The radiation has been positively identified as due to actinium itself by the excellent agreement between theoretical and experimental growth curves.

BERKELEY, CALIFORNIA RECEIVED MAY 27, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

The Kinetics of Hypobromite Decomposition

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This study has been undertaken to determine the order of decomposition of hypobromites in weakly acid and weakly alkaline solutions, as well as the effect of *p*H on the reaction velocity.

Earlier investigations show that bromate formation in strongly alkaline solutions is second order with respect to concentration of hypobromite; as the alkalinity of the solution is decreased, a third order reaction appears and may become predominant under the proper experimental conditions. Liebhafsky and Makower[1] from a consideration of their own work, that of Skrabal and Weberitsch[2] and that of Kretzschmar[3] infer that the rate of decomposition of hypobromite can be represented by the equation

$$-d[Br_2]/dt = k_{c''} [HBrO]^2 [BrO^-] \qquad (1)$$

Corresponding to the rate determining step

$$2HBrO + BrO^- = BrO_3^- + 2H^+ + 2Br^-$$

as originally suggested by Kretzschmar. Equation (1) can be translated into an alternate form by introducing the ionization constant, K_{HBrO}, of hypobromous acid and the ion product of water, K_w, namely

$$-d[Br_2]/dt = k_3 [HBrO]^3 [OH^-] \qquad (2)$$

where $k_3 = k_{c''} K_{HBrO}/K_w$. According to this equation the reaction is of the third order with respect to hypobromous acid at constant *p*H and varies with the latter as the first power of the OH^- concentration.

In a more recent paper Chapin[4] finds the reaction in line with the above to be of third order in strongly acid solutions and of second order in solutions of *p*H 9 or higher. The hydrogen-ion concentration was determined by Chapin colorimetrically after first destroying the oxidizing agents in solution.

In this work the rate was followed at 25° in solutions of various constant hydrogen-ion concentrations in the range *p*H 6.4 to 7.8. Constant *p*H was maintained with Na_2HPO_4–NaH_2PO_4 buffers, while the hydrogen-ion concentration was determined with a glass electrode and vacuum tube voltmeter.

Experimental

Apparatus

Constant Temperature Bath.—The water bath used was of large capacity and was maintained at 25 ± 0.05°.

Glass Electrode.—The electrode used was of the type described by Robertson[5] and others, and was made of Corning 015 glass. Before and after every experiment the electrode was calibrated by two buffers whose *p*H fell on either side of that of the solution studied. A straight line relationship was assumed between these voltages and *p*H, an assumption amply borne out by calibration of the electrode over the *p*H range 2 to 8.5.

Vacuum Tube Voltmeter.—The vacuum tube voltmeter was of the usual type. Plate current deflections were compensated by an external e. m. f. whose value was measured with a Leeds and Northrup student type potentiometer.

Reaction Vessel.—The reaction vessel consisted of a three-necked liter flask.

Analytical

At intervals samples were removed from the reaction vessel and analyzed for hypobromite content and total oxidizing power. The hypobromite concentration was determined by adding a definite volume of solution to an excess of standard arsenite solution and titrating the excess with iodine. Toward the end of the titration excess bicarbonate and starch were added and the titration continued to the well-known blue end-point.

The total oxidizing power was determined by adding definite volumes of sample to solutions of potassium iodide acidified with hydrochloric acid, and titrating the liberated iodine with thiosulfate, using starch as an indicator. The difference between total oxidizing power and total hypobromite represents the concentration of bromate.

Procedure

In this study the hypobromite solutions were kept at constant *p*H during the course of an experiment with mixtures of Na_2HPO_4 and NaH_2PO_4 as buffers. (In two cases mixtures of KH_2PO_4–K_2HPO_4 were used.) The former was about 0.13 molar, while the latter was 0.5 molar. By mixing the two in various proportions with the hypobromite solution, the *p*H range of 6.4 to 7.8 could be easily covered.

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(1) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1037 (1933).

(2) Skrabal and Weberitsch, *Monats.*, **36**, 237 (1915).

(3) Kretzschmar, *Z. Elektrochem.*, **10**, 789 (1904).

(4) Chapin, THIS JOURNAL, **56**, 2211 (1934).

(5) Robertson, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 5 (1931).

The reacting mixture was prepared as follows: 10 cc. of concentrated sodium hydroxide solution was diluted to 100 cc. with water and cooled by ice. To this cold sodium hydroxide was added with vigorous agitation about 400 cc. of fairly strong bromine water. The straw-yellow solution so obtained was quickly diluted with 500 cc. of the buffer solution and immediately placed in the bath. The electrodes were then inserted in the bath, using a long agar-agar bridge to avoid contamination of solution with calomel, connections made, and a sample removed for hypobromite analysis.

To make frequent sampling possible, a series of ten 250-cc. Erlenmeyer flasks, each containing a measured volume of arsenite solution, was prepared; and in the early stages of a run the samples were pipetted directly into these and the bottles tightly stoppered. The excess arsenite in these solutions was titrated at a convenient time, usually in about fifteen minutes.

To determine the total oxidizing power, which remains practically constant during the course of an entire experiment, 10-cc. samples were withdrawn at various intervals and titrated as described above.

The glass electrode voltage was measured periodically and found to be quite constant during the course of an experiment, indicating that the buffers functioned well, and that the *p*H remained constant.

Calculation and Results

In the tables time is expressed in minutes, while all concentrations are in moles per liter. The concentration of hypobromite is that calculated from the cc. of arsenite solution required, while that of bromate is given by the difference of total oxidizing power and cc. of arsenite solution used. The original concentration of hypobromite was obtained from the equation

$$a = (a - x) + 3(C_{BrO_3^-}) \qquad (3)$$

where a is the starting concentration of hypobromite, $(a - x)$ the concentration of hypobromite found in the first analysis, while $C_{BrO_3^-}$ is the concentration of bromate at the same time. This expression follows on the assumption that no bromate was formed directly on addition of bromine solution to the buffer except through the intermediate stage of hypobromite, and that for three moles of hypobromite decomposed one mole of bromate was formed.

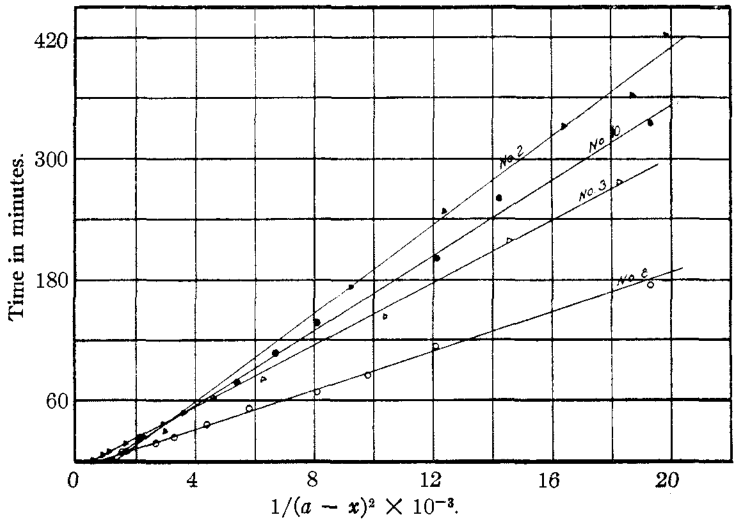

Fig. 1.—Plot of t against $1/(a - x)^2$ for several experiments.

The starting time was obtained by plotting $C_{BrO_3^-}$ against time and extrapolating to $C_{BrO_3^-} = 0$. The difference between the starting time so obtained and that actually recorded as zero when the first sample was taken for analysis, represents the correction to be added to the observed time.

For all experiments the specific reaction constants were calculated in the usual manner from

$$k_1 = \frac{2.3}{t}\frac{a}{a-x}$$

$$k_2 = \frac{1}{at}\frac{x}{a-x} \text{ and}$$

$$k_3' = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

No constancy was observed in the values of either k_1 or k_2. For the sake of brevity, results for k_3' from several experiments are presented in Fig. 1, where a plot of t against $1/(a - x)^2$ is seen to yield the straight lines expected for a third order reaction. From these and other similar curves it is to be concluded that at 25° and at constant *p*H the rate of decomposition is proportional to $(a - x)^3$.

Results from twelve separate experiments are presented in Table I. Columns (1) and (2) are self-explanatory. Column (3) gives the initial concentrations of hypobromite while Columns (4) and (5) give the concentrations of buffer salts used, all in moles per liter. Column (6) gives the values of k_3' obtained from the slopes of the lines when t is plotted against $1/(a - x)^2$ as described above.

A perusal of these constants shows that the values of k_3' vary considerably among themselves. If this variation is due to variation in the hydroxyl-ion concentration, it should be possible to evaluate the time constant, k_3, as follows. The rate of decomposition of hypobromite may in general be represented by the equation

$$-dx/dt = k_3'' \, [OH]^{\nu} \, (a - x)^3 = k'(a - x)^3 \qquad (4)$$

TABLE I

DATA AND RESULTS ON HYPOBROMITE DECOMPOSITION AT 25°

(1) Expt.	(2) pH	(3) a, moles/liter	(4) $C_{Na_2HPO_4}$, moles/liter	(5) $C_{NaH_2PO_4}$, moles/liter	(6) k'_3	(7) $k''_3 = k'_3/OH$	(8) $k_3 = k''_3/Z^2$
4	6.4	0.0362	..	0.25	6.18	2.46×10^8	2.77×10^8[a]
7	6.4	.0387	..	.25	9.00	3.58	4.05
11	6.4	.0521	0.013	.20	7.41	2.95	3.44
12	6.6	.0373	.013	.20	14.79	3.72	4.49
2	6.8	.0285	.013	.20	23.70	3.75	5.04
10	6.8	.0328	.020	.18	27.05	4.28	5.75
9	6.9	.0441	.026	.15	17.57	2.21	3.18
1	7.0	.0362	.026	.15	21.74	2.17	3.40
8	7.2	.0367	.032	.13	47.80	3.04	5.86
6	7.4	.0332	.039	.10	41.95	1.67	4.44
3	7.6	.0469	.020[b]	.18	32.60	0.82	3.28
5	7.8	.0406	.026[b]	.15	51.75	0.82	5.45
						2.6×10^8	4.4×10^8

[a] Omitted from calculation of mean. [b] K_2HPO_4–KH_2PO_4 buffer mixtures.

since in any one experiment the pH is constant. The hydroxyl-ion concentration can be obtained directly from the pH measurements and the ion product of water at 25°, namely, $K_w = [OH^-][H^+] = 1.0 \times 10^{-14}$. The constant y on the basis of previous work may be expected to be unity. Assuming this, $k''_3 = k'_3/OH$. Values of k''_3 thus calculated are given in Column (7) of Table I.

Although these values all have the same order of magnitude, they nevertheless deviate from the mean to an extent greater than would be expected from the uncertainty involved in the measurements, about 0.1 of a pH unit. It seems inadvisable to correct for this variation by changing the value of y. Better concordance can be obtained by allowing for the ionization of HBrO. In the above calculations the concentration of HBrO was assumed to be the analytically determined quantity $(a - x)$, which involves besides HBrO also BrO^-, Br_3^- and Br_2. Under the conditions of these experiments the concentrations of Br_3^- must be quite small and may be neglected. If we assume, further, that the concentrations of bromine in these solutions are also small, then $(a - x)$ involves only HBrO and BrO^-; and, with a knowledge of the ionization constant of hypobromous acid, K_{HBrO}, the concentrations of both HBrO and BrO^- may be calculated.

The value of the ionization constant of hypobromous acid used was that given by Chapin[4] and based on the data of Liebhafsky and Makower,[1] namely, $K_{HBrO} = 2.5 \times 10^{-8}$. The concentration of hypobromous acid, [HBrO], is given, then, by

$$[HBrO] = Z(a - x) \qquad (5)$$

where $Z = K_w/(K_w + K_{HBrO}[OH])$, and the rate equation becomes on substitution of (5)

$$\frac{d(HBrO)}{dt} = k_3[HBrO]^3\,[OH] = -Z\frac{dx}{dt} = k_3Z^3[a - x]^3\,[OH] \qquad (6)$$

and

$$\frac{-dx}{dt} = k_3Z^2[OH][a - x]^3 \qquad (7)$$

Comparison with (4) yields

$$k_3 = k'_3/Z^2[OH] = k''_3/Z^2 \qquad (8)$$

The values of k''_3/Z^2 from equation (8) are given in Table I, Column 8. The deviations from the mean are now considerably less than those for Column 7 and are much closer to those expected from the uncertainty of experiment. Omitting the lowest result for Experiment No. 4 the mean value of $k_3 = 4.4 \times 10^8$ when the time is in minutes and concentrations in moles per liter.

Discussion

These results indicate that under the conditions outlined above in the pH range 6.4 to 7.8 the decomposition of hypobromous acid is a reaction of the third order with respect to HBrO, and first order with respect to hydroxyl-ion concentration. As was pointed out before, the rate law (6) has an alternative form

$$d[HBrO]/dt = k_4[HBrO]^2[BrO^-] \qquad (9)$$

where $k_4 = k_{C''}$ of Liebhafsky and Makower, and still another form

$$\frac{d[HBrO]}{dt} = k_c\,\frac{[Br_3^-]^3\,[OH^-]^4}{[Br^-]^6} \qquad (10)$$

also mentioned by the above authors. Although they give values for k_3 and k_c, no value is given for k_4. It would be of interest, therefore, to calculate these rate constants and compare them with those of Liebhafsky and Makower, and also with those of Kretzschmar.

It can readily be shown that $k_4 = k_3K_w/K_{\text{HBrO}}$ and $k_c = k_3K_h^3/K_wK_3^3$ where K_h, the hydrolytic constant of bromine, is given by

$$K_h = [\text{HBrO}]\,[\text{Br}^-]\,[\text{H}^+]/[\text{Br}_2]$$

and

$$K_3 = [\text{Br}_2]\,[\text{Br}^-]/[\text{Br}_3^-]$$

For K_h both Liebhafsky[6] and Jones and Baeckström[7] found at 25° the value 5.8×10^{-9}. For K_3 Linhart,[8] Bray and Connolly[9] and Jones and Baeckström[7] give respectively 0.062, 0.0625 and 0.063; choosing $K_3 = 0.063$ and the values indicated for the other constants it is found that $k_4 = 175.5$ and $k_c = 2.1 \times 10^{22}$, while $k_3 = 4.4 \times 10^8$. These values are to be compared with Liebhafsky and Makower's estimates of $k_3 = 7.9 \times 10^9$ and $k_c = 2.4 \times 10^{23}$.

Liebhafsky and Makower remark on the fact that Kretzschmar's value of $k_4 = 100$ at 25° leads to low results for both k_3 and k_c, namely, 10^6 and 3×10^{19}, respectively. This is to be ascribed to their assumption of $K_{\text{HBrO}} = 10^{-10}$. If the value given by Chapin, and based on their own results, namely, 2.5×10^{-8}, is employed, the results become quite concordant with ours as may be seen from Table II.

TABLE II

SUMMARY OF RATE CONSTANTS

	Liebhafsky and Makower (based on Skrabal)	Kretzschmar	Prutton and Maron	
			from k_3''	from k_3
k_3	7.9×10^9	2.5×10^8	2.6×10^8	4.4×10^8
k_4	....	100	105	175.5
k_c	2.4×10^{23}	1.2×10^{22}	....	2.1×10^{22}

It is seen that the agreement between our results and Kretzschmar's is quite good if the uncorrected values are used, while Liebhafsky and Makower's calculations appear to be somewhat higher.

Foerster and Jorre[10] found for hypochlorites and Kretzschmar found for hypobromites that the general rate law

$$d[\text{HXO}]/dt = k[\text{HXO}]^2\,[\text{XO}^-] \qquad (11)$$

corresponding to the reaction

$$2\text{HXO} + \text{XO}^- \longrightarrow \text{XO}_3^- + 2\text{H}^+ + 2\text{X}^- \quad (12)$$

is obeyed, and considered reaction (12) to be rate determining. Similarly Liebhafsky and Makower[1] find the above rate law to be "of general importance in the formation of the halate ion, XO_3^-, through the decomposition of these lower valent halogen compounds," but realize that the probability of a trimolecular reaction is not very high, and hence the actual mechanism is more complex than appears from the equation. The first part of their conclusion is questioned in a very recent paper by Skrabal.[11]

In view of this divergence of opinion it seems advisable to the authors to refrain from any inferences as to the mechanism until more data of the type given here and extending over a wider range of hydroxyl-ion concentrations are available.

Summary

1. The rate of hypobromous acid decomposition has been studied at 25° in solutions of constant pH in the range 6.4 to 7.8.

2. The decomposition is found to be of the third order with respect to hypobromous acid and first with respect to the hydroxyl-ion concentration. The complete rate equation is

$$d[\text{HBrO}]/dt = k_3[\text{HBrO}]^3\,[\text{OH}]$$

where $k_3 = 4.4 \times 10^8$, the time being in minutes while concentrations are in moles per liter.

3. Specific reaction rate constants are calculated also for the following rate equations

$$d[\text{HBrO}]/dt = k_4[\text{HBrO}]^2\,[\text{BrO}^-]$$

$$d[\text{HBrO}]/dt = k_c\,\frac{[\text{Br}_3^-]^3\,[\text{OH}^-]^4}{[\text{Br}^-]^6}$$

The constants are found to be $k_4 = 175.5$ and $k_c = 2.1 \times 10^{22}$.

4. A comparison is made between the results obtained here and those of other workers. The constants given by Kretzschmar are in general agreement with the above; Liebhafsky and Makower's values are somewhat higher.

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RECEIVED FEBRUARY 18, 1935

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(6) Liebhafsky, THIS JOURNAL, **56**, 1500 (1934).

(7) Jones and Baeckström, *ibid.*, **56**, 1517 (1934).

(8) Linhart, *ibid.*, **40**, 158 (1918).

(9) Bray and Connolly, *ibid.*, **33**, 1485 (1911).

(10) Foerster and Jorre, *J. prakt. Chem.*, **59**, 53 (1899).

(11) Skrabal, *Z. Elektrochem.*, **40**, 245 (1934).