## Summary

1. The salt effect of sodium chloride, in concentrations up to 0.2 *M*, upon the rate of hydration of acetopropionic anhydride is negligibly small at 0°.

2. The constants of hydrogen, acetate and formate-ion catalysis have been determined. They are in the order

$$k_{H_3O^+} < k_{CH_3COO^-} < k_{HCOO^-}$$

3. The hydration is retarded by the propionate ion and by the butyrate ion.

4. The results obtained with acetic, propionic and acetopropionic anhydrides have been collected. An examination of the catalytic constants suggests that, when the reaction is accelerated in a buffer solution, the collision complex formed between the anhydride and the anion of the buffer is of the order of stability of the mixed anhydride. In those buffer solutions in which the hydration is retarded there is reason to believe that a part of the initial anhydride has reacted with the anion of the buffer to form another anhydride.

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

# THE AUTOCATALYTIC REDUCTION OF BROMATE BY HYDROGEN PEROXIDE IN ACID SOLUTION

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RECEIVED DECEMBER 5, 1929 PUBLISHED APRIL 7, 1930

The autocatalytic reduction of bromate ion by hydrogen peroxide has been described briefly by Bray and Livingston.[1] At the acid concentration they used, over 0.7 *N*, some bromine is formed; its concentration, when hydrogen peroxide is present in excess, rises to a maximum and then gradually decreases to a constant value. We have found that the amount of bromine formed decreases rapidly as the concentration of acid is lowered, and that at moderate or low concentrations of acid (and bromide) the main reaction is

$$BrO_3^- + 3H_2O_2 = Br^- + 3O_2 + 3H_2O \tag{1}$$

The present investigation was undertaken to measure the rate of this autocatalytic reaction, and to test quantitatively the conclusion[1] that the autocatalysis is due to the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \tag{2}$$

followed by

$$Br_2 + H_2O_2 = O_2 + 2Br^- + 2H^+ \tag{3}$$

The progress of the reaction was followed by collecting the oxygen over water and measuring its volume. The temperature of the oxygen buret

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[1] Bray and Livingston, THIS JOURNAL, **45**, 1254 (1923).

and the barometric pressure were noted. The reaction mixture, 250 cc. in volume, was contained in a 500-cc. round-bottomed flask with a long neck, and was shaken vigorously enough to prevent supersaturation. The volume of the evolved oxygen was read frequently and the readings were plotted against the time in minutes. The type of curve obtained is shown in Fig. 1.

The experiments were performed in the dark in a thermostat at 25°. Measured quantities of water and solutions of sulfuric acid, potassium bromate and hydrogen peroxide, all at 25°, were placed in the reaction flask in the order named.

The stock solutions were standardized as follows. The reference for acids and bases was sodium carbonate, and that for potassium permanganate was sodium oxalate. Hydrogen peroxide (diluted "Perhydrol") was titrated with permanganate. Sodium thiosulfate was standardized iodimetrically by means of the permanganate solution.[2] Potassium bromate was determined iodimetrically against thiosulfate.

To test the stoichiometric relations expressed in Equation 1, complete analyses were made in three experiments while some bromate was still present. In one portion of the solution bromide was determined gravimetrically as silver bromide. The bromide concentration thus found was subtracted from the initial bromate concentration to find the bromate concentration in the sample. To another portion of the solution a measured amount of permanganate was added (to destroy the peroxide), and the small excess of permanganate together with the bromate was determined iodimetrically with thiosulfate.[3] From this result and the concentration of bromate as determined above, the concentration of hydrogen peroxide was calculated. While these data proved that the relation between the oxygen formed and the bromate and peroxide used up was almost exactly

$$3 \text{ moles of } O_2 = 1 \text{ mole of } BrO_3^- = 3 \text{ moles of } H_2O_2 \qquad (4)$$

there were slight deviations which indicated that the side reaction

$$2H_2O_2 = 2H_2O + O_2 \qquad (5)$$

could not be completely neglected. Further work showed that this reaction alone took place after the bromate had been completely reduced.

The initial concentrations in moles per liter are shown in Table I in the second to fourth columns. The two experiments of a pair, labeled A and B, were performed simultaneously under identical conditions, except that the concentration of one substance was varied.

The first step toward the interpretation of the results was made by drawing tangents to the oxygen–time curves as close to the origin as possible. The readings in the first five minutes were usually somewhat irregu-

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[2] Bray and Miller, THIS JOURNAL, **45**, 2204 (1924).

[3] *Cf.* Ref. 1, p. 1257.

lar and could be given little weight. The initial rates, cc. of oxygen per min. from 250 cc., are shown in the fifth column of Table I. On account of the initial discrepancies no claim for absolute accuracy can be made, but it is believed that the ratio of the rates in each pair of experiments shows definitely the effect of varying the concentration of one substance. Thus in Expts. 2A and 2B the results in Col. 5 (or 6) show that the rate is doubled when the concentration of hydrogen peroxide is doubled, and therefore that the reaction is first order with respect to the peroxide. The other pairs of experiments furnish evidence that the reaction is also first order with respect to hydrogen ion and bromate ion. The corresponding rate law is

$$-d(BrO_3^-)/dt = (1/3)d(O_2)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) \qquad (6)$$

The values of $k_1$ in the last column of the Table were calculated by means of Equation 6 by dividing the initial rate, expressed in the unit moles per liter per minute (sixth column), by the product of the initial concentrations. Although these values are not accurate, it seemed justifiable to conclude that $k_1 = 0.04 \pm 0.01$.

TABLE I

INITIAL CONCENTRATIONS AND INITIAL RATES

| | Concentrations, moles/liter | | | Cc. $O_2$ per min. from 250 cc. | $-d(BrO_3^-)/dt \times 10^7$ | $k_1 \times 10^3$ |
|---|---|---|---|---|---|---|
| Expt. | $(H^+)$ | $(BrO_3^-)$ | $(H_2O_2)$ | | | |
| 1A | 0.1 | 0.00587 | 0.036 | 0.017 | 9 | 43 |
| 1B | .1 | .01174 | .036 | .036 | 19 | 45 |
| 2A | .12 | .00978 | .0385 | .037 | 20 | 44 |
| 2B | .12 | .00978 | .077 | .074 | 40 | 44 |
| 3A | .12 | .00489 | .0363 | .017 | 9 | 43 |
| 3B | .24 | .00489 | .0363 | .033 | 18 | 41 |
| 4A | .24 | .00493 | .0362 | .034 | 18 | 42 |
| 4B | .36 | .00493 | .0362 | .052 | 28 | 43 |

The calculation of the amounts of oxygen formed by the bromide catalysis, Reaction 5, was then undertaken. The method involves the calculation of the *rate* of this reaction at a series of times in each experiment, the plotting of these rates against the time and the graphic integration from zero time to any designated time. The results of these calculations are shown in the lower half of Table II: $x$ is the concentration of bromide in moles per liter, and the amount of oxygen due to the catalysis is expressed as percentage of the total amount formed. It is to be noted that the oxygen due to catalysis exceeds 0.3% only near the end of Expts. 2B and 3A.

The rates upon which these calculations were based were calculated by means of the differential equation

$$-d(H_2O_2)/dt = {}^1/_2d(O_2)/dt = k_3(H_2O_2)(Br^-)(H^+) \qquad (7)$$

which has been established by Bray and Livingston.[4] The values of $k_3$,

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[4] (a) Ref. 1, THIS JOURNAL, **45**, 1258–1271 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923); (c) Livingston, *ibid.*, **48**, 45 (1926); (d) *ibid.*, **48**, 53 (1926); (e) Bray and Livingston, *ibid.*, **50**, 1654 (1928).

TABLE II

PROPORTION OF OXYGEN DUE TO BROMIDE CATALYSIS

| Expt. | 1A | 1B | 2A | 2B | 3A | 3B | 4A | 4B |
|---|---|---|---|---|---|---|---|---|
| Ionic strength, $\mu$ | 0.156 | 0.162 | 0.190 | 0.190 | 0.185 | 0.365 | 0.365 | 0.545 |
| $\nu$ | .96 | .93 | .95 | .95 | .97 | .99 | .99 | .99 |
| $\gamma_{HBr}$ | .66 | .66 | .65 | .65 | .65 | .60 | .60 | .58 |
| $10^3 k_3$ | 22 | 22 | 20 | 20 | 20 | 17 | 17 | 16 |

PERCENTAGE OF OXYGEN DUE TO BROMIDE CATALYSIS

| $10^4 x$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 10 | 0.21 | 0.10 | 0.10 | 0.15 | 0.20 | 0.09 | 0.11 | 0.07 |
| 20 | .23 | .11 | .10 | .19 | .23 | .12 | .12 | .09 |
| 40 | | | .11 | .23 | .57 | .18 | .18 | .13 |
| 80 | | | .13 | .33 | | | | |
| 90 | | | .15 | .60 | | | | |

given in Table II, are based on the early experimental data in sulfuric acid solution.[4a] They exceed by only 5 to 15% the values calculated later[4d] by means of the relation $k_3 = 0.043\gamma^2$, where $\gamma$ is the activity coefficient of hydrobromic acid in the presence of excess sulfuric acid.[4c] The ionic strength of each solution, $\mu$, the proportion of the ionic strength due to the sulfuric acid, $\nu$, and the corresponding values of $\gamma_{HBr}$ are shown in the table.

Equation 7 was used in the form

$$-d(H_2O_2)/dt = {}^1/_2 d(O_2)/dt = k_3(D-3x)(x)(H^+) \qquad (8)$$

Values of $D - 3x$ and $x$ at various times were determined from the amounts of total evolved oxygen on the assumption that Equations 1 and 4 are correct. The amounts of oxygen formed catalytically (calculated as explained above) turned out to be so small that it was unnecessary to repeat the calculation to obtain more exact values.

TABLE III

EXPERIMENTAL DATA CORRECTED FOR BROMIDE CATALYSIS

| | 1A Times, min. | | 1B Times | | 2A Times | | 2B Times | |
|---|---|---|---|---|---|---|---|---|
| $10^4 x$ | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. |
| 1 | 89 | 113.3 | 48 | 61.8 | 45 | 59.1 | .. | 33.8 |
| 2 | 155 | 183.1 | 92 | 98.0 | 87 | 91.4 | 44 | 56.8 |
| 3 | 208 | 234.2 | 120 | 123.9 | 113 | 114.0 | 65 | 74.4 |
| 5 | 291 | 308.7 | 157 | 160.8 | 144 | 145.6 | 93 | 100.8 |
| 10 | 426 | 428.5 | 214 | 217.6 | 193 | 193.7 | 139 | 143.8 |
| 15 | 512 | 511.1 | 252 | 254.4 | 224 | 224.8 | 170 | 172.7 |
| 20 | 581 | 578.6 | 282 | 282.3 | 250 | 248.9 | 195 | 195.3 |
| 30 | 696 | 696.8 | 326 | 325.6 | 287 | 286.3 | 231 | 231.3 |
| 40 | | | | | 318 | 317.6 | 262 | 261.5 |
| 50 | | | | | 347 | 346.6 | 289 | 289.7 |
| 60 | | | | | 376 | 376.0 | 318 | 318.4 |
| 70 | | | | | 409 | 408.5 | 349 | 350.2 |
| 80 | | | | | 447 | 449.5 | 385 | 390.3 |
| 90 | | | | | 512 | 516.2 | 441 | 456.1 |
| 95 | | | | | | | 489 | 530.8 |

TABLE III (*Concluded*)

| $10^4 x$ | 3A Times |  | 3B Times |  | 4A Times |  | 4B Times |  |
|---|---|---|---|---|---|---|---|---|
|  | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. |
| 1 | 120 | 125.6 | 63 | 54.6 | 41 | 46.1 | 20 | 20.8 |
| 2 | 190 | 194.1 | 81 | 79.1 | 63 | 69.5 | 31.5 | 32.0 |
| 3 | 238 | 242.2 | 99 | 96.7 | 80 | 85.4 | 39.5 | 39.9 |
| 5 | 307 | 310.6 | 121 | 120.0 | 106 | 107.8 | 50.5 | 51.1 |
| 10 | 419 | 419.0 | 154 | 155.8 | 143 | 142.7 | 68.5 | 68.8 |
| 15 | 494 | 494.3 | 177 | 180.0 | 167 | 166.7 | 81 | 81.0 |
| 20 | 560 | 557.4 | 198 | 200.8 | 187 | 186.7 | 91 | 91.3 |
| 30 | 678 | 676.1 | 240 | 239.0 | 225 | 224.2 | 111 | 110.4 |
| 40 | 828 | 826.2 | 290 | 287.2 | 271 | 270.8 | 135 | 134.4 |
| 45 | 1000 | 962.8 | 337 | 330.9 | 308 | 311.6 | 156 | 155.4 |
| 47 |  |  | 389 | 366.3 | 333 | 342.4 | 171 | 171.2 |

These results were used to correct the values of $x$, the bromide concentration. In Table III are shown the corrected values of $x$ and the corresponding "observed" times for all the experiments;[5] in Fig. 1 the same data for Expts. 4A and 4B are represented by circles. The "calculated" times, also shown in Table III, correspond to the smooth curves in Fig. 1 and will be explained later.

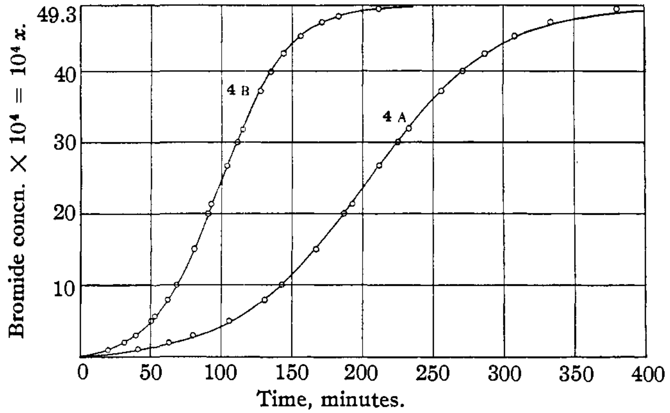

Fig. 1.—Experimental data corrected for bromide catalysis, *cf.* Table III. The smooth curves are calculated from Equation 13 and the constants of Table IV.

The results of Judson and Walker[6] and of Skrabal and Weberitsch[7] leave no doubt that the reduction of bromate by bromide, Equation 2, is represented by the differential equation

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[5] No attempt was made to correct for the discrepancies observed in the first five minutes. If this had been done, the values of $10^4 x$ in the table would have been decreased by about 0.05 in Expts. 1A, 1B and 4A; 0.1 in Expts. 2A and 2B; and 0.15 in Expt. 4B; and might have been slightly increased in Expts. 3A and 3B.

[6] Judson and Walker, *J. Chem. Soc.*, **73**, 418 (1898).

[7] Skrabal and Weberitsch, *Monatsh.*, **36**, 211 (1915).

$$-d(BrO_3^-)/dt = k_2(BrO_3^-)(Br^-)(H^+)^2 \quad (9)$$

and is rapid enough to account qualitatively for the autocatalysis. Our problem was to determine whether the data of Table III could be accurately represented by the sum of Equations 6 and 9

$$-d(BrO_3^-)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) + k_2(BrO_3^-)(Br^-)(H^+)^2 \quad (10)$$

Since the concentration of hydrogen ion remains constant throughout each experiment, this equation may be simplified to

$$dx/dt = k'(C - x)(D - 3x) + k''(C - x)(x), \text{ or}$$

$$\frac{dx/dt}{C - x} = Dk' + x(k'' - 3k'), \text{ where} \quad (11)$$

$$k' = k_1(H^+),\ k'' = k_2(H^+)^2 \quad (12)$$

and $C - x$, $D - 3x$ and $x$ represent the concentrations in moles per liter of bromate ion, hydrogen peroxide and bromide ion, respectively.

The form of Equation 11 suggested a method of evaluating the constants, namely, to determine rates by drawing tangents at a series of points on each $x$–$t$ curve, to divide each rate by the corresponding concentration of bromate, and to plot these values of rate/bromate against $x$. If Equation 10 or 11 is correct, a straight line will result; the slope will be $k'' - 3k'$ and the intercept on the ordinate axis, $Dk'$. In applying this method tangents were drawn at points on the original oxygen–time curves by means of a tangentimeter,[8] kindly furnished by Dr. R. L. Hasche. These rates were changed to the unit, moles of bromide per liter per minute, and small corrections were applied for the bromide catalysis, $(k_3/6)(D - 3x)(x)(H^+)$.

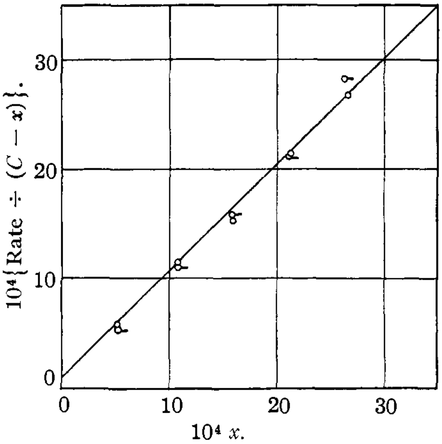

Fig. 2.—Evaluation of constants by use of Equation 11, Expts. 1A and 1B. Intercept $= 1 \times 10^{-4} = 0.036k'$. Slope $= 0.972 = k'' - 3k'$.

The application of the method to Expts. 1A and 1B is shown in Fig. 2. The straight line corresponds to the values 98 and 0.028 for $k_2$ and $k_1$, respectively. The latter number is much smaller than any in Table I, but it is evident that the line in Fig. 2 could have been drawn to give a smaller intercept and, therefore, a still smaller value for $k_1$. On the other hand, since the line could not have a much greater slope than that shown, the value of $k_2$ has been determined within 2 or 3%. The method yielded definite slopes in the other experiments also, but the intercepts were relatively so small that $k'$ (and $k_1$) could not be determined. Details will not

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[8] Latschow, This Journal, **47**, 793 (1925).

be given since the values of $k'' - 3k'$ were entirely consistent with the constants determined by the method now to be described.

Integration of Equation 11 leads to the following

$$\log\left(\frac{x + \alpha}{C - x}\right) = \log\left(\frac{\alpha}{C}\right) + \beta t, \text{ where} \tag{13}$$

$$\alpha = Dk'/(k'' - 3k') \text{ and } \beta = (Ck'' + (D - 3C)k')/2.303 \tag{14}$$

If these equations agree with the experimental data, a straight line will result when log $[(x + \alpha)/(C - x)]$ is plotted against the time, $t$; the slope will be $\beta$ and the intercept on the ordinate axis log $(\alpha/C)$. Since both $\alpha$ and $\beta$ involve $k'$ and $k''$, a method of approximations was employed in evaluating these rate constants. The ratio $k'/k''$ is always very small, and $\alpha$ is nearly negligible in comparison with $x$ except in the early stages of each experiment. Accordingly Equation 13 was first tested by plotting log $[x/(C - x)]$ againt $t$. Although log $[x/(C - x)]$ is equal to minus infinity when $x$ is zero,[9] it was found, as indicated by the dotted curves in Fig. 3, that each curve rapidly approached a straight line with increase in $x$. The slope and intercept of each line yielded values of $\beta$ and $\alpha$, as a first but close approximation in that experiment. Log $(x + \alpha)/(C - x)$ was then plotted against $t$, another $\beta,\alpha$ pair was determined from the position of the new line, and the process was repeated when necessary. The values of $k_1$ and $k_2$ in Table IV correspond to the straight lines finally selected. However, other

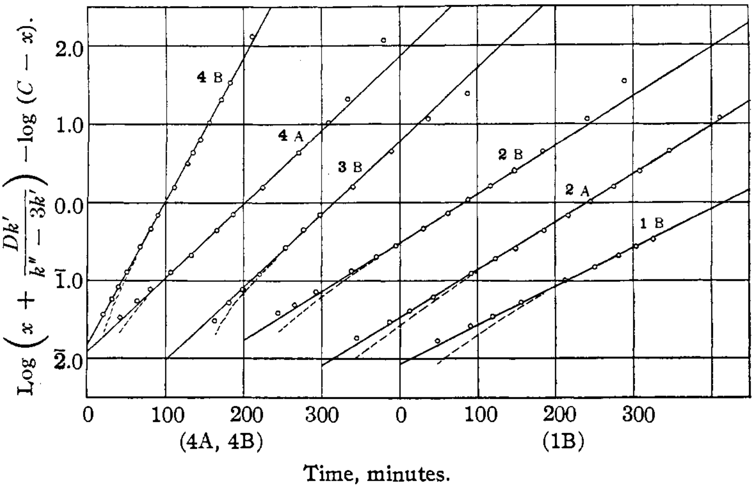

Fig. 3.—Evaluation of constants by use of Equation 13.

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[9] Integration of $dx/dt = k(C - x)(x)$ leads to the equation log $[(x + x_0)/(C - x)] = \log(x_0/C) + tCk/2.303$, where $x_0$ is the initial value of $x$. It is evident that a "pure" autocatalytic reaction will never start unless $x_0$ has a finite value. Ostwald, "Lehrbuch der allgem. Chem.," **1902**, Vol. II, Part 2, pp. 265–267, discussed in detail a hypothetical case in which $x$ was formed in a second independent reaction. Our results furnish an actual example.

pairs of constants, properly chosen within the limits specified, would satisfy fairly well the actual data in each experiment.

TABLE IV

CONSTANTS EVALUATED BY USE OF EQUATION 13

| Expt. | $k_1 \times 10^3$ | $k_2$ | $\mu$(Table II) | $k_2/\gamma^4_{HBr}$ |
|---|---|---|---|---|
| 1A | 30 ±1.5 | 98∓2 | 0.156 | 515 |
| 1B | 26.5±1.5 | 98∓2 | .162 | 515 |
| 2A | 24.2±1.5 | 100∓2 | .190 | 550 |
| 2B | 25.7±1 | 101∓1 | .190 | 555 |
| 3A | 24 ±2 | 97∓2 | .185 | 535 |
| 3B | 23 ±5 | 76∓4 | .365 | 585 |
| 4A | 30 ±2 | 76∓1 | .365 | 585 |
| 4B | 48 ±2 | 65.6∓0.4 | .545 | 580 |

The *times* at various values of $x$, *calculated* by means of Equations 13, 14 and 12 and the constants of Table IV, are shown in Table III. These correspond to the smooth curves in Fig. 1 and the straight lines in Fig. 3. The calculated times at low and high values of $x$ are somewhat greater than the observed times in six of the eight experiments, but are less in the remaining two, Expts. 3A and 3B. If the results in these two experiments prove to be incorrect, then the differences in the remaining cases indicate that a little oxygen is formed in the first five minutes by catalytic decomposition of the peroxide, when the bromide concentration, $x$, is very small; and that the values of $x$ are slightly less than we have assumed. At the present time, however, we are not justified in rejecting Expts. 3A and 3B; and the differences at low and high values of $x$ may be considered to be due to accidental errors in the zero setting of the oxygen buret and to correspond to the initial discrepancies referred to in Footnote 5. Corrections in $x$ would greatly diminish the differences between calculated and observed times; the values of $k_2$ would not be changed appreciably, and those of $k_1$ would be altered by only a few per cent., being increased in Expts. 3A and 3B and decreased in the remaining cases. Thus in Expt. 2A, when $x$ was decreased by $10^{-4}$, the differences between calculated and observed times were found to be negligible throughout the experiment when $k_1$ and $k_2$ were assigned the values 0.022 and 100, respectively.

The value of $k_2$ is 99 ± 2 in the five experiments at ionic strengths between 0.156 and 0.19, but is much smaller in the three remaining experiments where the ionic strength is two or three times as great. This is in qualitative accord with Brönsted's theory of reaction rates,[10] which requires $k_2/\gamma^2_{HBr}\ \gamma^2_{HBrO_3}$ to be a true constant in dilute solutions. A definite test of this law is not possible on account of the lack of, or uncertainties in, the activity coefficients of bromic and hydrobromic acids in

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[10] (a) Brönsted, *Z. physik. Chem.*, **102,** 169 (1922); (b) *ibid.*, **115,** 337 (1925); (c) "The Velocity of Ionic Reactions," Columbia University Press, **1927.**

the presence of sulfuric acid. Our results are in reasonable agreement with those of Skrabal and Weberitsch.[7]

The values of $k_1$ do not show the expected decrease with increasing ionic strength. The result is within ±15% of 0.026 in seven experiments, but is much greater in the last experiment at the highest ionic strength. It therefore, seems possible that another term should be added to Equation 10. If there is such an additional reaction, it is appreciable only at low concentration of bromide ion and high concentration of hydrogen ion. We may, therefore, conclude that, with this possible exception (and after making the small correction for bromide catalysis), the kinetic data are accurately represented by Equation 10.

In the two independent reactions of Equation 10 the following rate-determining steps are possible, or even probable

$$BrO_3^- + H^+ + H_2O_2 = X = HBrO_2 + H_2O + O_2 \qquad (15)$$
$$BrO_3^- + 2H^+ + Br^- = Y = HBrO_2 + HBrO \qquad (16)$$

where $X$ and $Y$ are critical complexes, as postulated by Brönsted.[10] The products shown in these equations are those usually assumed in bromate and bromide reactions.[11] The later steps will then involve a number of reactions such as the following, each of which must have a relatively high specific reaction rate

$$HBrO_2 + H_2O_2 = HBrO + H_2O + O_2 \qquad (17)$$
$$HBrO + H_2O_2 = H^+ + Br^- + H_2O + O_2 \qquad (18)$$
$$HBrO_2 + Br^- + H^+ = 2HBrO \qquad (19)$$

Equation 1 is the sum of Equations 15, 17 and 18; of 16, 17 and 18 (counted twice); and of 16, 19 and 18 (counted three times).

## Summary

The autocatalytic reaction is accurately represented by the equation $BrO_3^- + 3H_2O_2 = Br^- + 3H_2O + 3O_2$ in dilute solutions when the concentration of hydrogen ion is less than 0.4 $N$. The catalytic decomposition of hydrogen peroxide due to bromide ion is appreciable only toward the end of the reaction.

The rate of the reaction at 25° in the dark was studied by measuring the volume of oxygen evolved. The results agreed closely with the assumption of two independent reactions

$$-d(BrO_3^-)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) + k_2(BrO_3^-)(Br^-)(H^+)^2$$

where $k_1$ and $k_2$ have the values 0.026 ± 15% and 99 ± 2% in 0.12 $N$ sulfuric acid.

Methods of evaluating the specific reaction rates $k_1$ and $k_2$ are discussed.

A mechanism is suggested.

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[11] *Cf.* the "primary" reactions suggested by Bray, *Z. physik. Chem.*, **54**, 467, 490, 560 (1906).