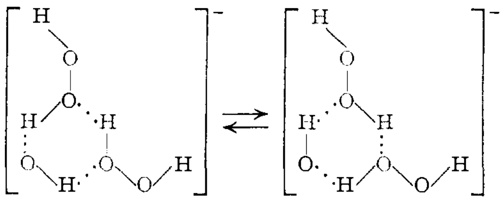
(ref. 13, p. 349). These two mechanisms may be schematically represented by the equations

$$H_2O_2{\cdot}H_2{*}O_2 + OH^- \overset{k_8}{\rightleftarrows} H_2O_2{\cdot}HO_2^- + H{*}OH \tag{VIII}$$

and

$$H_2O_2{\cdot}H{*}O^- + H_2O_2 \overset{k_9}{\rightleftarrows} H_2{*}O_2{\cdot}OH^- + H_2O_2 \tag{IX}$$

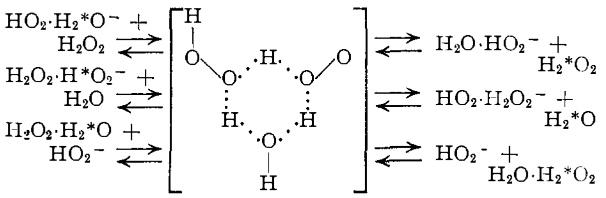
Both mechanisms form the same activated complex



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

$$H_2O_2{\cdot}H_2O + HO_2^- \overset{k_{10}}{\rightleftarrows} HO_2^- + H_2O{\cdot}H_2O_2 \tag{X}$$

$$HO_2{\cdot}H_2O^- + H_2O_2 \overset{k_{11}}{\rightleftarrows} H_2O_2 + H_2O{\cdot}HO_2^- \tag{XI}$$

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.

[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 *p*H 8 there is evidence that one or more *p*H-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.

[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).

Experimental

Materials.—General Chemical (Allied Chemical and Dye Corp.) Reagent Grade Chemicals were used. The Na_2SO_3 was analyzed for sulfite content.[4] The H_2O_2, a "30%" solution supplied in a polyethylene bottle, was analyzed periodically.[4] Because of its high purity, the solution was quite stable. Ethylenediaminetetraacetic acid (EDTA) sodium salts ("Sequestrenes") were obtained from Geigy Chemical Corporation. Laboratory-distilled water was used for kinetic runs. Conductivity water, swept free of carbon dioxide with nitrogen, was used for dissociation constant determinations.

Solutions.—The Na_2SO_3 and H_2O_2 solutions were prepared less than 2 hr. before use. The desired *p*H and ionic strength were obtained by use of buffers and Na_2SO_4. Dilute H_2SO_4 and NaOH were used for small adjustments of *p*H of buffered solutions or to achieve the operating *p*H in solutions containing no buffer. For all experiments except one, 0.2 g./l. of EDTA tetrasodium salt was included in the Na_2SO_3 and H_2O_2 solutions. The EDTA salt greatly retarded the reaction of sulfite with oxygen[5] and the decomposition of H_2O_2.

Spectrophotometric Method.—Five-ml. portions of H_2O_2 and Na_2SO_3 solutions were brought to 25.0 ± 0.1° and mixed rapidly. After a time, *t*, the reaction was greatly retarded by adding 0.9 ml. of 11 *N* NaOH. The optical density of the solution at 290 mμ (due to HO_2^-)[6] was measured with a Beckman Model DU spectrophotometer, and the values were plotted as a function of time elapsed after addition of the NaOH solution. The density data were extrapolated to time of NaOH addition, giving a value proportional to the H_2O_2 concentration at that time. By performing several such experiments, varying only *t*, the necessary rate data were obtained. This method was used for a number of runs in carbonate buffers but was abandoned in favor of the much more convenient polarographic method.

Polarographic Method.—The apparatus consisted of two solution chambers, connected by capillary tubing to an all-glass, jet-mixing chamber, which, in turn, was connected to the reaction chamber. The entire assembly was immersed in a constant-temperature (±0.05°) bath. Five-ml. portions of the Na_2SO_3 and H_2O_2 solutions were pipetted into the solution chambers, and Linde purified nitrogen was passed through the reaction and solution chambers to remove air. The nitrogen flow was stopped, and, after the solutions had reached reaction temperature, the direction of nitrogen flow was reversed so that the solutions were forced through the jet-mixing chamber and into the reaction chamber, which contained the dropping mercury electrode. Mixing of the solutions required about 1 sec. The mercury pool-saturated KCl anode with its saturated KCl–agar bridge was inserted and a constant polarizing potential of −1.3 v. (*vs.* the mercury anode) applied to the dropping mercury electrode. The polarographic current was recorded as a function of reaction time, using a Brown Elektronik Strip Chart Recorder having a full-scale pen traverse time of 2 sec. Reliable chart readings could be made 30 sec. after the start of the reaction; by this time, the electrodes had reached poised operation. Most reactions were followed 80%, or more, toward completion. Chart readings were taken arbitrarily at the upper edge of the trace envelope swept out by the oscillating pen (one oscillation per mercury drop). No capacitive damping of the oscillations was used, since this interfered with the ability of the instrument to follow rapid changes in H_2O_2 concentration. The empirical relation between chart readings and H_2O_2 concentration was established using solutions of known H_2O_2 content.

The concentrations of H_2O_2 and Na_2SO_3 used in the experiments were limited so that the temperature rise during reaction was never greater than about 0.2°. In general, the rise was much smaller.

For each set of experimental conditions, duplicate runs were made. The positions of the H_2O_2 and Na_2SO_3 solutions in the solution chambers were reversed for the second run. The chart readings for the two runs were averaged. In general, the readings agreed quite well. There was a small, consistent difference, however, which was due to a small inequality in the volumes of solution delivered from the solution chambers. Averaging the data should have reduced error in rate constants due to this inequality.

Determination of Stoichiometry.—Nitrogen was passed through the Na_2SO_3 and H_2O_2 solutions to free them of air, and then they were mixed under a nitrogen atmosphere by pipetting one solution into the other and shaking. This mixing operation required about 15 seconds. Reaction was allowed to proceed at room temperature under nitrogen atmosphere until 99.9% (or more) complete. At the end of the reaction period, the remaining Na_2SO_3 or H_2O_2 was determined iodometrically. For comparison, a number of the experiments were repeated in the presence of air.

***p*H Determinations.**—*p*H Determinations were made using a Beckman Model G instrument equipped with 1170 calomel and 1190-80 glass electrodes calibrated against borate and phthalate buffers. Temperature of solutions was 25.0 ± 0.1°.

***p*H Changes during Reactions.**—For those kinetic runs conducted under conditions of poor buffering and at a *p*H at which the rate was sensitive to small changes in *p*H, it was important to know how *p*H changed during the course of the reaction. This information was obtained by performing duplicates of the kinetic runs in a water-jacketed beaker equipped with *p*H electrodes. The Na_2SO_3 solution was placed in the beaker and swept free of air with nitrogen. After the solution had reached 25°, reaction was started by lowering a weighed quantity of 30% H_2O_2, contained in a small glass dish, into the solution and stirring it with nitrogen. Measurements of *p*H were made at recorded times until no further change occurred. When the total *p*H change was small, only the initial and final values were measured; intermediate values were estimated. In the *p*H range 7–8, it was necessary to carry out these reactions in the absence of air. Even though EDTA was present, H_2O_2 promoted the reaction between sulfite and O_2,[7] causing too large a decrease in *p*H (in this *p*H range, the decrease in *p*H results from conversion of the weak acid, HSO_3^-, to the stronger acid, HSO_4^-).

Determination of Dissociation Constants.—Dissociation constants, defined by $K = 10^{-pH}$ (A)/(HA), were determined for the acids $H_2PO_4^-$, $H_2AsO_4^-$ and HSO_3^- at 25°. (HA) and (A) are the molarities of the acid and conjugate base, respectively. These constants were used to calculate the molarities of the HA or A species in certain of the kinetic reaction mixtures. The *K* values were calculated from *p*H values of solutions containing known concentrations of A and HA. Sodium sulfate was used to give an ionic strength of 1.0. Air was eliminated from the water used in preparing the solutions to avoid oxidation of the sulfite and interference of CO_2. The solutions were also protected from air during *p*H measurements. The *K* values found were: $H_2PO_4^-$, 3.5×10^{-7}; $H_2AsO_4^-$, 4.1×10^{-7}; HSO_3^-, 2.8×10^{-7}.

Results and Discussion

Reaction Products and Stoichiometry.—Only two oxidation products have been reported to result from reaction of sulfite with a number of oxidizing agents.[8] These are sulfate and dithionate. Using hydrogen peroxide as the oxidizing agent, Albu and Schweinitz[9] found that only 0.24% of the peroxide was used in converting sodium sulfite to dithionate. The remainder of the peroxide was used in production of sulfate.

Two moles of sulfite should be consumed for each mole of peroxide reacted in the dithionate-forming reaction and only one mole of sulfite per mole of peroxide in the sulfate-forming reaction. Hence, stoichiometric measurements may be employed to ascertain the contributions of the sulfate and dithionate-forming reactions to the total re-

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[4] The analyses of sodium sulfite and hydrogen peroxide were carried out by D. G. Bush, of these Laboratories.

[5] K. Meyer and L. Roth, *Z. wiss. Phot.*, **49**, 10 (1954).

[6] G. Bredig, H. L. Lehmann and W. Kuhn, *Z. anorg. allgem. Chem.*, **218**, 16 (1934).

[7] H. L. J. Bäckström, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 15 (entire issue) (1927).

[8] K. B. Rao and G. G. Rao, *Analyt. Chim. Acta*, **13**, 313 (1955).

[9] H. W. Albu and H. D. Schweinitz, *Ber.*, **65**, 729 (1932).

action. In this way, Higginson and Marshall[10] found that the oxidation of sulfite by hydrogen peroxide occurs exclusively, or nearly so, *via* the sulfate-forming reaction at pH 0.5 (bisulfate buffer) and pH 9 (borate buffer). At pH 5 (acetate buffer), however, the stoichiometry varied between 1.00 and 1.04 moles of sulfite consumed per mole of peroxide reacted, the value depending on order of addition of reactants.

Stoichiometry of the peroxide–sulfite reaction has been determined for a number of the conditions under which the kinetic runs described here were carried out. Measurements were made in pH 10 carbonate and phosphate buffers, in pH 7.5 phosphate buffer and in an unbuffered medium at pH 7.5, all at ionic strength 1.0. Each solution contained 0.2 g./l. of EDTA tetrasodium salt. Care was taken to remove dissolved air from the solutions in order to avoid the H_2O_2-induced reaction of sulfite with oxygen.[7] In no case did the stoichiometry depart by more than 0.5% from one mole of sulfite consumed per mole of peroxide reacted. When air was present in the solutions, however, the consumption of sulfite during reaction was higher. For example, when 0.01 M H_2O_2 was reacting with 0.04 M Na_2SO_3 in pH 10 phosphate buffer, the ratio of moles of sulfite to moles of peroxide consumed was 1.00 in the absence of dissolved air and 1.025 in presence of air. Similar results were obtained in pH 10 carbonate buffer. When peroxide was present in excess in the reaction mixtures, air had less effect on the stoichiometry. The results of the stoichiometric measurements indicate that in the kinetic experiments the peroxide–sulfite reaction occurred primarily *via* the sulfate-forming reaction. In no instance should any significant error be introduced in the kinetic treatment of the rate data by assuming that one mole of sulfite was consumed for each mole of peroxide which reacted.

Kinetic Order and Catalysis of the Reaction.—Hydrogen peroxide–sulfite reactions carried out in phosphate buffers at constant pH above a value of about 8 conform closely to second-order kinetics (first order in both hydrogen peroxide and sodium sulfite), as shown by good linearity of second-order plots and the absence of any marked effect on the values of second-order rate constants of changing the initial sulfite concentration eightfold. The second-order rate constants, k_2, derived from the slopes of second-order plots, are given in Table I. The constant, k_2, is defined by

$$dx/dt = k_2(A_0 - x)(B_0 - x) \qquad (1)$$

where x is the decrease in molarity of hydrogen peroxide (dissociated + undissociated) due to reaction, and A_0 and B_0 are the initial concentrations of hydrogen peroxide and sodium sulfite (including all sulfite species, $SO_3^=$, HSO_3^-, etc.), respectively.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE H_2O_2-Na_2SO_3 REACTION IN PHOSPHATE BUFFERS

T = 25.0°; ionic strength = 1.0[a]; initial H_2O_2 concn. = 1.12×10^{-2} M

pH	Initial Na_2SO_3 concn., $M \times 10^2$	k_2, l. mole^{-1} sec.$^{-1}$ Exp.	Calcd.
12.75	3.95	0.0077	0.0062
11.41	3.95	.090	.083
11.41	0.553	.085	
11.23	3.95	.110	.103
10.80	3.95	.153	.149
10.36	3.95	.181	.179
10.36	0.553	.179	
10.08	3.95	.189	.189
10.08	1.12	.186	
10.08	0.553	.183	
9.78	3.95	.195	.195
9.42	3.95	.200	
8.98	3.95	.218	
8.98	0.553	.215	
8.53	.553	.332	
8.23	.553	.707	
7.92	.553	2.27	

[a] Ionic strength due to Na_2SO_3, phosphate buffer salts and EDTA salts; no Na_2SO_4 added.

In the pH range 9.4–10.4, the value of k_2 shows only minor dependence on pH, indicating absence of acid catalysis. Thus, in this pH region, an uncatalyzed or solvent-catalyzed reaction predominates. The decrease in k_2 at the higher pH values correlates well with the decrease in concentration of H_2O_2 due to dissociation and can be explained by assuming that the HO_2^-–$SO_3^=$ reaction is much slower than the H_2O_2–$SO_3^=$ or kinetically indistinguishable HO_2^-–HSO_3^- reaction. For example, the k_2 values in the fourth column of Table I were calculated assuming the rate of the HO_2^-–$SO_3^=$ reaction to be zero. Equation (2) was used

$$k_2 = k_0\, 10^{-pH}/(10^{-pH} + K_A) \qquad (2)$$

where k_0 is the second-order rate constant for the uncatalyzed H_2O_2–$SO_3^=$ reaction, taken = 0.202 l. mole^{-1} sec.$^{-1}$, and K_A is the acid dissociation constant of H_2O_2 at 25° and ionic strength 1.0, taken = 5.6×10^{-12} (estimated from data of Evans and Uri[11]).

The marked increase in k_2 at pH values below about 8.5 was found to be due primarily to catalysis by phosphate buffer salts. For pH values greater than about 8.5, there is no important catalysis by the phosphate buffer, as shown by the data of Table I and Table II, where it is seen that, for a given pH, there is no significant change in the value of k_2 when the phosphate buffer is left out of the reaction mixture. Arsenate buffer at pH 9.89 also had no appreciable effect on the value of k_2. In addition, Table II shows that, for the pH values concerned, there is no important salt effect. It will be noted (Table II) that in the absence of any added salt or buffer, raising the pH from 10.08 to 11.36 causes a decrease in k_2 similar to that observed in phosphate buffers. This fact is consistent with the theory that this decrease is due to the dissociation of the H_2O_2 and indicates that this effect of pH is in no way directly related to the presence of phosphate buffer salts.

In a detailed study of catalysis by phosphate buffers, twenty-four kinetic runs were made in three series of buffers, having pH values of 6.96,

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(10) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

(11) M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).

TABLE II

EFFECT OF REACTION ENVIRONMENT ON SECOND-ORDER RATE CONSTANT

$T = 25.0°$; initial H_2O_2 concn. = initial Na_2SO_3 concn. = 1.12×10^{-2} *M*

Salt	Ionic strength	*p*H	k_2, l. mole^{-1} sec.$^{-1}$
Phosphate buffer[a]	0.20	8.86	0.238
None added	.034	10.08	.196
None added	.046	11.36	.108
Na_2SO_4	.20	10.08	.204
Na_2SO_4	1.0	10.08	.210
Na_2SO_4	1.0	9.80	.216
Arsenate buffer	1.0	9.89	.187

[a] Initial Na_2SO_3 concn. = 5.53×10^{-3} *M* for this experiment.

7.26 and 7.62. Within each constant-*p*H series, the ionic strength was held constant at 1.0 with sodium sulfate while the buffer concentration was varied from the maximum possible value (the buffer salts alone giving ionic strength 1.0) down to a value one quarter this great. Initial H_2O_2 concentration was 0.001 *M* in each run, while initial Na_2SO_3 concentration varied between 0.001 and 0.007 *M*. It was found that at constant *p*H the rate of the reaction is linearly related to buffer concentration, the mean departure of the data from straight lines being 2.3%. (The straight lines were constructed so as to minimize the sum of the squares of the *percentage* deviations of the experimental points from the lines.) In addition, the relation between the slopes of these lines and *p*H shows that, in the *p*H region 7–8, the rate along the phosphate-catalyzed reaction path is proportional to the product, $10^{-pH}(H_2PO_4^-)$. These facts, along with the rate of the uncatalyzed reaction determined at higher *p*H, allow the following partial formulation of the empirical rate equation for reaction in phosphate buffers of *p*H higher than about 7

$$dx/dt = k_0(H_2O_2)(SO_3^{=}) + k_p 10^{-pH}(H_2PO_4^-)(H_2O_2)(SO_3^{=}) + r_c \quad (3)$$

where k_0 and k_p are the rate constants for the uncatalyzed and phosphate-catalyzed reactions, respectively, and (H_2O_2) is the molarity of undissociated hydrogen peroxide. At 25° and ionic strength 1.0, $k_0 = 0.20$ l. mole^{-1} sec.$^{-1}$ and $k_p = 1.7 \times 10^{10}$ l.^{3} mole^{-3} sec.$^{-1}$. The values of $(SO_3^{=})$ and $(H_2PO_4^-)$ used in evaluating these constants were calculated using the known concentrations of the salts and the dissociation constants given in the experimental section.

The term r_c must be included in equation 3 to account for contributions to the over-all reaction by catalyzed reactions other than the phosphate-catalyzed reaction. Evidence for the existence of such catalyzed reactions is to be found in the fact that extrapolation (along the constant-*p*H plots) of reaction rates to zero phosphate buffer concentration leads to reaction rates higher than the rate of the uncatalyzed reaction. The magnitude of r_c decreases rapidly with increasing *p*H, explaining failure to detect its existence at *p*H near 10. At the highest phosphate buffer concentration, the rate data for *p*H in the 7–8 region indicate that the phosphate-catalyzed reaction is first order in both sulfite and H_2O_2. As buffer concentration is made lower, however, there is evidence of a small deviation from first-order dependence of the over-all rate on sulfite, indicating that one or more of the rate terms which contribute to r_c contain $(SO_3^{=})$ to a power other than unity.

To learn more about the nature of r_c, twenty-seven kinetic runs were made at *p*H values between 7 and 8 in absence of phosphate buffer. Initial H_2O_2 concentration was 0.001 *M*, and initial Na_2SO_3 concentration varied between 0.003 and 0.01 *M*. The data indicate that the reaction continues to be first order in H_2O_2 under these conditions; however, the rate shows a somewhat greater than first-order dependence on sulfite. Using these data, the following approximate expression for r_c has been derived

$$r_c = [9.5 \times 10^{12} + 9 \times 10^{14}(SO_3^{=})]10^{-1.8pH}(H_2O_2)(SO_3^{=}) \quad (4)$$

where r_c has the units mole l.$^{-1}$ sec.$^{-1}$. Reaction rates calculated using equations 3 and 4 (with $(H_2PO_4^-) = 0$ and for *p*H in the 7–8 range) differ from the experimental values by a mean amount of 5%. In only three of the twenty-seven cases do the calculated rates differ from the experimental values by more than 8%. While equation 4 may be used to obtain an approximate value of r_c, it is felt that agreement with experiment is not good enough to justify any extensive kinetic interpretation of the equation. It does appear, however, that r_c includes contributions from several catalyzed reactions, at least one of which is higher than first order in $SO_3^{=}$. Hydronium-ion catalysis is also indicated.

Catalysis of the hydrogen peroxide–sulfite reaction was observed in an arsenate buffer of *p*H 8.10 ($H_2AsSO_4^-$ concentration = 6.5×10^{-3} *M* and ionic strength = 1.0). The second-order rate constant, k_2, is 1.30 l. mole^{-1} sec.$^{-1}$, while it can be estimated that at this same *p*H in absence of added buffer the value would be about 0.25 l. mole^{-1} sec.$^{-1}$. It will be recalled that at a higher *p*H (9.89) there was no noticeable catalysis by arsenate buffer, the uncatalyzed reaction being predominant. In this respect, the catalytic behavior of arsenate buffer appears to be similar to that of phosphate.

The reaction is also catalyzed by carbonate buffers. The catalyzed reaction comes into prominance at higher *p*H than is the case for phosphate or arsenate catalysis, being considerable even at *p*H 10. Behavior in carbonate buffers is different in another important respect. The reaction deviates considerably from second order when reactant concentrations are such that the product, $(H_2O_2)(SO_3^{=})$, is greater than about 10^{-5} *M*.[2] At lower reactant concentrations, the reaction appears to approximate second-order behavior. In Fig. 1, second-order plots for the reaction in phosphate and carbonate buffers are compared. Deviation from second-order (non-linearity) and catalysis (greater slope) for the carbonate buffer are apparent. Because of the unusual behavior in carbonate buffers, rate data for a number of the experiments are given in detail in Table III. Most of these reactions were followed both polarographi-

TABLE III

KINETIC DATA FOR REACTIONS IN CARBONATE BUFFER[a]

(Per cent. of H_2O_2 reacted *vs.* reaction time.) $T = 25.0°$; ionic strength = 1.0; *p*H 10.10

Reaction time (min.)	A_0 = 0.01121 M B_0 = 0.0395 M	A_0 = 0.01128 M[c] B_0 = 0.0397 M	A_0 = 0.01118 M B_0 = 0.02031 M	A_0 = 0.01123 M B_0 = 0.01426 M	A_0 = 0.01122 M B_0 = 0.01122 M	A_0 = 0.01124 M B_0 = 0.00851 M	A_0 = 0.01125 M B_0 = 0.00553 M	A_0 = 0.00168 M B_0 = 0.00470 M
0.5	24.3 (23.0)[b]	(21.8)	15.1 (14.0)	11.9 (11.8)	9.1		(8.1)	
0.75	33.3				(13.1)	(10.3)	10.9	14.5
1	41.3 (42.3)	(39.3)	26.6 (26.3)	21.2 (19.7)	17.3	15.5	14.8	
1.5	55.0		36.4	29.2	24.3	20.9	18.4 (17.1)	25.1
2	65.9 (66.2)	(64.5)	44.8 (45.3)	36.1 (36.2)	30.4 (30.2)	25.8 (24.7)	21.6	
2.5	74.7		52.1	42.0		30.2	24.5	32.7
3	81.4 (81.4)	(80.0)	58.3	47.5	40.3	34.2		
3.5	86.2		63.8 (64.7)	52.2			29.3	39.3
4	90.5	(89.0)	68.7	56.6 (56.5)	48.3	40.7		
4.5	93.4 (93.6)		72.7	60.1			33.0 (32.5)	45.8
5	95.4		76.4	63.7	54.7 (54.9)	45.9 (45.7)	36.0	51.8
6	98.0		82.8 (83.0)	69.5	59.8	50.2	38.3	56.8
7			86.5	73.9 (74.4)				
8			89.8		67.6	56.5	41.8 (41.5)	66
9			92.3 (92.8)		(70.6)	(59.3)		68
10					72.9	61.1	43.9	71
11				85.5	75.0			
12			96.5	(87.8)			45.6	76
13						65.5	(46.0)	
14					80.1 (80.3)	66.9 (66.8)		81
15				91.1	81.4		47.2	
16							47.9	
18				(93.9)		69.9	(47.4)	
20					(85.8)	(71.1)		
21					86.5	71.8		

[a] 0.3 M Na_2CO_3–0.1 M $NaHCO_3$. [b] Figures in parentheses are for spectrophotometric method; all others are for polarographic method. [c] No EDTA salts in this reaction mixture.

cally and spectrophotometrically. The agreement between the two sets of data is good.

Several experiments were run in which the composition of the carbonate buffer was varied from that used in obtaining the data of Table III. The results indicate that, when the reactant concentrations are sufficiently low so that second-order behavior is approximated, the rate of the reaction is directly proportional to HCO_3^- concentration and, for a given HCO_3^- concentration, independent of *p*H.

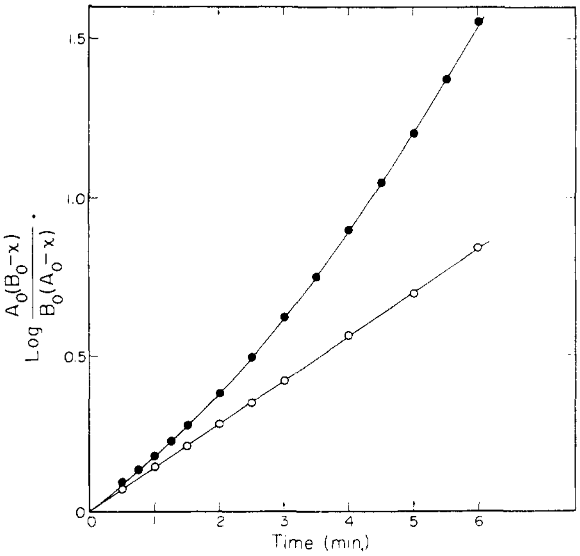

Fig. 1.—Second-order plots: ○, 0.01123 M H_2O_2–0.0395 M Na_2SO_3 in phosphate buffer (*p*H 10.08); ●, 0.01122 M H_2O_2–0.0395 M Na_2SO_3 in carbonate buffer (*p*H 10.10); $T = 25°$; ionic strength = 1.0.

The buffers which catalyze the H_2O_2–$SO_3^=$ reaction share a common feature: they contain proton-donating acids, such as $H_2PO_4^-$. It is probable that these species, or some of them, are the active catalysts and that they owe their catalytic activity to their acidity. Thus, it would appear that the reaction may be subject to general acid catalysis, as is believed to be the case for a number of other oxidation reactions of hydrogen peroxide with anions.[12] If the reaction is subject to general acid catalysis, it is possible that the divergence from first-order dependence on sulfite concentration noted at *p*H below 8 is due to catalysis of the reaction by acidic species formed through association of sulfite ion and hydrogen ion (HSO_3^-, for example). The divergence from first order is in the direction expected to result from such catalysis, as revealed by the form of equation 4.

Effect of Temperature.—The effect of temperature on k_2 of the uncatalyzed reaction was determined at low ionic strength and at a *p*H near 10 (Table IV). The slope and the intercept of the Arrhenius plot give 15.2 kcal./mole for the energy of activation and 3×10^{10} l. mole^{-1} sec.$^{-1}$ for the frequency factor.

Effect of EDTA Salts.—One run was made without EDTA salts present in the solutions. The buffer was carbonate, and the kinetic data are

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[12] J. O. Edwards, *J. Phys. Chem.*, **56**, 279 (1952).

TABLE IV

EFFECT OF TEMPERATURE

Ionic strength = 0.034; initial H_2O_2 concn. = initial Na_2SO_3 concn. = 1.12×10^{-2} *M*

T, °C.	*p*H	k_2, l. mole $^{-1}$ sec. $^{-1}$
0.4	9.95	0.0196
15.0	10.18	.0829
25.0	10.08	.196
35.0	9.95	.464

shown in the third column of Table III. Some effect is to be expected in the absence of EDTA salts, owing to loss of sulfite through reaction with the oxygen of the air and through loss of H_2O_2 through decomposition. However, the importance of these side reactions relative to the peroxide-sulfite reaction was minimized by choosing conditions leading to rapid peroxide–sulfite reaction. The experiment was run to see if there was any important, unanticipated effect of EDTA salts on the rate of the reaction. On comparing the second and third columns of Table III, it is obvious that there was no such effect.

Effect of Metal Ions.—The chemicals used in the experiments probably contained traces of ions that usually show catalytic activity. To determine whether or not metal-ion catalysis might have played an important part in the experiments, a run was made in an unbuffered solution to which sufficient Fe^{+++} and Cu^{++} were added to double the maximum expected level of these ions in the kinetic experiments. EDTA salts were also present and Na_2SO_4 was used to give an ionic strength of 1.0. The *p*H varied from 8 to 6.6 during the course of the reaction. For comparison, an identical run was made without the added metal ions. The polarographic method was used. The added metal ions had no detectable effect on the rate of disappearance of H_2O_2 from the reaction mixture. It is unlikely that metal-ion catalysis was of any importance in the kinetic runs.

Effect of Light.—No attempt was made to protect the solutions during reaction from the illumination in the room, since it was believed that the reactants absorbed a negligible amount of radiation from this source. However, as a precaution, one reaction in *p*H 10 carbonate buffer was carried out in the beam of a Kodak Signet 500 slide projector placed 16 inches from the reaction vessel. There was no detectable effect of this high-intensity illumination on the reaction rate.

Errors.—For *p*H values above about 8 and for an initial H_2O_2 concentration of 0.01 *M*, the probable errors in k_2 for several representative initial sulfite concentrations are: B_0 = 0.04 *M*, 1.5%; B_0 = 0.01 *M*, 2.0%; B_0 = 0.0055 *M*, 3.2%. These errors were calculated using assumed values for the probable errors in the various quantities used in calculating k_2.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Deuterium Isotope Effects in the Bromine Oxidation of Ethanol and of Acetaldehyde[1]

BY LOUIS KAPLAN

RECEIVED OCTOBER 21, 1957

The rate of oxidation of ethanol-1,1-d_2 by bromine in aqueous solution has been measured over a range of alcohol concentrations from one to 41% by weight, and over a *p*H range from two to ten. In unbuffered acid solution the ratio of the rates of oxidation of ordinary to that of dideutero alcohol is close to four, proving that a methylene C–H bond is broken in the rate-determining step of the reaction. From the isotope effect and the reaction kinetics it is concluded that ethyl hypobromite plays no role in the oxidation of ethanol, neither as the precursor of acetaldehyde nor as the active oxidant. Under the same conditions acetaldehyde is oxidized at a rate four times that of acetaldehyde-1-*d*, in accord with the suggestion that the aldehyde is oxidized, *via* its hydrate, by a mechanism very similar to that for ethanol. At *p*H 5.5 and 10.3 the isotope effects for the alcohol oxidation are 2.4 and 3.0, respectively. The significance of these lower values cannot be assessed in the absence of detailed knowledge of the reaction products and kinetics under these conditions.

Introduction

In an earlier investigation[2] of the oxidation of ethanol-1-*t* by bromine it was found that the rate of removal of a tritium atom from the methylene carbon was about 0.15 that for a protium atom. From this isotope effect and the previously investigated[3] reaction kinetics it was concluded that ethyl hypobromite is not a precursor of acetaldehyde in the oxidation. The possibility remained that ethyl hypobromite or an ethanol–bromine complex might be formed in the rate-determining step of the reaction and oxidize a different molecule of ethanol in a subsequent fast step. It was pointed out that such a mechanism could account for the isotope effect observed in the competitive system studied with tritium, but should result in little or no difference between the separately measured reaction rate constant for ethanol from that for ethanol-1,1-d_2. The present paper presents the results of a comparison of the reaction rates of these two compounds in dilute unbuffered solutions comparable to those used in the tritium studies, as well as at higher alcohol concentrations and higher *p*H. An estimate has also been made of the deuterium isotope effect in the concurrent oxidation of acetaldehyde.

Experimental

Reagents.—Ethanol was the U. S. Industrial Chemicals Co. absolute grade. It was found to contain less than five parts per million of aldehyde.

Ethanol-1,1-d_2 was prepared by a procedure similar to that used for the tritium-labeled compound.[2] To a sus-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 132nd Meeting, American Chemical Society, New York, N. Y., September, 1957.

[2] L. Kaplan, THIS JOURNAL, **76**, 4645 (1954).

[3] L. Farkas, B. Perlmutter and O. Schächter, *ibid.*, **71**, 2829 (1949).