

separation of ammonium iodide to obtain the imide in a fairly high state of purity.

Some of the properties of germanous imide are described.

CHICAGO, ILLINOIS

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

THE RATE OF THE FOURTH ORDER REACTION BETWEEN BROMIC AND HYDROBROMIC ACIDS. THE KINETIC SALT EFFECT

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Introduction

While reactions of high order are not common, the reduction in acid solution of bromate or chlorate by a halide,¹ and that of iodate by iodide at very low concentration of iodide,² are of the fourth order. Their rates are represented by differential equations of the form

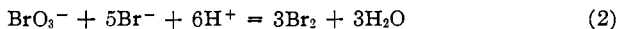
$$-d(\text{XO}_3^-)/dt = k(\text{XO}_3^-)(\text{Y}^-)(\text{H}^+)^2$$

According to Brönsted,³ k should decrease rapidly with increasing ionic strength, and the function $k\gamma_n/\gamma_{\text{HXO}_3}^2\gamma_{\text{HY}}^2$ should be constant at low ionic strengths. Since γ_n , the activity coefficient of a neutral substance, differs but little from unity, the kinetic salt effect may be represented by the equation

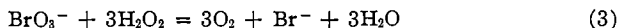
$$k/\gamma_{\text{HXO}_3}^2\gamma_{\text{HY}}^2 = \chi \quad (1)$$

where χ is a true constant.

To study this kinetic salt effect, an investigation of the reduction of bromic acid by hydrobromic acid was undertaken. The reaction



was first studied by Judson and Walker,⁴ and their conclusion that its rate might be represented by an equation of the above form was later confirmed by Skrabal and Weberitsch.⁵ Still later, Bray and Davis⁶ investigated the autocatalytic reduction of bromate ion by hydrogen peroxide



¹ Skrabal, *Z. Elektrochem.*, **30**, 123 (1924); "International Critical Tables." Vol. VII, p. 149.

² Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

³ J. N. Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927.

⁴ Judson and Walker, *J. Chem. Soc.*, **73**, 418 (1898).

⁵ Skrabal and Weberitsch, *Monatsh.*, **36**, 211 (1915).

⁶ Bray and Davis, *THIS JOURNAL*, **52**, 1427 (1930).

and proved that the differential equation expressing its rate was

$$-d(\text{BrO}_3^-)/dt = k_1(\text{H}_2\text{O}_2)(\text{BrO}_3^-)(\text{H}^+) + k(\text{BrO}_3^-)(\text{Br}^-)(\text{H}^+)^2 \quad (4)$$

The results of the latter investigation gave promise that this indirect method of studying the reduction of bromic acid by hydrobromic acid should yield accurate values of the specific rate. The determination of k by this method has the added advantage that, since bromine is not an end-product, errors due to the accumulation of bromine and the consequent formation of tribromide ion are eliminated.

Experimental Procedure

The experimental procedure of Bray and Davis was closely followed except that perchloric acid was substituted for sulfuric. This substitution abolished two difficulties inherent to sulfuric acid solutions: the obscurity cast upon the interpretation of activity data, and the uncertainty in the hydrogen-ion concentration resulting from the relatively weak second dissociation of that acid.

The experiments were performed in the dark at the three temperatures 25, 45 and 65°. Measured quantities of water, perchloric acid, potassium bromate and hydrogen peroxide, all at the reaction temperature, were placed in the reaction flask in that order. Zero time was taken as the instant the stopcock was closed, immediately after adding the hydrogen peroxide. In the runs in which bromide ion was added, a measured solution of potassium bromide was introduced just preceding the introduction of the hydrogen peroxide solution, and in the same manner.

Considerable care was taken to prevent the discrepancies referred to by Bray and Davis in the gas evolution during the first few minutes of the experiments. Blank experiments performed by adding water to water in the reaction flasks indicated that introducing a solution to the reaction mixture by removing the stopper from the reaction flask, running in the solution from a pipet and then replacing the stopper produced an error which might be as high as two or three cc. extra evolved gas at 25°. This error was presumably due to the introduction of air at room temperature (18–22°) to the reaction flask which was at 25°. It was found that these disturbances could be largely eliminated by adding the solution through a stopcock in the top of the reaction flask, without stopping the shaker. Experiments showed that when the amount of added solution was small (25 cc.) this method completely eliminated initial errors, but that when the amount of added solution was large (150 cc.) some such effect might persist, although of much lesser magnitude. In the experiments at higher temperatures any slight difference in temperature between the added solution and the reaction mixture was sufficient to introduce an initial disturbance, the magnitude of which increased rapidly with the temperature difference and the amount of the added solution.

To check the stoichiometric relations expressed in Reaction 3, 3 moles O_2 produced = 1 mole BrO_3^- used = 3 moles H_2O_2 used, complete analyses were made in several experiments while 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 original bromate concentration to find the bromate concentration of the sample. Another portion of the solution was analyzed iodimetrically for total oxidizing power, and the peroxide concentration was obtained by subtracting the oxidizing power of the bromate from this total. In four experiments carried out in this manner at 25° the ratio of moles O_2 produced to moles BrO_3^- used was found to be 3.00 ± 0.09 and the ratio of moles O_2 produced to moles H_2O_2 used, 1.00 ± 0.02 . In three experiments at higher temperatures these ratios were 3.00 ± 0.07 and 1.00 ± 0.04 , respectively. All of these results were obtained in $0.1 M (H^+)$.

This method of analysis was adopted after it had been found that the presence of bromate caused an error in the titration of hydrogen peroxide with permanganate. Thus, in $0.1 M$ perchloric acid solutions in which the amount of hydrogen peroxide present corresponded to 22.8 cc. of $0.002 M$ potassium permanganate, 0.05 cc. less permanganate was used when the concentration of bromate was $0.0027 M$, and 4.7 cc. less when this concentration was $0.0044 M$. This error was overlooked by Bray and Davis, presumably because the bromate concentrations were very low in their titrations.

The Rate Law of the Autocatalytic Reduction. Calculation of the Constants.—In order to test the validity of the rate law, Equation 4, runs were made over as wide a range of hydrogen-ion concentrations as was possible, and a series of experiments was performed (at 25°) in which a small amount of potassium bromide was added to the reaction mixture at the beginning of each run.

Since the concentration of hydrogen ion remains constant throughout each experiment, Equation 4 may be at once reduced to

$$dX/dt = k'(C - X)(D - 3X) + k''(C - X)(X) \quad (5)$$

or, for added Br^-

$$dX/dt = k'(C - X)(D - 3X) + k''(C - X)(A + X) \quad (5a)$$

where $k' = k_1(H^+)$, $k'' = k(H^+)^2$ and X , $C - X$, $D - 3X$, represent the instantaneous concentration in moles per liter of bromide ion (formed by reduction of bromate ion), bromate ion and hydrogen peroxide, respectively. A , C , D , are the original concentrations of bromide ion, bromate ion and peroxide.

Integration of Equation 5 or 5a yields

$$\log \frac{X + \alpha}{C - X} = \log \frac{\alpha}{C} + \beta t \quad (6)$$

where

$$\alpha = \frac{Dk'}{k'' - 3k'} \text{ and } \beta = \frac{Ck'' + (D - 3C)k'}{2.303} \quad (6a)$$

or, for added bromide

$$\alpha = \frac{Ak'' + Dk'}{k'' - 3k'} \quad \beta = \frac{(A + C)k'' + (D - 3C)k'}{2.303} \quad (6b)$$

If the equations agree with the experimental data, a straight line of slope β and intercept $\log \alpha/C$ should result when values of $\log (X + \alpha)/(C - X)$ are plotted against t . As both α and β involve k' and k'' , a method of approximation similar to that described in detail by Bray and Davis⁶ was used. As a first approximation α is assumed equal to 0 (or A if bromide has been added) and values of $\log (X/(C - X))$ are plotted against t . As α is relatively small when X is large, a curve is obtained which rises from minus infinity when $X = 0$ and which rapidly approaches a straight line as X increases in value. The intercept of this line yields an approximate value of α , which is then used in plotting values of $\log (X + \alpha)/(C - X)$ against t as a second approximation. This process is repeated until no change in α is obtained by further approximations. The results of the work at 25° are summarized in Tables I and II.

TABLE I
EXPERIMENTS AT 25°, WITHOUT ADDED BROMIDE

Run	H ⁺	Initial (BrO ₃ ⁻)	Initial (H ₂ O ₂)	μ	$k_1(10^3)$	k
25	0.0502	0.00500	0.0314	0.0552	29=5	276±15
21	.0502	.0100	.0327	.0602	31=9	240±20
23	.0502	.00700	.0327	.0572	30=7	252±15
8	.0493	.0109	.0251	.0593	47=8	248±15
Mean				.0580	34	254
13	.104	.00994	.0348	.114	32=8	216±14
14	.100	.00700	.0331	.107	54=6	219±16
15	.100	.00700	.0334	.107	31=4	210±14
16	.100	.00700	.0329	.107	27=6	200±15
19	.100	.00500	.0334	.105	30=8	208±20
18	.100	.00500	.0334	.105	25=5	220±14
17	.100	.00300	.0334	.103	35=9	230±30
20	.100	.00300	.0334	.103	35=9	230±30
85	.100	.00500	.0296	.105	35=8	219±10
86	.100	.00500	.0296	.105	36=9	223±10
Mean				.106	34	211
134	.200	.00500	.0521	.205	21	187
135	.200	.00500	.0521	.205	23	195
Mean				.205	22	191
132	.300	.00500	.0514	.305	22	172
133	.300	.00500	.0514	.305	25	168
Mean				.305	23	170
128	.500	.00500	.0509	.505	54	144
131	.500	.00500	.0493	.505	42	146
Mean				.505	46	145

TABLE II
 EXPERIMENTS AT 25° WITH ADDED BROMIDE

Run	H ⁺	Initial BrO ₃ ⁻	Initial H ₂ O ₂	Initial Br ⁻	μ	$k_1(10^3)$	k
77	0.0500	0.00500	0.0272	0.00194	0.0569	30	258 ± 10
72	.0500	.00500	.0275	.00194	.0569	120	260 ± 10
71	.0500	.00500	.0275	.00194	.0569	45	255 ± 10
Mean					.0569		257
53	.100	.00500	.0287	.00186	.107	43	210 ± 20
54	.100	.00500	.0287	.00186	.107	143	209 ± 15
59	.100	.00500	.0273	.00186	.107	180	224 ± 15
63	.100	.00500	.0273	.00194	.107	126	225 ± 15
55	.100	.00500	.0264	.000778	.106	36	225 ± 15
57	.100	.00500	.0273	.000748	.106	96	229 ± 15
67	.100	.00500	.0300	.00780	.106	68	229 ± 15
73	.100	.00500	.0272	.00778	.106	85	219 ± 15
74	.100	.00500	.0272	.00778	.106	59	216 ± 14
Mean					.106		220
129 ^a	.100	.00500	.0252	.000780	.805	35	141

^a Run 129 was made in 0.7 *N* NaClO₄ solution.

At a hydrogen-ion concentration below 0.05 *N*, the reaction is too slow to be measured accurately by oxygen evolution; at values of hydrogen-ion concentration above 0.3 *N*, slight deviations from the rate law were noted, coincident with the accumulation of appreciable amounts of bromine in the reaction mixture. At all other values of the hydrogen-ion concentration the straight lines obtained by the approximation method were very good, although other pairs of constants properly chosen within the limits specified would satisfy fairly well the actual data in each case.

The agreement between the values of k in Tables I and II, without and with added bromide, is satisfactory: thus at $\mu = 0.06$, the values are almost identical, 254 and 257; and at $\mu = 1.06$, 211 and 220 are within the estimated limits. On the other hand, the error in k_1 is so greatly increased by the presence of bromide that the values in Table II have little if any significance.

The decrease in k with increasing ionic strength will be discussed in a later section and the limiting value at zero ionic strength will be calculated. k_1 also shows a general decrease with increasing ionic strength, but the values are not sufficiently accurate to justify a similar quantitative treatment.

The Effect of Temperature.—The results of the work at 45 and 65° are summarized in Tables III and IV, respectively.

The plotted values of the logarithms of the specific rates against $1/T$ for $\mu = 0.105$ are shown in Fig. 1. From the slopes of these lines, a heat of activation of 16,000 ± 300 cal. was obtained for the fourth order reaction, and an approximate value of 15,000 ± 1000 cal. for the third order reaction.

TABLE III
 EXPERIMENTS AT 45°

Run	H ⁺	Initial BrO ₃ ⁻	Initial H ₂ O ₂	μ	k ₁ (10 ³)	k
90	0.100	0.005	0.0146	0.105	114 ± 56	1150 ± 165
91	.100	.005	.0146	.105	112 ± 50	1100 ± 120
92	.100	.005	.0265	.105	161 ± 48	1090 ± 70
93	.100	.005	.0265	.105	198 ± 81	1140 ± 140
Mean				.105	146	1120
96	.0500	.005	.0564	.055	284 ± 81	1340 ± 170
97	.0500	.005	.0564	.055	264 ± 35	1330 ± 80
Mean				.055	274	1335
98	.025	.005	.0548	.030	308 ± 35	1550 ± 180
99	.025	.005	.0548	.030	312 ± 40	1570 ± 140
Mean				.030	310	1560

 TABLE IV
 EXPERIMENTS AT 65°

Run	H ⁺	Initial BrO ₃ ⁻	Initial H ₂ O ₂	μ	k ₁ (10 ³)	k
108	0.0125	0.00500	0.0564	0.0175	1480 ± 380	10000 ± 600
109	.0125	.00500	.0564	.0175	1520 ± 350	10200 ± 600
Mean				.0175	1500	10100
104	.0250	.00500	.0449	.0300	1080 ± 400	8000 ± 500
105	.0250	.00500	.0449	.0300	1000 ± 300	8280 ± 630
Mean				.0300	1040	8140
106	.0500	.00500	.0414	.055	855 ± 260	6610 ± 740
107	.0500	.00500	.0414	.055	793 ± 160	6850 ± 510
Mean				.055	824	6730
111	.100	.00500	.0615	.105	714 ± 230	5140 ± 650
112	.100	.00500	.0615	.105	745 ± 260	5070 ± 730
Mean				.105	729	5105
115 ^a	.100	.00500	.0464	.106	730	5650

^a Run 115 had an initial concentration of 0.00078 *M* added bromide.

The Kinetic Salt Effect of the Fourth Order Reaction.—The measurements at 65° were carried to sufficiently low ionic strengths to permit a test of Equation 1 by calculations of the necessary activity coefficients from the theory of Debye and Hückel. The limiting expression for the activity coefficient γ_i of an ion of valence *Z* is, at 65°⁷

$$\log \gamma_i = -0.6 Z^2 \sqrt{\mu} \quad (7)$$

From Equation 7, the logarithm of the activity coefficient product, Equation 1, becomes

$$\log \gamma_{\text{H}^+}^2 \gamma_{\text{Br}^-} \gamma_{\text{BrO}_3^-} = -0.6(1^2 + 1^2 + 1^2 + 1^2) \sqrt{\mu} = -2.4 \sqrt{\mu}$$

If *k* is proportional to this activity coefficient product, a straight line of slope -2.4 will result when values of log *k* are plotted against $\sqrt{\mu}$. From

⁷ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, p. 500.

the plot, Fig. 2, it is evident that such a line is rapidly being approached as the ionic strength decreases.

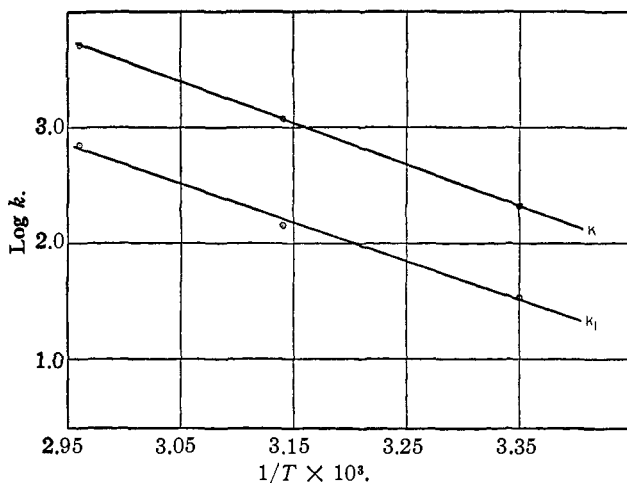


Fig. 1.—Variation of the constants with the temperature.

A further test of Equation 1 may be obtained from the data at 25° by calculating values of χ from the measured activity coefficients of hydrobromic acid. This introduction of activity coefficients should eliminate the observed discrepancy that the values of k for perchloric acid solutions are considerably higher than those obtained by earlier investigators^{4,5,6} for sulfuric acid solutions.

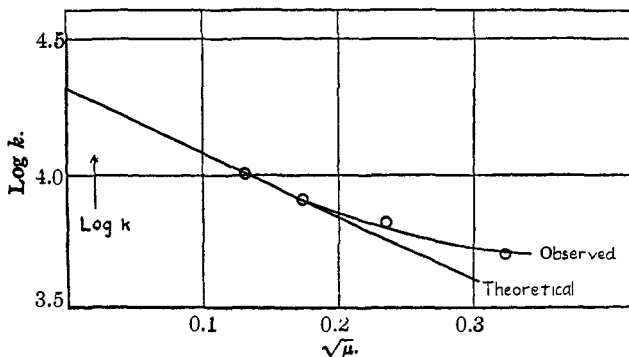


Fig. 2.—Kinetic salt effect at 65°.

In the absence of data for the activity coefficient of bromic acid, γ_{HBrO_3} was assumed to be equal to γ_{HBr} , and Equation 1 was applied in the form

$$k/\gamma_{\text{HBr}}^4 = \chi \quad (8)$$

γ_{HBr} , in the presence of perchloric acid, was assumed to have the same value as in a solution of pure hydrobromic acid at the same ionic strength.

Any error introduced by such assumptions as these should not interfere with the accuracy of the extrapolation to zero ionic strength.

Livingston⁸ has measured γ_{HBr} in solutions of pure hydrobromic acid, and in certain sulfuric acid solutions, and has suggested a method for calculating it in sulfuric acid solutions to which his measurements do not apply. The work of Harned and James⁹ shows that at constant ionic strength γ_{HBr} is lowered when Na^+ or K^+ is substituted for H^+ in a bromide solution. No attempt was made to allow for this effect except in the experiments listed in the last four lines of Table V in which the concentration of Na^+ was high. The activity coefficients of these investigators^{8,9} were corrected to agree, at low ionic strengths, with recent values of γ_{HCl} determined by Randall and Young.¹⁰

The values of the specific rates as determined by Skrabal and Weberitsch,⁵ Judson and Walker,⁴ Bray and Davis⁶ and ourselves, together with the values of γ_{HBr} and χ (Equation 8), are summarized in Table V. This table contains also the results of eight runs which were made to test the effect of the addition of the inert salt, NaClO_4 , upon the value of χ . The details of these are given in Table Va.

TABLE V
SUMMARY OF DATA FOR THE FOURTH ORDER REACTION AT 25°

Experimenter	Run	μ	k	γ_{HBr}	$\chi = \frac{k}{\gamma_{\text{HBr}}^4}$	Acid
Judson and Walker	11	0.912	63	0.562	632	HBr, HBrO ₃
Skrabal and Weberitsch	2	.251	80	.629	512	H ₂ SO ₄
Skrabal and Weberitsch	6	.141	95	.670	472	H ₂ SO ₄
Skrabal and Weberitsch	8	.306	72	.609	525	H ₂ SO ₄
Skrabal and Weberitsch	9	.110	120	.756	367	H ₂ SO ₄
Skrabal and Weberitsch	10	.150	103	.664	531	H ₂ SO ₄
Skrabal and Weberitsch	11	.116	167	.700	696 ^a	H ₂ SO ₄
Skrabal and Weberitsch	12	.216	156	.721	586 ^a	H ₂ SO ₄
Skrabal and Weberitsch	13	.209	159	.748	510 ^a	H ₂ SO ₄
Skrabal and Weberitsch	15	.066	148	.738	500 ^a	H ₂ SO ₄

⁸ Livingston, *THIS JOURNAL*, **48**, 45 (1926). A lower limit for the values of γ_{HBr} in sulfuric acid solutions is given which holds when the ionic fraction of the sulfuric acid is 0.6 or greater. In only three of the experiments summarized in Table V was this condition not fulfilled; Runs 11, 12, 13, of Skrabal and Weberitsch. In these three runs γ_{HBr} was calculated from the following equation of Livingston

$$\gamma_{u'} = \gamma_{u \text{ pure}} \frac{m' \neq}{m \neq}$$

where $\gamma_{u'}$ is the desired activity coefficient; $\gamma_{u \text{ pure}}$ is the activity coefficient in a strong electrolyte at the given ionic strength; $m' \neq$ is the effective mean molality calculated assuming the first dissociation of H_2SO_4 to be complete and the second dissociation constant to have an average value of 3×10^{-2} at these ionic strengths; and $m \neq$ is the mean molality calculated assuming the second dissociation to be complete.

⁹ Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

¹⁰ Randall and Young, *THIS JOURNAL*, **50**, 989 (1928).

TABLE V (Concluded)

Experimenter	Run	μ	k	γ_{HBr}	$x = \frac{k}{\gamma_{\text{HBr}}^4}$	Acid
Bray and Davis	1A	0.156	98	0.661	515	H ₂ SO ₄
Bray and Davis	1B	.162	98	.661	515	H ₂ SO ₄
Bray and Davis	2A	.190	100	.653	550	H ₂ SO ₄
Bray and Davis	2B	.190	101	.653	555	H ₂ SO ₄
Bray and Davis	3A	.185	97	.653	535	H ₂ SO ₄
Bray and Davis	3B	.365	76	.601	585	H ₂ SO ₄
Bray and Davis	4A	.365	76	.601	585	H ₂ SO ₄
Bray and Davis	4B	.545	66	.581	580	H ₂ SO ₄
Young and Bray	21	.0602	240	.820	530	HClO ₄
Young and Bray	23	.0572	252	.822	553	HClO ₄
Young and Bray	8	.0593	248	.820	547	HClO ₄
Young and Bray	13	.114	216	.789	553	HClO ₄
Mean of runs						
Young and Bray	14, 15, 16	.107	210	.792	533	HClO ₄
Young and Bray	18, 19, 85, 86	.105	217	.793	549	HClO ₄
Young and Bray	128, 131	.505	145	.772	408	HClO ₄
Young and Bray	132, 133	.305	170	.766	492	HClO ₄
Young and Bray	134, 135	.205	191	.771	540	HClO ₄
Young and Bray	120, 121	.305	156	.753	485 ^b	HClO ₄
Young and Bray	122, 123	.405	165	.752	516 ^b	HClO ₄
Young and Bray	124, 125	.175	188	.771	532 ^b	HClO ₄
Young and Bray	126, 127	.805	144	.787	375 ^b	HClO ₄

^a Experiment performed at 26° corrected to 25°.

^b NaClO₄ added. For details see Table Va.

TABLE Va

EXPERIMENTAL RESULTS AT 25° IN THE PRESENCE OF NaClO ₄						
Run	H ⁺	BrO ₃ ⁻	H ₂ O ₂	NaClO ₄	μ	k
120	0.100	0.00500	0.0135	0.200	0.305	159 ± 19
121	.100	.00500	.0135	.200	.305	154 ± 15
Mean						156
122	.100	.00500	.0562	.300	.405	165 ± 30
123	.100	.00500	.0562	.300	.405	165 ± 10
Mean						165
124	.100	.00500	.0536	.070	.175	190 ± 17
125	.100	.00500	.0536	.070	.175	187 ± 14
Mean						188
126	.100	.00500	.0540	.700	.805	145 ± 11
127	.100	.00500	.0540	.700	.805	144 ± 5
Mean						144

The values of k are plotted against the ionic strength in Fig. 3; in Fig. 4 are plotted values of χ on a corresponding scale. From this plot it is evident that the introduction of the measured activity coefficients of hydrobromic acid in the manner prescribed by Brønsted does eliminate a pronounced trend in the measured rate constants at ionic strengths less than 0.2 and does, in the same region, reconcile the measurements in

sulfuric acid to those in perchloric. It may be added that the specific effect of potassium ion on the activity of hydrobromic acid is of the nature to counteract the decrease in χ at higher ionic strengths; and that in perchloric acid solutions the use of the activity coefficients of Harned and James does in fact give values of χ which are constant to $\mu = 0.5$.

Extrapolation to $\mu = 0$ of the sulfuric acid results leads to a value of χ_0 between 500 and 560. This result agrees satisfactorily with the more accurate extrapolation of the perchloric acid values, $\chi_0 = 540 \pm 15$.

Fig. 4.

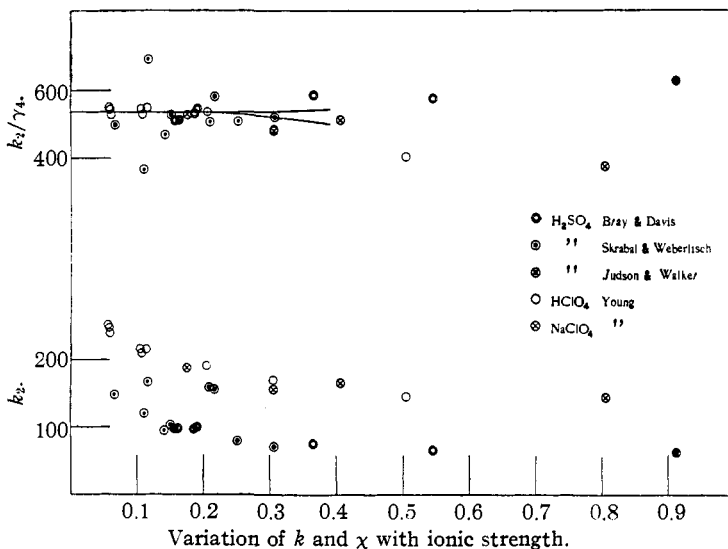
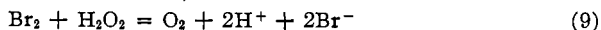


Fig. 3.

Mechanism of the Autocatalytic Reduction.—As was pointed out above, in the runs in which the hydrogen-ion concentration was 0.3 M or greater, slight deviations from the rate law were observed which seemed to be correlated with the appearance of appreciable amounts of bromine in the solution during the latter parts of the experiments.

This accumulation of bromine increases fairly rapidly with the acid concentration, so that at 0.5 M hydrogen ion, sufficient bromine is present to be measured accurately. The determination of the bromine concentrations at various times was undertaken in order to compare the observed rate of oxygen evolution (Reaction 3) with that calculated for the reaction



which, according to Bray and Livingston,¹¹ obeys the law

¹¹ (a) Bray and Livingston, *THIS JOURNAL*, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923); (c) Livingston, *ibid.*, **48**, 53 (1926); (d) Bray and Livingston, *ibid.*, **50**, 1654 (1928).

$$\frac{dO_2}{dt} = \chi_2 \frac{(Br_2)(H_2O_2)}{(H^+)(Br^-)\gamma_{HBr}^2} \quad (10)$$

At an acid concentration of 0.5 *M*, duplicate runs were made having initial concentrations of 0.00503 *M* bromate ion and 0.0455 *M* hydrogen peroxide. In one of these, the bromine concentration was determined from time to time by extraction with carbon tetrachloride, running the extractions into slightly acidic solutions of potassium iodide and titrating the liberated iodine with a 0.01 *N* thiosulfate solution. The results of these titrations, together with the calculated concentrations of bromine corrected for tribromide,¹² are given in the third and fourth columns of Table VI. In the other of the duplicate runs the evolved oxygen was measured frequently, and the concentrations of bromide ion, bromate ion, and hydrogen peroxide were calculated in the usual manner. Since the stoichiometric relationships for the formation of bromine must be those of Equation 2, these concentrations were corrected as follows: from the bromide ion concentration, $\frac{5}{3}$ that of the total bromine was subtracted; from the bromate, $\frac{1}{3}$ that of the bromine; and from the hydrogen ion, twice that of the bromine. These corrected concentrations form the last four columns of Table VI.

TABLE VI
CONCENTRATIONS AT VARIOUS TIMES
Millimoles per Liter

Time, minutes	Br ⁻ uncorrected	Br ₂	Br ₂ corrected for Br ₃ ⁻	Br ⁻ corrected	BrO ₃ ⁻	H ⁺	H ₂ O ₂
0	0	0	0	0	5.03	500	45.5
28	2.39	2.39	2.64	500	38.9
32	2.92	0.11	0.10	2.74	2.08	500	36.6
35	3.39	.19	.18	3.07	1.59	500	35.2
39	3.94	.36	.34	3.34	0.98	499	33.6
44	4.43	.40	.37	3.76	.48	499	32.1
49	4.76	.27	.25	4.31	.19	500	31.2
53	4.91	4.91	.12	500	30.8

The observed rates of evolution of oxygen, obtained by taking tangents to the oxygen time curve at the times given in Table VI, form the first row of Table VII. (The units are moles per minute from 250 cc. of solution.) The corresponding rates of oxygen evolution from Reaction 9, calculated from¹³

$$V_o = \frac{dO_2}{dt} = \frac{0.0275}{4} \frac{(Br_2)(H_2O_2)}{(H^+)(Br^-)}$$

¹² The bromine concentration was corrected for tribromide using the value of 16.2 [Lewis and Randall, THIS JOURNAL, 38, 2348 (1916)] for the equilibrium constant of the reaction $Br_2 + Br^- \rightleftharpoons Br_3^-$.

¹³ The value of the specific rate, $\chi_2 = 0.0275$ at $\mu = 0.5$, is based on the steady state measurements and χ_2 values given in Ref. 11 (b) (c) (d).

are given in the second row of Table VII. It is evident that this reaction fails to account for much of the oxygen formed, and does not provide for the oxidation of enough hydrogen peroxide.

For comparison with these results, there are listed in the fifth and third rows of the table the corresponding rates of the third and fourth order reactions

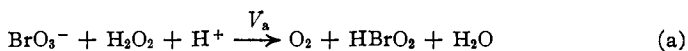
$$\begin{aligned} V_a &= (0.03/4)(\text{H}_2\text{O}_2)(\text{BrO}_3^-)(\text{H}^+) \\ \text{and} \quad V_b &= (220/4)(\text{BrO}_3^-)(\text{Br}^-)(\text{H}^+)^2 \end{aligned}$$

and in the fourth row the sum, $V_b + V_c$. The values of V_a are negligible in comparison with those of V_b or V_c . An examination of the remaining data in the table leads at once to the following conclusion. During the reduction of one mole of BrO_3^- by Br^- in the presence of hydrogen peroxide, there is formed one mole of oxygen in addition to that due to Reaction 9.

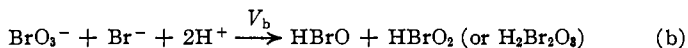
TABLE VII
RATES OF OXYGEN EVOLUTION AT VARIOUS TIMES
Moles $\times 10^{-4}$ per Min. from 250 Cc.

Time	32	35	39	44	49
1 $d\text{O}_2/dt$ (observed)	1.21	1.06	0.72	0.63	0.38
2 $d\text{O}_2/dt$ due to reduction of Br_2 by $\text{H}_2\text{O}_2 = V_c$	0.18	0.26	.40	.37	.23
3 Rate of the fourth order reaction = V_b	.783	.670	.449	.247	.113
4 Sum of Rows 2 and 3 = $V_b + V_c$.96	.93	.85	.62	.34
5 Rate of the third order reaction = V_a	.0029	.0020	.0012	.0006	.0002

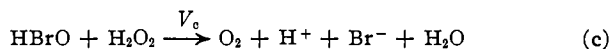
A mechanism for the autocatalytic reduction of bromate ion by hydrogen peroxide may now be postulated with a considerable degree of surety. In agreement with other investigators, we shall assume that the most probable rate-determining steps in the third and fourth order reactions are



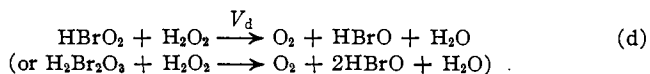
and



Bray and Livingston have furnished almost conclusive evidence that the rate-determining step in the reduction of bromine by hydrogen peroxide, Reaction 9, is



and that the hydrolysis equilibrium is maintained during this reaction. The empirical conclusion stated in the preceding paragraph requires that some product of the fourth order reaction (b), other than HBrO , reacts as rapidly as it is formed, with production of oxygen. Consequently, the next step may be written



where $V_d = V_b$. Equation 3 is the sum (a) + (b) + (c), or (b) + (d) + 2(c).

The results presented in this section have thus led to the conclusion that, under the conditions of these experiments, hydrogen peroxide, rather than hydrobromic acid, acts as the reducing agent at every stage of Reaction 3 except the first step of the reduction of bromate ion by bromide ion.

Summary

The rate of the autocatalytic reduction of bromate ion by hydrogen peroxide may be expressed by the equation

$$[-d(\text{BrO}_3^-)/dt] = k_1 (\text{H}_2\text{O}_2)(\text{BrO}_3^-)(\text{H}^+) + k (\text{BrO}_3^-)(\text{Br}^-)(\text{H}^+)^2$$

over hydrogen-ion concentrations ranging at 25° from 0.05 *M* to 0.5 *M* and at 65° from 0.0125 *M* to 0.105 *M*.

The heat of activation of the fourth order reaction, calculated in the usual manner, is 16,000 ± 300 calories; that of the third order reaction, 15,000 ± 1000 calories.

The expression for the kinetic salt effect of the fourth order reaction

$$\frac{k}{\gamma_{\text{HBr}}^2 \gamma_{\text{HBrO}_3}^2} = \chi$$

is the limiting law at 65°.

The rate law for the fourth order reaction in perchloric and sulfuric acid solutions of ionic strengths less than 0.2 is

$$-d(\text{BrO}_3^-)/dt = 540 \pm 15(\text{BrO}_3^-)(\text{Br}^-)(\text{H}^+)^2 \gamma_{\text{HBr}}^4 \text{ at } 25^\circ$$

A mechanism is given for the autocatalytic reduction of bromate ion by hydrogen peroxide, in which the reduction takes place in steps and hydrogen peroxide acts as the reducing agent for the intermediates HBrO and HBrO₂ (or H₂Br₂O₃). Definite evidence is presented in support of this mechanism.

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