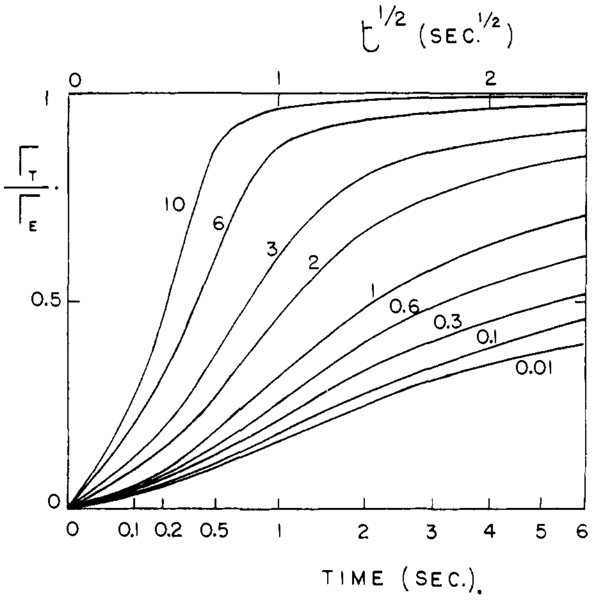

Fig. 4.—Variations of Γ_t/Γ_e with $t_{1/2}$ for the data of Fig. 3.

ments to avoid oscillations of the drop—to speed up attainment of equilibrium.[1a]

Influence of the Sphericity.—The sphericity of the solid-solution interface is not considered in equation 2. This simplification is quite permissible when the diffusion layer thickness is very small in comparison with the radius of curvature of the mercury drop, *e.g.*, for drop times shorter than 2–4 seconds. For longer drop times equilibrium should be approached somewhat more rapidly than the results deduced from equation 2 indicate, but not to the point of invalidating the foregoing conclusions. From comparison of the Ilkovic equation for polarographic diffusion currents with modified forms of this equation in which sphericity is considered, one concludes that the increase in diffusion rate resulting from sphericity does not exceed 5–10% for drop times as large as 10–15 seconds. The increase in adsorption rates caused by sphericity is probably of the same order of magnitude. Detailed calculations were not performed because we were primarily interested in the order of magnitude of diffusion rates at the dropping mercury electrode.

Comparison with a Very Approximate Treatment.—A *very approximate* calculation of Γ_t/Γ_e can be made when $C^0 \gg a$ as was shown by several authors (see ref. 1a for bibliography). Thus, the flux for the diffusion current for an electrode process, as calculated by Ilkovic,[4] is substituted for $D(\partial C/\partial x)_{x=0}$ in eq. 3; and it then follows very simply that Γ_t/Γ_e varies linearly with $t^{1/2}$. It is seen from Fig. 4 that departure from this simple relationship is not too pronounced for values of Γ_t/Γ_e somewhat smaller than unity. Even when the condition $C^0 \gg a$ is not fulfilled, Γ_t/Γ_e still varies fairly linearly with $t^{1/2}$. It readily can be shown that this result is to be expected for adsorption for the linearized isotherm.[6] The foregoing conclusions also hold for adsorption on a plane.

Acknowledgments.—The support of the Office of Naval Research is gladly acknowledged. This problem was initially discussed with Dr. T. W. Hildebrandt before his departure from Oak Ridge.

BATON ROUGE, LOUISIANA

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(6) Expand the error function in equation 5 of ref. 1a for small arguments and retain only the first two terms.

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

Kinetics of Hydrogen Exchange between Hydrogen Peroxide and Water Studied by Proton Magnetic Resonance[1,2]

BY M. ANBAR, A. LOEWENSTEIN AND S. MEIBOOM

RECEIVED DECEMBER 16, 1957

The kinetics of hydrogen exchange between H_2O_2 and water have been investigated using the PMR method in the *p*H range of 2.5 to 6.5. The reaction was found to be both acid and base catalyzed. In the acid region, $pH < 4.5$, the reaction involves H_3O^+ and H_2O_2, while in the basic region it was found to involve HO_2^-, H_2O_2 and H_2O. The reaction constants are 1.6×10^7 l. mole^{-1} sec.$^{-1}$, and 7.3×10^7 l.^{2} mole^{-2} sec.$^{-1}$, respectively.

Introduction

The rate of exchange of hydrogen atoms bonded to oxygen is generally too fast to be measured by isotope labelling methods. Erlenmeyer and Gartner[3] found, by deuterium labelling, that hydrogen exchanges quickly and completely between hydrogen peroxide and water. Attempts to measure the rates of hydrogen exchange between two oxygen atoms (mainly between alcohols and water) are reported by Swain and Labes.[4]

In this paper we report measurements, by the PMR technique, of the rate of proton exchange between H_2O_2 and H_2O as function of *p*H and of H_2O_2 concentration. At sufficiently slow exchange rates the PMR spectrum of aqueous H_2O_2 solutions is expected to consist of two lines, corresponding to the protons in the H_2O_2 and H_2O, respectively. With increasing exchange rate, the two lines broaden and eventually merge into a single broad line which narrows on further increase of rate.[5,6]

In the H_2O_2–H_2O system, at room temperature, it was actually found that the exchange rate is never slow enough for the two lines to be separated, and a single line was always observed. However, the width of this line was found to be strongly dependent on the *p*H and on the H_2O_2 concentration of the solution.

The half-widths of the lines were used to evaluate the exchange rate, using the basic theory given by

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[1] This research has been sponsored in part by the Air Force Office of Scientific Research of the Air Research and Development Command, U.S.A.F., through its European Office under Contract No. AF61 (052)-03.

[2] Taken in part from a thesis presented by A. Loewenstein to the Hebrew University, Jerusalem, in partial fulfillment of the requirements to the Ph.D. degree.

[3] H. Erlenmeyer and H. Gartner, *Helv. Chim. Acta*, **17**, 970 (1934).

[4] C. G. Swain and M. M. Labes, THIS JOURNAL, **79**, 1084 (1957), ref. 4.

[5] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[6] E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 630 (1957); A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).

Gutowsky, McCall and Slichter.[7] The greatest line width was observed at a *p*H of about 4.5, the width being of the order of 25 cycles in 9 *M* H_2O_2 solutions, corresponding to an exchange half-time of the H_2O_2 hydrogen atoms of about 5×10^{-4} seconds. In view of the high rate of hydrogen exchange in pure water,[8] the slowness of the exchange in the H_2O_2–H_2O system is rather surprising. However, relatively slow exchange rates have been found in ethyl alcohol.[9,10] Both acid and base catalysis have been observed in these systems.[8,9]

Experimental

The PMR spectrometer used was the same as described in a previous communication.[6] The sample holders consisted of cylindrical glass tubes of about 3 mm. inner diameter and were rotated by an air turbine. Effective T_2's of pure water of about 1 sec., as measured from the decay of the "wiggles" on fast passage, were obtained.

In the present investigation the PMR spectra consisted of a single line, the width of which had to be measured accurately. The broader lines (width at half-height more than about 3 cycles) were recorded on slow passage and the width was measured from the record. An accurate frequency calibration was obtained by repeating the line at a known frequency difference, the double oscillator described[11] being used for this purpose. In case the line was narrower than about 3 cycles, the direct measurement of width became inaccurate. Instead, the width was determined from the decay of the "wiggles" on fast passage. The two methods gave consistent results in the range where both could be applied. Immediately before and after the measurement of a solution a water sample was measured by the fast passage method. The effective T_2 thus obtained was used to correct the measured line width of the solution. The observed difference between the line width of the solution and of the water was attributed to exchange broadening.[12]

Analytical reagent H_2O_2 3 wt. % ("Merck Superoxol") was used. It was diluted to the desired H_2O_2 concentration with distilled water. The concentration was determined by titration with standardized $KMnO_4$. The mole fractions of H_2O_2 were calculated using density values taken from Schumb, Satterfield and Wentworth.[13]

The *p*H was adjusted by adding small quantities of $HClO_4$ (0.1*N*) or NaOH (0.1*N*). The *p*H was measured using a glass electrode with a Metrohm type E184c *p*H meter. The reference *p*H was phthalate buffer at *p*H 3. The precision in *p*H readings was about ±0.02 *p*H unit. The relative values of *p*H determinations, Δ*p*H, are estimated at an accuracy of ±0.05 *p*H unit in the acid range and ±0.1 *p*H unit in the basic range. The effect of H_2O_2 concentration on the glass electrode *p*H readings is relatively small in the range of H_2O_2 concentrations[14] under investigation, and no corrections were applied.

Measurement of Rate Constants.—A theoretical equation for the exchange broadening of two lines of different intensities has been given by Gutowsky and co-workers.[5,15] Using this equation, theoretical line shapes were calculated for different exchange rates and concentrations. The width at half height of the calculated lines was then plotted as function of exchange rate. Figure 1 gives a set of typical plots. In this figure the dimensionless quantity $u = \Delta/\delta\omega$ is plotted as function of $r = \tau_A\delta\omega$, for different values of p. Here Δ is the line width in radians per second, $\delta\omega$ half the frequency difference of the lines of H_2O_2 and H_2O in radians per second, τ_A the average lifetime in seconds of an H_2O_2 molecule, and p the fraction of H_2O_2 protons in the solution. In the present case p, the proton fraction is also the mole fraction.

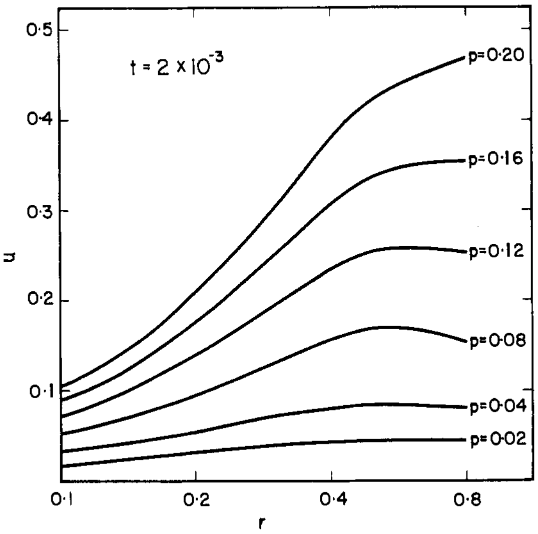

Fig. 1.—Calculated line width as function of exchange rate, for different mole fractions, p, of H_2O_2. The line width is characterized by the dimensionless quantity $u = \Delta/\delta\omega$, where Δ is the line width in radians per second at half height, and $\delta\omega$ is half the frequency difference in radians per second between the H_2O_2 and H_2O protons. The exchange rate is given by $r = \tau_A\delta\omega$, where τ_A is the mean lifetime in seconds of a hydrogen atom in H_2O_2. The graphs apply for a natural line width characterized by $t = 1/(T_2\delta\omega) = 2 \times 10^{-3}$, where T_2 is the relaxation time in seconds in the absence of exchange.

From the observed line width and a knowledge of $\delta\omega$, the mean time between hydrogen exchanges of an H_2O_2 molecule, τ_A, can be found with the help of these plots. The reciprocal of τ_A, which will be referred to as the "specific rate," R, is defined by

$$R = \frac{1}{\tau_A} = \frac{1}{[H_2O_2]}\frac{d[H_2O_2]}{dt} \qquad (1)$$

In the case of fast exchange ($r = \tau_A\delta\omega \ll 1$), the following approximate equation can be derived from equation 3 of ref. 15

$$u/_2 = 4p(1-p)^2 r + t \qquad (2)$$

where $t = 1/(T_2\delta\omega)$ and T_2 is the relaxation time characterizing the line width in the absence of exchange.

As mentioned in the introduction, the exchange rate is too high for the H_2O_2 and H_2O lines to be observed separately. The chemical shift, $2\delta\omega$, cannot therefore be measured directly.[16] An indirect

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[7] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[8] S. Meiboom, Z. Luz and D. Gill, *ibid.*, **27**, 1411 (1957).

[9] J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).

[10] I. Weinberg and J. R. Zimmerman, *J. Chem. Phys.*, **23**, 748 (1955).

[11] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

[12] Owing to decomposition of the H_2O_2, the measured solutions were saturated with oxygen, which because of its paramagnetism should broaden the observed lines. This additional broadening could be neglected in our case, as follows from the observation that sufficiently basic H_2O_2 solutions gave T_2 values nearly equal to those in water.

[13] W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publ. Corp., New York, N. Y., 1955, p. 194.

[14] J. R. Kolczynski, E. M. Roth and E. S. Shanley, THIS JOURNAL, **79**, 531 (1957).

[15] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[16] A rough estimate shows that lowering of the temperature would not slow down the reaction sufficiently to obtain splitting, even if the activation energy would be appreciable.

way is to measure the frequency shift of the combined H_2O_2–H_2O line as a function of the mole fraction, p, of H_2O_2. As an internal frequency reference a small amount of tetramethylammonium bromide was added to the measured solutions. The results are given in Fig. 2. Extrapolation of the line to $p = 1$ gives a relative chemical shift, $\nu(H_2O_2) - \nu(H_2O)$, of 175 cycles/sec. This figure applies for a proton frequency of 31.65 Mc./sec. It should be stressed, however, that the $\delta\omega$ needed in the rate computation is the frequency difference of the protons in H_2O_2 and H_2O, *in the solution measured*. It is not self-evident that this frequency difference is independent of concentration. In fact, there is ample evidence that in highly associated systems, as the one under investigation, the chemical shift of a given molecular species is concentration dependent.[17]

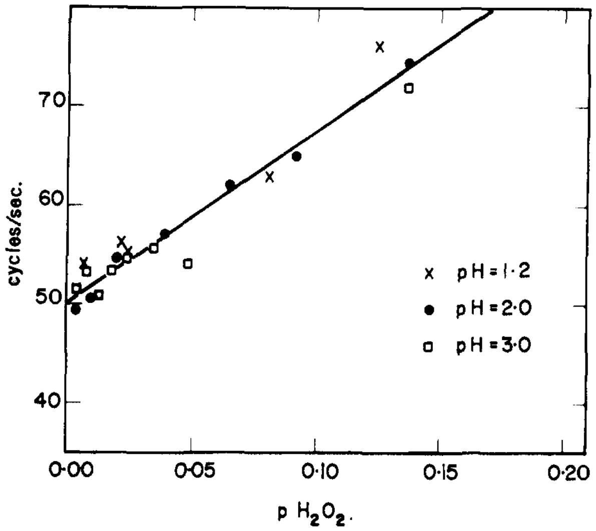

Fig. 2.—Frequency difference between the H_2O_2–H_2O resonance and a tetramethylammonium bromide reference, as function of H_2O_2 mole fraction. Different symbols refer to different pH values. Proton frequency 31.65 Mc/sec.

Evidence that the above figure of 175 cycles/sec. for the relative chemical shift is too low follows from the fact that if this figure is used, some of the observed line widths at low H_2O_2 concentrations were greater than the theoretical maximum line width, showing that the actual frequency difference is larger. It seems very difficult to measure the chemical shift as a function of concentration. We have therefore, somewhat arbitrarily, based our calculations on a relative chemical shift of 200 cycles/sec. Because of this uncertainty the numerical values of the rates given below may be in error up to an estimated factor of 2. However, the dependence of the rates on H_2O_2 concentration and on pH would not be significantly affected by a change of $\delta\omega$. This is because most of the measurements were made in the range where eq. 2 applies, in which $\delta\omega$ appears only as a factor.

The specific rate R, defined in eq. 1 is shown in Fig. 3 as a function of the pH and of the H_2O_2 concentration. It is apparent that the reaction is both acid and base catalyzed. The specific rate is, within experimental accuracy, proportional to H^+ concentration in the acid region (pH < 4) and inversely proportional to H^+ concentration in the basic region (pH > 5). In the acid region the specific rate is essentially independent of H_2O_2 concentration, while in the basic region it increases with H_2O_2 concentration. In the latter region a log–log plot of the specific rate *vs.* H_2O_2 concentration at constant pH has a slope of 1.4. As the measurements at the different H_2O_2 concentrations were done on different days, at which the temperature or some other uncontrolled factor might have changed, it was felt that a deviation from first power dependence might not be significant. An additional series was therefore measured, in which the pH was kept constant, and the H_2O_2 concentration changed. The results of this series are given in Fig. 4. The slope of the line is found to be 1.15.[18]

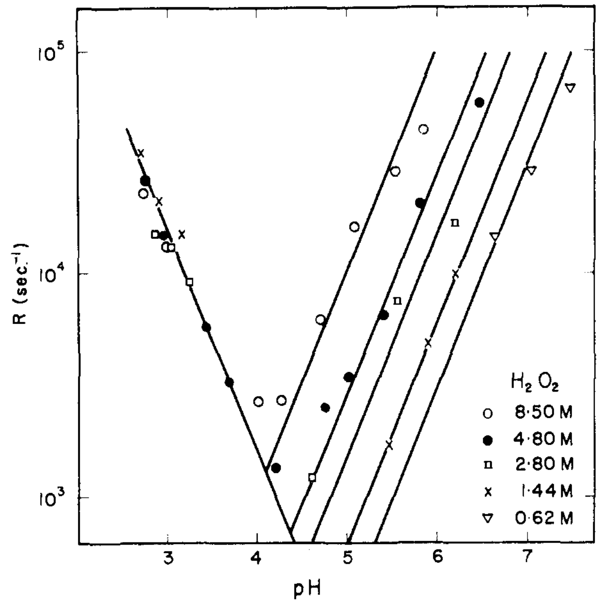

Fig. 3.—Specific rate, R, as defined in eq. 1, as function of pH, for different H_2O_2 concentrations; $T = 27 \pm 2°$.

In view of this result it will be assumed in the following discussion that the reaction is first order in H_2O_2 concentration in the acid region and second order in the basic region.

Discussion

We consider the H_2O_2–H_2O system as consisting of the several species: H_2O, H_2O_2, H_3O^+, $H_3O_2^+$, OH^- and HO_2^-, which are in chemical equilibrium. The concentration of the ionic species is very small under the experimental conditions and a hydrogen atom will therefore spend only a very small fraction of its time bound to these ions. The contribution of

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[17] It has been observed that in aqueous solutions of acetone the frequency difference between the protons of the CH_3 group and those of H_2O is dependent on the acetone concentration (J. T. Arnold, W. A. Anderson, private communication). See also, A. D. Cohen and C. Reid, *J. Chem. Phys.*, **25**, 790 (1956); B. N. Bhar, *Arkiv Fysik*, **12**, 171 (1957).

[18] If a correction to the pH meter readings would have been applied, according to ref. 14, it would lower the rate constants at high H_2O_2 concentrations and consequently make the slope of the line approach unity. This correction was not applied because of insufficient data for the range of H_2O_2 concentrations studied by us.

the ions to the line broadening can therefore be neglected. Hence, we have only to consider those mechanisms which transfer hydrogen atoms from H_2O_2 or its ions to H_2O or its ions. For the interpretation of the experimental results we will first consider the elementary reactions

$$HO_2H^* + HOH \underset{}{\overset{k_1}{\rightleftarrows}} HO_2H + H^*OH \qquad (I)$$

$$H_2O_2 + H_3O^+ \overset{k_2}{\rightleftarrows} H_3O_2^+ + H_2O \qquad (II)$$

$$H_2O_2 + HO^- \overset{k_3}{\rightleftarrows} HO_2^- + H_2O \qquad (III)$$

$$H^*O^+OH + OH^- \overset{k_4}{\rightleftarrows} H^*O\dagger^- + HOOH \qquad (IV)$$

$$H_3O_2^+ \overset{k_5}{\rightleftarrows} OH^+ + H_2O \qquad (V)$$

The reactions of HO_2^- with H_2O_2 and of OH^- with H_2O, which are both probably fast reactions, do not contribute to hydrogen transfer between H_2O_2 and H_2O and have no effect on our measurements. Reaction IV, the nucleophilic attack of the hydroxyl on the H_2O_2 molecule, and reaction V, postulated by Waters (ref. 13, p. 374), both involve an oxygen exchange accompanying the hydrogen exchange. It has been shown that no appreciable oxygen exchange occurs between H_2O_2 and H_2O,[19] and hence reactions IV and V can be disregarded in our case.

Reaction I would give a *p*H independent contribution to the exchange rate. The experimental results (Fig. 3) show that this reaction contributes very little to the over-all rate of exchange. The upper limit for its rate constant is estimated at

$$k_1 < 30 \text{ l. mole}^{-1} \text{ sec.}^{-1} \text{ at } T = 27 \pm 2°$$

Reaction II is in agreement with the results in the acid region (*p*H < 4). For this reaction

$$\frac{1}{\tau_A} = R = \frac{1}{[H_2O_2]}\frac{d[H_2O_2]}{dt} = k_2[H_3O^+]$$

which indicates R to be proportional to hydrogen ion concentration and independent of H_2O_2 concentration. It is found that

$$k_2 = 1.6 \pm 0.2 \times 10^7 \text{ l. mole}^{-1} \text{ sec.}^{-1} \text{ at } T = 27 \pm 2°$$

In the basic region (*p*H > 5) the specific rate of hydrogen exchange has been found to be inversely proportional to hydrogen ion concentration and proportional to H_2O_2 concentration. Because of the latter dependence, reaction III cannot describe the main exchange mechanism. From an estimate of the intercept in a plot of R at constant *p*H in the basic region as function of H_2O_2 concentration, the upper limit of k_3 is

$$k_3 < 3 \times 10^{11} \text{ l. mole}^{-1} \text{ sec.}^{-1} \text{ at } T = 27 \pm 2°$$

In the basic region it follows from the kinetic data that in the exchange reaction are involved either two H_2O_2 molecules and an OH^- ion, or an H_2O_2 molecule, an H_2O molecule and an HO_2^- ion. The possible over-all reactions can be written as

$$HO_2H + HO_2H + H^*O^- \overset{k_6}{\rightleftarrows} HO_2H^* + HO_2H + HO^- \qquad (VI)$$

$$HO_2H + H^*OH + HO_2^- \overset{k_7}{\rightleftarrows} HO_2H^* + HOH + HO_2^- \qquad (VII)$$

As will be shown in the following discussion, reaction VII is much more probable than reaction VI. For reaction VII the over-all rate constant is given by

$$\frac{1}{\tau_A} = \frac{1}{[H_2O_2]}\frac{d[H_2O_2]}{dt} = k_7[H_2O][HO_2^-] = \frac{k_7K_A[H_2O_2][H_2O]}{[H^+]}$$

where

$$K_A = \frac{[HO_2^-][H^+]}{[H_2O_2]}$$

Taking $K_A = 2.24 \times 10^{-12}$ (ref. 13, p. 257), it is found from Figs. 3 and 4

$$k_7 = 7.3 \pm 1.0 \times 10^7 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} \text{ at } 27 \pm 1°.$$

It should be emphasized that equations VI and VII represent over-all reactions and do not describe mechanisms. A mechanism involving a termolecular step is most improbable, in view of the observed high rate of exchange. Two mechanisms may involve the OH^- ion as reactant: the first being an interaction of OH^- with a dimer molecule of H_2O_2: such dimer molecules have been postulated in other mechanisms (ref. 13, p. 346). The second mechanism implies the precursory formation of a complex $H_2O_2{\cdot}OH^-$ which reacts with H_2O_2; the formation of such a complex seems probable in view of the "salting in" effect in H_2O_2 solutions

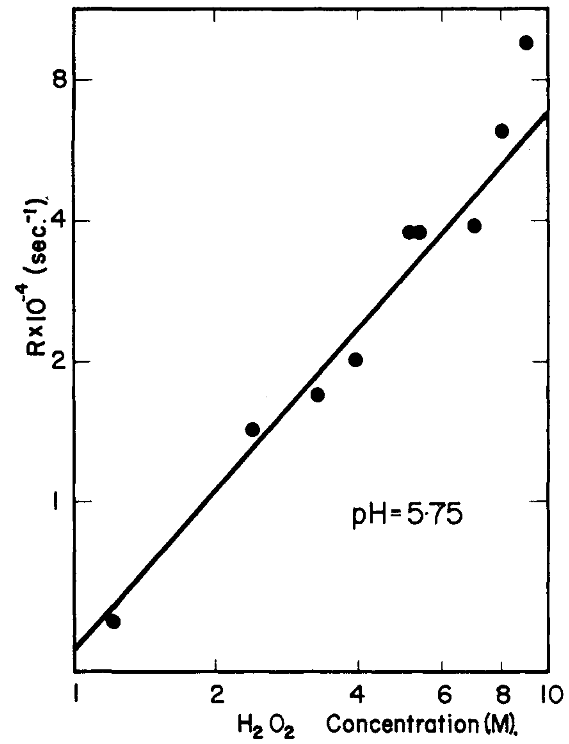

Fig. 4.—Specific rate, R, as function of H_2O_2 concentration, at *p*H 5.75, $T = 27°$. This graph gives a special set of measurements, and was not derived from Fig. 3.

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[19] M. Anbar and H. Taube (1955), unpublished results. Using O^{18} as a tracer, no exchange between H_2O_2 and H_2O was detected in 0.5 N NaOH for 14 days, and in 68% $HClO_4$ for ten days, at room temperature. For exchange studies at milder conditions of acidity or alkalinity see ref. 13, pp. 297, 386.

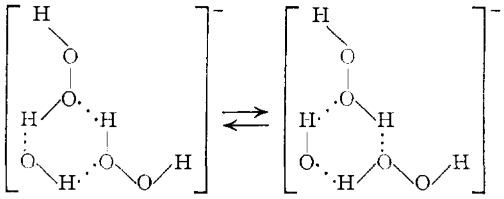
(ref. 13, p. 349). These two mechanisms may be schematically represented by the equations

$$H_2O_2{\cdot}H_2{*}O_2 + OH^- \overset{k_8}{\rightleftarrows} H_2O_2{\cdot}HO_2^- + H{*}OH \qquad \text{(VIII)}$$

and

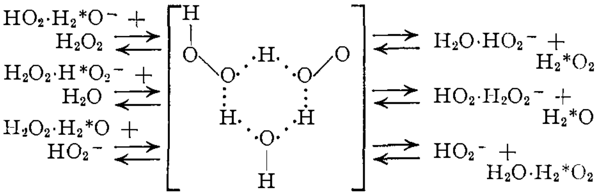
$$H_2O_2{\cdot}H{*}O^- + H_2O_2 \overset{k_9}{\rightleftarrows} H_2{*}O_2{\cdot}OH^- + H_2O_2 \qquad \text{(IX)}$$

Both mechanisms form the same activated complex



The low concentration of OH^- in the solution implies a very high reaction rate for reactions VIII and IX. Assuming equilibrium constants for the complex formation as high as 0.1, we get $k_8 = k_9 > 10^{13}$ l. mole^{-1} sec.$^{-1}$. It is hard to understand why these interactions would be more than 30 times faster than the interaction of OH^- with H_2O_2.

The concentration of HO_2^-, on the other hand, is more than 100-fold that of OH^- even at the most dilute H_2O_2 solutions used in this study; thus it seems more probable that HO_2^- is one of the reacting species in our mechanism. There are three possibilities of precursory complex formation: a hydrated hydrogen peroxide—$H_2O_2{\cdot}H_2O$, a hydrated perhydroxyl ion—$HO_2{\cdot}H_2O^-$ and a peroxyhydrated perhydroxyl ion—$H_2O_2{\cdot}HO_2^-$. Each of these complexes has been postulated before, either to interpret physical properties of the H_2O_2–H_2O system, or in interpreting reaction kinetics (ref. 13, p. 346). These three precursory complexes may form an identical cyclic activated complex.



The formation of a six-membered cyclic activated complex in an aqueous system seems rather plausible compared to linear activated complexes. It should be noted that this mechanism involves a transient formation of an asymmetric H_2O_2 molecule, which is a consequence of the mode of hydration or perhydroxidation of the HO_2^- ion (ref. 13, p. 321). The hydrogen transfer mechanism in this activated complex is considered analogous to the Grothuss mechanism of proton transfer in aqueous solutions.[20]

Assuming equal equilibrium constants for the formation of $HO_2{\cdot}H_2O_2^-$ and $HO_2{\cdot}H_2O^-$, the concentration of the first will be 100-fold less than that of the second in 0.5 M H_2O_2 solution. The equilibrium constant of formation of $H_2O_2{\cdot}H_2O$ is most probably lower than that of $HO_2{\cdot}H_2O^-$, but its concentration may be comparable with that of the latter, due to the relatively low HO_2^- concentration. It may be concluded, therefore, that the most probable reactions responsible for the proton exchange between H_2O_2 and H_2O are

$$H_2O_2{\cdot}H_2O + HO_2^- \overset{k_{10}}{\rightleftarrows} HO_2^- + H_2O{\cdot}H_2O_2 \qquad \text{(X)}$$

$$HO_2{\cdot}H_2O^- + H_2O_2 \overset{k_{11}}{\rightleftarrows} H_2O_2 + H_2O{\cdot}HO_2^- \qquad \text{(XI)}$$

As we have no estimate for the values of the equilibrium constants for the formation of these complexes, we shall assume arbitrarily that they are equal to 0.1. The rate constants obtained by this approximation, $k_{10} = k_{11} = 7 \times 10^8$ l. mole^{-1} sec.$^{-1}$, are reasonable compared to the estimated upper limit for the reaction rate of OH^- with H_2O_2.

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[20] *Cf.*, E. S. Shanley, E. M. Roth, G. M. Nichols and M. Kilpatrick, THIS JOURNAL, **78**, 5190 (1956).

REHOVOT, ISRAEL

[COMMUNICATION NO. 1913 FROM THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

Kinetics of the Hydrogen Peroxide–Sulfite Reaction in Alkaline Solution

BY PAUL M. MADER

RECEIVED DECEMBER 13, 1957

The uncatalyzed (or water-catalyzed) hydrogen peroxide–sulfite reaction is first-order in peroxide and in sulfite, shows little salt effect and has an activation energy of 15.2 kcal./mole at ionic strength 0.034. The increase in rate observed in phosphate, arsenate and carbonate buffers may be due to acid catalysis. The reaction is first-order in each of the two reactants for the catalyzed reaction in the first two buffers but deviates from simple kinetics in carbonate buffers. Below pH 8 there is evidence that one or more pH-dependent reactions exist which have higher than first-order dependence on sulfite. This higher-order dependence may be due to catalysis by acids, such as HSO_3^-, formed through association of sulfite and hydrogen ions.

Introduction

An interest in the rate at which hydrogen peroxide oxidizes sulfite arose during a study of reactions occurring in photographic developer solutions exposed to air. Although the reaction has been investigated by an isotopic tracer technique,[1,2] the amount of attention given to the study of its rate appears to be small.[3] This paper describes the results of a kinetic study of the sulfite–hydrogen peroxide reaction. In the rate experiments, the disappearance of hydrogen peroxide was followed either polarographically or spectrophotometrically.

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[1] E. R. S. Winter and H. V. A. Briscoe, THIS JOURNAL, **73**, 496 (1951).

[2] J. Halperin and H. Taube, *ibid.*, **74**, 380 (1952).

[3] R. Best, *Trans. Ill. Acad. Sci.*, **47**, 201 (1955).