

is the hydrate form, but neither composition nor temperature conditions of formation were specified.

Polymorphism of sulfanilamide has been described by Watanabe,<sup>5</sup> working in Japan. By means of X-ray study three forms of the solid were defined. The crystals studied were all obtained from alcohol; hence Watanabe could not have obtained the hydrate which is the main feature of this investigation.

Since 37° is body temperature, the sulfanilamide hydrate or transition thereof may hypothetically bear some relation to therapeutic activity, perhaps as a water carrier in biological coupled reactions or as an energy transfer mechanism.

The behavior in buffers bears out the hypothesis that sulfanilamide and its isomers may behave as ampholytes, with minimum solubility at an "isoelectric point" (pH 4.5–5.0 at 37°). The solubility increase for sulfanilamide at pH 1.2 appears to be exceptionally large.

The similarity of "isoelectric point" of sulfanilamide with that of blood serum proteins may be involved in therapeutic activity.

(5) Watanabe, *Naturwissenschaften*, **29**, 116 (1941); *Chem. Abs.*, **36**, 695 (1942).

The authors are indebted to Dr. G. L. M. Christopher for help rendered in the preparation of this paper and to Dr. M. L. Crossley for the encouragement to carry through this type of investigation.

### Summary

1. The aqueous solubilities of orthanilamide, metanilamide and sulfanilamide have been determined in the range 23–50°.

2. Heats of solution calculated from the solubility data are: orthanilamide 7820; metanilamide 9570; sulfanilamide below 37°, 10,860, above 37°, 9050 cal./mole.

3. The discontinuity in the solubility curve of sulfanilamide at 37° represents a transition, confirmed by dilatometry, and shown by analysis to involve a monohydrate.

4. Solubilities in buffered solutions of pH 1.2 to 12.4 at 37° exhibit a minimum for all three isomers at pH 4.5–5.0, with striking increase above pH 9 and below pH 3, especially for sulfanilamide below pH 2.

BOUND BROOK, NEW JERSEY

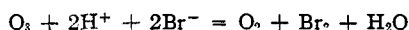
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

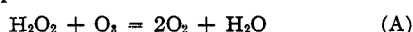
## Reactions in Solutions Containing O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sup>+</sup> and Br<sup>-</sup>. The Specific Rate of the Reaction O<sub>3</sub> + Br<sup>-</sup> →

BY HENRY TAUBE

When ozone and bromide ion are mixed in acid solution, the net reaction



takes place so rapidly that a direct measure of the specific rate is not possible. In the present paper, experiments on the measurement of this specific rate by an indirect method are reported. The system studied contained acid, O<sub>3</sub>, Br<sup>-</sup> at a relatively low concentration and H<sub>2</sub>O<sub>2</sub>. Hydrogen peroxide possesses the properties that at low (Br<sup>-</sup>), it rapidly reduces bromine to Br<sup>-</sup>,<sup>1</sup> that the reaction with Br<sup>-</sup> under the present conditions is negligibly slow, and that the direct interaction with ozone is also slow.<sup>2</sup> The net reaction which takes place in this mixture is



It has been shown<sup>2</sup> that this reaction is ac-

celerated by Br<sup>-</sup>, and that the catalytic decomposition of ozone



which accompanies reaction A in a mixture of H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and acid is suppressed by low concentrations of Br<sup>-</sup>.

The experiments consisted of a study of the variation of the rate of A with (O<sub>3</sub>), (H<sub>2</sub>O<sub>2</sub>), (H<sup>+</sup>) and (Br<sup>-</sup>). Analysis of the data showed that three distinct paths are available for reaction A. Mechanisms for these paths, consistent with the data, and with other work in this field are proposed.

### Experimental

Acid solutions of O<sub>3</sub> at 0° were prepared as described<sup>2</sup>; redistilled water was used for the most part. Merck's inhibitor free Superoxol was used to make up the solution of H<sub>2</sub>O<sub>2</sub>. A stock supply of sodium perchlorate solution was prepared by neutralizing perchloric acid with c. p. sodium carbonate.

(1) Bray and Livingston, *THIS JOURNAL*, **60**, 1663 (1928).

(2) Taube and Bray, *ibid.*, **62**, 3357–3373 (1940).

The method of handling the solutions was the same as that described in the earlier article. Usually nine cells were filled for a single experiment; these were placed in an ice-bath shielded from light and analyzed at intervals. The time of emptying, less than one-tenth minute, was small compared to the shortest interval between successive quenchings, one and one-half minutes.

The rates were obtained by plotting the values of  $(O_3)$  or  $(H_2O_2)$  against time in minutes, and measuring the slopes at intervals on the curve. Each experiment yields values of the rates for a fairly wide range of  $(O_3)$  and  $(H_2O_2)$ ; for each experiment a table was computed listing corresponding values of time,  $(H_2O_2)$ ,  $(O_3)$ , rates and suitable functions of these variables. The system is not nearly as sensitive to traces of impurities as it is in the absence of  $Br^-$  and results were reproducible.

All experiments were carried out at  $0^\circ$ . Except where otherwise stated, the ionic strength was maintained at 0.20 by the addition of sodium perchlorate solution. The units used throughout are: concentration in moles per liter and time,  $t$ , in minutes.

In all experiments for which rate data are presented,  $(H^+)$  and  $(Br^-)$  were sufficiently high to eliminate reaction B almost completely, so that  $\Delta(H_2O_2) = \Delta(O_3)$ . For the analysis in most cases the cell content was forced into an acidified solution of sodium bromide, and potassium iodide and ammonium molybdate solutions were then added. After the hydrogen peroxide had reacted completely with the iodide ion, the total iodine (equivalent to the sum of the ozone and hydrogen peroxide) was determined. One cell in each run was allowed to proceed to completion,

and the final concentration of the reagent in excess then determined. This permitted the concentration of hydrogen peroxide and ozone at any time to be calculated from the corresponding value of their sum. Orienting experiments showed that this method gave the same results as the method of separate analysis.<sup>2</sup>

In most of the experiments,  $(Br^-)$  added was small compared to  $(H_2O_2)$  or  $(O_3)$ ; when  $(Br_2)$  was appreciable, appropriate corrections were made in calculating the concentration of ozone and hydrogen peroxide.

**Results**

Figure 1 presents data on the variation of the rate of reaction A with  $(Br^-)$  at low values of  $(H^+)$  and at low values of the ratio  $(O_3)/(H_2O_2)$ . The specific rate  $k_1$ , which is plotted as ordinate, is defined by

$$-d(H_2O_2)/dt = -d(O_3)/dt = k_1(O_3)$$

For each line in the figure, the only variable is the concentration of  $Br^-$ . The results show that the rate law consists of at least two terms. One of these varies directly with  $(Br^-)$ ; its value is given by the slope of the straight lines through points of constant  $(H^+)$ ,  $(H_2O_2)$  and  $(O_3)$  and varying  $(Br^-)$ . The slopes of the lines (*cf.* table under Fig. 1) are nearly constant and independent of  $(H^+)$ . The slight variation as  $(O_3)$  decreases and time increases is discussed in connection with Fig. 2. The other term represented by the intercept on the vertical axis is independent of  $(Br^-)$ ; the variation of this term with  $(H^+)$  over a wide range is discussed below.

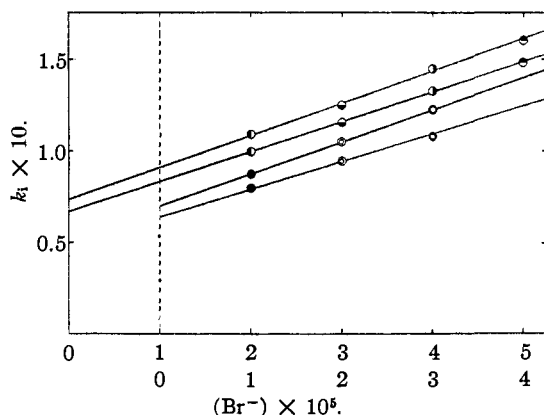


Fig. 1.—Variation of  $k_1$  with  $(Br^-)$ ;  $\mu = 0.20$ ;  $(H_2O_2) = 12.5 \times 10^{-4} M$ . The lower row of values for the abscissa refers to lines 3 and 4, the lines being numbered from top to bottom. Points represented by the same symbol are results of the same experiment; the upper one always is a result later in an experiment after  $(O_3)$  has decreased to the designated value. To eliminate  $(H_2O_2)$  as a variable, the data were corrected to the recorded value of  $(H_2O_2)$  using the law of variation with  $(H_2O_2)$  demonstrated in Fig. 2; the maximum correction was about 6%.

line	$(O_3) \times 10^4$	$(H^+) \times 10^3$	slope
1	2	1.16	1750
2	3	1.16	1600
3	1	2.60	1750
4	2	2.60	1520

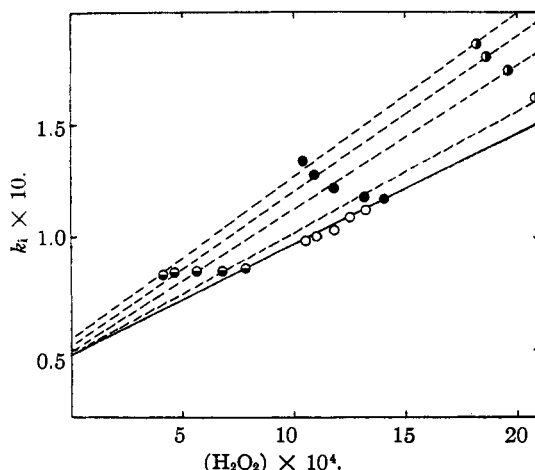


Fig. 2.—Variation of  $k_1$  with  $(H_2O_2)$ , at  $3 \times 10^{-5} M Br^-$ ,  $1.16 \times 10^{-2} M HClO_4$ ,  $\mu = 0.20$ . All points from one experiment are distinguished by the same symbol. The open circles distinguish an experiment in which the method of handling the solutions was changed (see text). Numbering the lines from top to bottom: for line 1,  $(O_3) = 0.5 \times 10^{-4} M$ ; for 2,  $1.0 \times 10^{-4} M$ ; 3,  $2 \times 10^{-4} M$ ; 4,  $3.25 \times 10^{-4} M$ ; 5,  $4.2 \times 10^{-4} M$ .

Figure 2 shows the variation of  $k_i$  with  $(\text{H}_2\text{O}_2)$  at  $1.16 \times 10^{-3} M \text{HClO}_4$ ,  $3 \times 10^{-5} M \text{Br}^-$  and low values of the ratio  $(\text{O}_3)/(\text{H}_2\text{O}_2)$ . Along each line, the only variable is  $(\text{H}_2\text{O}_2)$ ; from line to line,  $(\text{O}_3)$  differs. It is again apparent that there are at least two terms in the rate law. The peroxide independent term, which is represented by the finite limiting value of  $k_i = 0.048 \pm 0.002$  at zero peroxide, can be identified with the bromide dependent term of Fig. 1. This follows since the coefficient obtained by dividing the value of the intercept by the concentration of  $\text{Br}^- (0.048/3 \times 10^{-5}) = 1600$  is the same as the slope of the lines in Fig. 1. The peroxide dependent part of the rate law then corresponds to the  $(\text{Br}^-)$  independent term of Fig. 1.

The experiment in Fig. 2 represented by the open circles was an experiment in which five cells were rapidly and consecutively filled. During the experiment, the ozone concentration fell to one-third of its initial value; these points are seen to fall in line with the initial points in the other experiments and prove that  $k_i$  is independent of  $(\text{O}_3)$  (*i. e.*, rate is proportional to  $(\text{O}_3)$ ) for these conditions. In all the other experiments, the process of filling the cells was interrupted to make analyses. This probably occasioned a loss of ozone from the main body of the solution and the variation of  $k_i$ , *ca.* 40% for an 8-fold variation in  $(\text{O}_3)$ , with  $(\text{O}_3)$  shown by the lines through these points is therefore mainly due to this cause; these results have been included for the sake of completeness, but the lower line is taken as the

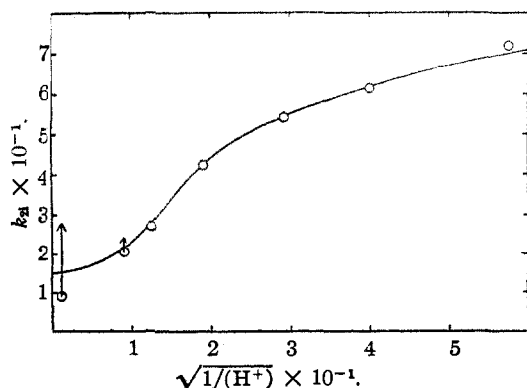


Fig. 3.—The variation of  $k_2$  with  $(\text{H}^+)$ ;  $\mu = 0.2$ .  $(\text{O}_3) = 3.0 \times 10^{-4} M$ ,  $\text{H}_2\text{O}_2 = \text{ca. } 14.0 \times 10^{-4} M$  for the series.  $(\text{Br}^-) = 2 \times 10^{-5} M$  except in the two experiments at lowest  $\text{H}^+$  where it was  $5 \times 10^{-5} M$ . In the two experiments at high  $(\text{H}^+)$ , the bottom of the arrow is the value if the maximum correction for path III is applied; top is the value if no correction for path III is applied (see text).

best representation of the rate of reaction for these conditions.

The results of Figs. 1 and 2 may be summarized by the equation

$$k_i = 1600 \pm 100 (\text{Br}^-) + k_H (\text{H}_2\text{O}_2) \quad (\text{I})$$

Line 2 in Fig. 1 passes through the most accurate data and the slope of this line was taken as the numerical coefficient of the first term of rate law I.

In rate law I,  $k_H$  is not a true constant but varies with  $(\text{H}^+)$ . A number of experiments were performed to study this variation; these results are presented in Fig. 3. At values of  $(\text{H}^+) < 1.15 \times 10^{-3} M$ ,  $(\text{Br}^-)$  was raised to  $5 \times 10^{-5} M$  to suppress reaction B.  $k_H$ , at any value of  $(\text{H}^+)$  within the range for which rate law I is valid, can readily be calculated by the use of this equation from the measured value of  $k_i$ . As will be shown later, at high  $(\text{H}^+)$ ,  $\text{Br}^-$  is present at the steady state largely as  $\text{Br}_2$ , and a new path for reaction A is available. Corrections, consistent with the later findings, are applied to the experimental values  $k_i$  to allow for these effects; these corrections are necessary only at the two highest values of  $(\text{H}^+)$ . There is an uncertainty in applying the correction for the new path due to bromine in the present range of values for  $(\text{O}_3)/(\text{H}_2\text{O}_2)$ ; the uncertainty is in such a direction that  $k_H$  is greater than the plotted value. For the point at highest  $(\text{H}^+)$ ,  $k_H$  may well be twice as great as the plotted value; for the next point, only slightly greater. In spite of this uncertainty, the results indicate that  $k_H$  approaches limiting values both at high and at low  $(\text{H}^+)$ .

When  $(\text{H}^+)$  and the ratio  $(\text{O}_3)/(\text{H}_2\text{O}_2)$  are increased, the kinetics of the reaction change radically. In Fig. 4, the results of a series of experiments for this concentration region are presented. To represent these results, it was found convenient to define a specific rate  $k_{ii}$  (not necessarily a constant) by the equation

$$-d(\text{H}_2\text{O}_2)/dt = k_{ii} \sqrt{(\text{H}_2\text{O}_2)(\text{O}_3)}$$

A single experiment is represented by a series of points starting at the right and usually covers a 6–12 fold change in the concentration of hydrogen oxide. The lines have been drawn in to conform to the rate law

$$k_{ii} = 1.26 \sqrt{(\text{Br}_2)/(\text{H}^+)} + 1.41 \times 10^2 \sqrt{(\text{Br}_2)(\text{H}_2\text{O}_2)} \quad (\text{II})$$

$(\text{Br}_2) = (\text{Br}^-)_0/2$  where  $(\text{Br}^-)_0$  is the concentration of bromide ion added) and represent the data with satisfactory fidelity except at the lowest

value of  $(H^+)$  investigated in this series (upper part of the figure).

In preliminary work, the law of variation with the concentration of added  $Br^-$ ,  $(Br^-)_0$ , was tested over a wider range than is done in Fig. 4. These data are presented in Table I. The results, though not strictly comparable with those of Fig. 4 (the ionic strength was less and  $(H^+)$  was not accurately known) are consistent with them. These results again show that  $k_{ii}$  varies directly with  $\sqrt{(Br_2)}$ .

TABLE I

VARIATION OF  $k_{ii}$  WITH ADDED  $Br^-$   
 $HClO_4$  is ca. 0.15 M and  $\mu$  is ca. 0.15.  $(H_2O_2)_0 = 3.6 \times 10^{-4}$  M.

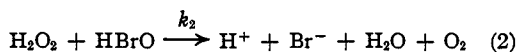
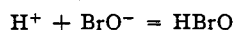
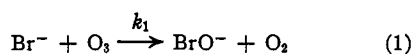
$(Br^-)_0 \times 10^6$	$(O_3) \times 10^4$	$k_{ii} \times 10^3$	$\frac{k_{ii}}{\sqrt{(Br_2)}}$
10	7.60	1.30	0.58
20	8.17	1.87	.59
40	7.17	2.64	.59
100	6.87	4.20	.59
300	6.90	7.80	.63

### Discussion

The rate laws obtained show that at each of the extremes—low  $(H^+)$ , low  $(O_3)/(H_2O_2)$  and high  $(H^+)$ , high  $(O_3)/(H_2O_2)$ —there are two paths for reaction A.

The first term of rate law I and the first term of rate law II both follow from the non-chain path represented by the following reactions (arrows designate rate determining steps).

#### PATH I



When reaction 1 is the sole rate determining step (*i. e.*,  $(Br_2)$  and  $(HBrO) \ll (Br^-)$ ), the simple rate law corresponding to the first term of rate law I follows. It will be shown that this condition is realized in the experiments at low values of  $(H^+)$  and  $(O_3)/(H_2O_2)$ . The numerical coefficient of this term therefore gives the value of  $k_1$ ; thus, the rate of interaction of  $O_3$  and  $Br^-$  at  $0^\circ$  and  $\mu = 0.2$  is  $1600 \pm 100$  l. mole $^{-1}$  min. $^{-1}$ .

The following considerations show that at low  $(H^+)$  and low  $(O_3)/(H_2O_2)$ ,  $(Br^-) \gg (HBrO)$ . At the steady state,  $k_1(O_3)(Br^-) = k_2(H_2O_2)(HBrO)$  and  $(Br^-)/(HBrO) = k_2(H_2O_2)/k_1(O_3)$ .

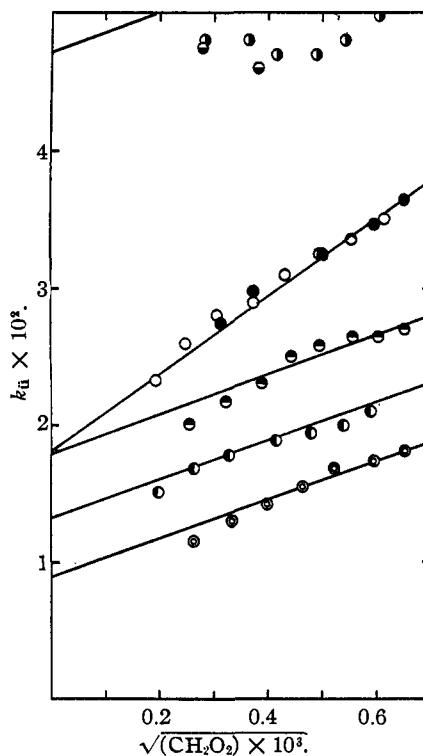


Fig. 4.—Variation of  $k_{ii}$  with  $(H_2O_2)$ ,  $(O_3)$ ,  $(H^+)$ ,  $(Br^-)_0$  at high  $(O_3)/(H_2O_2)$  and  $\mu = 0.20$ . All points obtained from a single experiment are distinguished with the same symbol.

Symbol	⊙	●	⊖	●	○	⊖	●
$(O_3)_0 \times 10^4$	16.46	12.3	14.32	7.54	15.11	14.45	13.2
$(H^+) \times 10^2$	20.1	8.86	4.48	20.2	20.2	0.63	0.63
$(Br^-)_0 \times 10^6$	2	2	8	8	2	2	2

Bray and Livingston,<sup>1</sup> from an analysis of Balint's<sup>3</sup> measurements on the rate of reaction of bromine and peroxide at  $0^\circ$ , report for  $k_2 K_{Br_2}$  a value of  $6.2 \times 10^{-4} \pm 9\%$ . For the same ionic strength (zero) Liebhfafsky<sup>4</sup> reports  $K_{Br_2}$  at  $0^\circ = 6.9 \times 10^{-10}$ . Thus  $k_2 = 9 \pm 1 \times 10^6$ .<sup>5</sup> When this value is substituted in the above expression together with  $k_1 = 1600$ ,  $(Br^-)/(HBrO) = 560$  when  $(H_2O_2) = (O_3)$ . For the experiments under consideration  $(H_2O_2)$  always exceeded  $(O_3)$  by more than a factor of 3 and  $(HBrO)$  becomes correspondingly less compared to  $(Br^-)$ .

To show that  $(Br_2)$  is small for the same conditions, the expression for the steady state concentration of  $Br^-$  when the hydrolysis is not complete and when  $(HBrO) \ll (Br^-)$  (*i. e.*,  $(O_3)/(H_2O_2)$  does not exceed ca. 25) is derived; the result is

(3) Balint, Thesis (in Hungarian), University of Budapest, 1910.

(4) Liebhfafsky, THIS JOURNAL, 66, 1500 (1934).

(5) This is the value calculated for  $\mu = 0$ ; the value  $\mu = 0.2$  should not differ widely since both molecules are neutral.

$$(\text{Br}^-) = \frac{\left( K_{\text{Br}_2}^2 + 8(\text{Br}^-)_0 K_{\text{Br}_2} \frac{k_1}{k_2} (\text{H}^+) \frac{(\text{O}_3)}{(\text{H}_2\text{O}_2)} \right)^{1/2} - K}{4 \frac{k_1}{k_2} (\text{H}^+) \frac{(\text{O}_3)}{(\text{H}_2\text{O}_2)}} \quad (\text{III})$$

Using the values  $k_1 = 1600$ ,  $k_2 = 9 \times 10^5$  and  $K_{\text{Br}_2} = 1.1 \times 10^{-9}$ ,  $(\text{Br}_2) = [(\text{Br}^-)_0 - (\text{Br}^-)]/2$  is calculated to be  $5 \times 10^{-7}$  for the most extreme case presented in Fig. 1 [lower right-hand point in Fig. 1;  $(\text{H}^+) = 2.65 \times 10^{-3}$ ,  $(\text{Br}^-)_0 = 3 \times 10^{-5}$ ,  $(\text{O}_3)/(\text{H}_2\text{O}_2) = 0.148$ ]. The point under consideration is actually below the line through the other points; this effect may be attributed to the fact that some of the  $\text{Br}^-$  is in the form of  $\text{Br}_2$  and the maximum rate is thus not observed.

A rate law of the form of the first term of rate law II follows from the mechanism above when  $(\text{Br}^-)$  and  $(\text{HBrO})$  are small compared to  $(\text{Br}_2)$ . It can readily be shown by using Equation III that this condition is realized for all the experiments in Fig. 4 except the two in the upper part of the diagram.

The rate law derived from the mechanism for this condition is

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = \sqrt{k_1 k_2 K_{\text{Br}_2}} \sqrt{\frac{(\text{Br}_2)}{(\text{H}^+)}} \sqrt{(\text{O}_3)(\text{H}_2\text{O}_2)}$$

where  $(\text{Br}_2) = (\text{Br}^-)_0/2$ . This has exactly the same form as the first term of rate law II. Comparing the coefficients of the theoretical and experimental laws we obtain the result:  $k_1 k_2 K_{\text{Br}_2} = 1.60$ . From the measured value of 1600 for  $k_1$  and the estimated value of  $1.1 \times 10^{-9}$  for  $K_{\text{Br}_2}$  at  $\mu = 0.20$  and  $0^\circ$ , we obtain for  $k_2$  a value of  $9.0 \times 10^5$ . The agreement with the value of  $9 = 1 \times 10^5$  calculated from Balint's results is good confirmation for the interpretation of the data. The limits of accuracy for the value of  $k_2$  from the present work are about the same as for Balint's.

On the interpretation given, a discrepancy in the observed direction between the experimental points and those predicted by rate law II is expected at  $6.3 \times 10^{-3} M \text{H}^+$  (experiments at the top of Fig. 4) since  $(\text{Br}^-)$  and  $(\text{Br}_2)$  have comparable values. However, a quantitative comparison of theoretical and experimental results is not possible since the contribution to the rate by the path corresponding to the second term of rate law II cannot be calculated accurately for this range of values for  $(\text{O}_3)/(\text{H}_2\text{O}_2)$ .

(6) Liebhfsky's value of  $K_{\text{Br}_2} = 6.9 \times 10^{-10}$  for  $0^\circ$  and low ionic strength is corrected approximately for the change to  $\mu = 0.2$  by dividing by  $\gamma_{\text{HBr}}$ . Livingston's value (THIS JOURNAL, 48, 45 (1926)) of  $\gamma_{\text{HBr}}$  at  $\mu = 0.2$  and  $25^\circ$  was used.

While the non-chain reactions of Path I give a consistent explanation for the first terms of both rate laws I and II, the last terms of these rate laws are best interpreted by chain reactions. Although the rate corresponding to the second term of rate law I is proportional to  $(\text{H}_2\text{O}_2)(\text{O}_3)$ , it cannot be explained by the direct interaction of ozone and hydrogen peroxide. The specific rate of interaction of these substances is 0.14 while  $k_{\text{H}}$  at  $2.6 \times 10^{-3} M$  is *ca.* 50. Experiments with inhibitors support the assumption of chain reactions. Table II presents data showing the effect of methanol in decreasing  $k_{\text{H}}$ .

TABLE II  
EFFECT OF  $\text{CH}_3\text{OH}$  ON  $k_1$  AT  $1.15 \times 10^{-4} M \text{HClO}_4$ ,  
 $3 \times 10^{-5} M \text{Br}^-$ ,  $4.18 \times 10^{-4} M \text{O}_3$

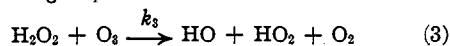
$(\text{CH}_3\text{OH}) \times 10^4$	$(\text{H}_2\text{O}_2) \times 10^4$	$k_1$	$k_{\text{H}}$
0	12.53	0.109	49
4	11.39	.076	25
10	11.18	.074	23
20	12.45	.074	21

Ethanol and phosphorous acid give similar results (the limiting value of  $k_{\text{H}}$  differing however for the different inhibitors) and a similar decrease in the rate under the conditions for which rate law II is valid is also observed. The fact that  $k_{\text{H}}$  (and the coefficient of the second term of rate law II) are not reduced to very low values is not inconsistent with the assumption of long chains. The radical which results from the reaction of the active intermediate with the "inhibitor" may itself catalyze the reaction<sup>7a</sup>; cases are known in which the resulting chains are longer than the original ones.<sup>7b</sup>

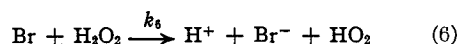
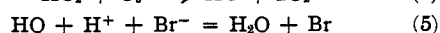
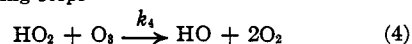
A rate expression of the form of rate law I follows (on the assumption of long chains) from the series of reactions (3)-(7).

PATH II

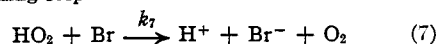
Chain initiating step



Chain continuing steps



Chain breaking step



Reactions 3 and 4 have been made plausible by other work<sup>2</sup>; 5, 6 (and 7 under limited conditions)

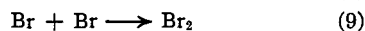
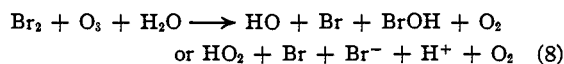
(7a) Taube and Bray, ref. 2, p. 3362.

(7b) Taube and Bray, ref. 2, p. 3363

find their exact analogy in experiments with  $H_2O_2 + O_3 + Cl^-$ .<sup>2</sup> Reaction 6 furthermore is a probable step in the photoreaction between peroxide and  $Br_2$ .<sup>8</sup>  $Br$  is presumably the intermediate which reacts with the inhibitors; the photochemical experiments of Dhar and Battacharya<sup>9</sup> indicate that  $Br$  and methanol do react.

If the reactions

PATH III



are substituted for the chain initiating and chain breaking steps, respectively, of Path II, the resulting mechanism (again assuming long chains) leads to a rate law of the form of the second term of rate law II. The following considerations show that these changes are not unreasonable. In going from the conditions for which rate law I is valid to those of II,  $(H^+)$ , and  $(O_3)$  are increased,  $(H_2O_2)$  is decreased.  $(Br_2)$  increases markedly with respect to  $(H_2O_2)$ , and reaction (8) becomes more probable than (3) on concentration considerations. Furthermore, increasing the ratio  $(O_3)/(H_2O_2)$  increases  $(Br)/(HO_2)$  and the chain breaking step (9) becomes more probable than (7).

It must be stressed that the second terms of rate laws I and II are limiting laws valid only for the extreme concentration ranges considered, where one or the other of the chain breaking steps (7) and (9) operate. Experiments which because of their complexity are not reported in detail suggest that in the intermediate range both chain breaking steps operate.

The variation of  $k_H$  with  $(H^+)$  observed in Fig. 3 can be explained if it is assumed the  $HO_2$  is a fairly strong acid with  $K_{\text{diss.}}$  *ca.*  $10^{-2}$ . On this basis, at  $(H^+) = 0.1 M$ , the free radical is present mainly as  $HO_2$  and a limit for  $k_H$  at high  $(H^+)$  is expected; at  $(H^+) = 10^{-3} M$ ,  $O_2^-$  will be the reactant, undergoing reactions similar to those of  $HO_2$ , and a limit for  $k_H$  at low acid will also result. Weiss,<sup>10</sup> Latimer<sup>11</sup> and Bray<sup>12</sup> suggest

(8) Callow, Griffith and McKeown, *Trans. Faraday Soc.*, **35**, 412-20 (1939).

(9) Dhar and Battacharya, *Z. anorg. allgem. Chem.*, **176**, 372 (1928).

(10) Weiss, *Trans. Faraday Soc.*, **31**, 968 (1935). Weiss promised publication of the experimental work on which his estimate is based. A search of the literature from 1935 to date failed to reveal this work.

(11) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 41.

(12) Bray, *THIS JOURNAL*, **60**, 86 (1938).

values of *ca.*  $10^{-6}$ , *ca.*  $10^{-6}$  and *ca.*  $8 \times 10^{-8}$ , respectively, but the evidence available for these low dissociation constants does not suffice to exclude the higher value indicated by the new kinetic data.<sup>13</sup> The experiments of Callow, Griffith and McKeown<sup>8</sup> and of Taube and Bray<sup>2</sup> on chain reactions of  $HO_2$  do not give a clue to the value of  $K_{HO_2}$  since the substance was not involved in the chain breaking steps for the concentration range in which quantitative results were available.

In conclusion, a correlation of the present results with those obtained in the  $O_3$ ,  $H_2O_2$ ,  $H^+$  and  $Cl^-$  system<sup>2</sup> may be interesting. In that case, the non-chain path corresponding to Path I contributed little to the reaction, due to the fact that the specific rate of interaction of  $O_3$  and  $Cl^-$  is much less than that for  $O_3$  and  $Br^- - 0.023$  compared to 1600. For the same reason,  $(Cl_2)$  at the steady state was always very small, and the path corresponding to Path III was absent. The path analogous to Path II accounted for most of the reaction at high  $Cl^-$ ; however, to eliminate  $HO$ ,  $(Cl^-)$  had to be increased to such an extent that complications due to the formation of  $Cl_2^-$  appeared. Analogous to the behavior in the present system, there appeared to be a change (at low  $Cl^-$ ) from  $Cl + Cl \rightarrow$  as chain breaking step to  $HO_2 + Cl \rightarrow$  when the ratio  $(O_3)/(H_2O_2)$  was decreased. Finally, the system with  $Br^-$  present is less sensitive to stray impurities than with  $Cl^-$ , since  $Br$  is less reactive than  $Cl$ .

The author is grateful to Professor William C. Bray for helpful discussions of this work.

### Summary

The rate of reaction A is studied over a wide range of the variables  $(O_3)$ ,  $(H_2O_2)$ ,  $(H^+)$  and  $(Br^-)$  at  $0^\circ$  and limiting rate laws, valid for extreme conditions, are obtained.

Three paths are necessary and sufficient to interpret the data. The results are consistent with the following conclusions:

Path I, a non-chain path, involves oxidation of  $Br^-$  by  $O_3$  to  $BrO^-$ , and reduction of hypobromous acid by peroxide. The specific rate of the former reaction is found to be  $1600 \pm 100$ , and the value of  $9 \times 10^6$  obtained for the latter reaction agrees with the value reported in the

(13) An alternative explanation, suggested by the Referee, for the variation of  $k_H$  with  $(H^+)$  is that  $HO_2$  forms a complex  $HO_2 \cdot H^+$ . Evidence for or against the existence of such a complex with a dissociation constant of  $10^{-2}$  could not be found in the literature.

literature. No evidence is found for the oxidation by  $O_3$  of  $Br^-$  by a free radical process.

Paths II and III are chain paths initiated by reaction of ozone with peroxide and bromine, respectively, to produce free radicals. The chain continuing steps are the same for both paths;

the nature of the chain breaking step depends on the ratio  $(O_3)/(H_2O_2)$ . An explanation of the variation of the rate by Path II with  $(H^+)$  is afforded by the assumption that  $HO_2$  is a fairly strong acid with  $K_{diss.} \text{ ca. } 10^{-2}$ .

ITHACA, NEW YORK

RECEIVED MARCH 25, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

## The System Sodium Nitrate–Dioxane–Water at 25°

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In connection with studies on the solubilities of salts in dioxane-water mixtures the formation of a two liquid system was observed in high dioxane solutions saturated with sodium nitrate. The experimental study of the phase relationships of such ternary systems involving a solid and two liquid components is in general rendered difficult by the problem of analysis for one of the liquid components in addition to the usually simple determination of the solid component. For solids forming no solid solvates with the liquid components the solubility curve is easily determined as a binary problem by using mixed solvents of known composition. Under favorable circumstances a binodal curve in such a system may be established by the synthetic method of titration with one of the liquid components, as in the system potassium carbonate–dioxane–water studied by Kobe and Stong.<sup>1</sup> Otherwise the analytical problem has usually been solved through the measurement of some physical property of the solution, or of the distillate from some ternary solution or phase, for the determination of the ratio of the two liquid components; examples of such properties are the refractive index (used for the study of the system lithium chloride–dioxane–water, by Lynch<sup>2</sup>), the density, or even the solubility of some reference salt in the unknown mixture of the two liquids. For more precise work it is desirable to attempt some direct determination of one of the liquid components. In the system silver nitrate–dioxane–water,<sup>3</sup> in which a solid dioxanate of silver nitrate appears at 25°, water was determined directly gravimetrically, with fairly accurate results, by volatilization of the solvents and absorption of water in barium mon-

oxide. In the present system, a more rapid and possibly more exact method was attempted, by the application of the Karl Fischer reagent for the direct volumetric determination of water.<sup>4</sup>

**Materials and Analysis.**—The sodium nitrate was a C. P. sample used without further purification, after grinding and drying at 110°. The dioxane was treated and dried as described in previous similar investigations.<sup>5</sup> The Karl Fischer reagent (active ingredients: iodine, sulfur dioxide and pyridine, in methanol as solvent) prepared according to the directions of Smith, Bryant and Mitchell,<sup>6</sup> was used with synthetic "anhydrous" methanol as back-titrating solution, and was standardized against a standard solution containing a known weight of pure water in the same methanol. The water content of the methanol and the effective titer of the reagent itself were calculated from a set of titrations using 1, 2 and 5 ml. (all at least in duplicate) of the standard solution of water (1 ml. containing 0.01793 g. of  $H_2O$  by preparation). The titer of the Karl Fischer reagent was found to fall with time, as expected (from 0.002582 to 0.001986 g. of water per ml. in fifty-eight days); in the actual use of the reagent, however, standardization titrations against the standard water solution were always run just before and just after any set of analyses, all being done within a few hours at most, so that the error from such changing strength could be kept low. It was found, moreover, that the water content of the back-titrating methanol also changed (increased) with time, so that a curve of this effect was used to estimate the water content of the methanol for some of the standardizations for which there had not been a satisfactory simultaneous determination of the water equivalent of the methanol. These corrections were, of course, small, inasmuch as relatively only small volumes of the methanol were used in back-titration, and the change in its water titer was only from 0.00033 to 0.00056 g. of water per ml., in the same period of fifty-eight days.

**Solubility Determinations.**—The methods for the preparation of complexes, temperature control, attainment of equilibrium, sampling of liquids for analysis and approximate density determination, were as used in previous investigations.<sup>3</sup> The equilibrium solutions were analyzed

(1) Kobe and Stong, *J. Phys. Chem.*, **44**, 629 (1940).

(2) Lynch, *ibid.*, **46**, 366 (1942).

(3) Skarulis and Ricci, *THIS JOURNAL*, **63**, 3429 (1941).

(4) Fischer, *Angew. Chem.*, **48**, 394 (1935).

(5) Davis and Ricci with Sauter, *THIS JOURNAL*, **61**, 3274 (1939).

(6) Smith, Bryant and Mitchell, *ibid.*, **62**, 3504 (1940).