valent bonds, because of the high central charge, that a high activation energy is needed to break them.

$Hg(CN)_2$ and $HgCN^+$ fit into neither of these categories. The only orbitals available for bonding are *s* and *p* orbitals of quantum number higher than those occupied by the electrons of Hg^{++}. Thus, these complexes, though "inert," are evidently "outer orbital" complexes with low charge on the central ion. However, even though this case may be unique we do not believe it to be anomalous. Hg^{++} ion is a very strong polarizing agent and CN^- is exceptionally polarizable. Thus if there are only one or two cyanides per Hg^{++} very strong, largely covalent bonds, requiring a high activation energy to break, should be found even though the formal charge on the central ion is only two. This gives rise to the very great thermodynamic stability of aqueous $Hg(CN)_2$: $(Hg(CN)_2\cdot)(Hg^{++})^{-1}(CN^-)^{-2} = 10^{32}$ [13] and by the same token to its non-lability. If the number of cyanides per Hg^{++} is increased to three or four the polarization interaction becomes saturated and the individual bonds become weaker. This is manifested in the relatively low association constant of $Hg(CN)_4^=$ with respect to $Hg(CN)_2$: $(Hg(CN)_4^=)(Hg(CN)_2)^{-1}\cdot(CN^-)^{-2} = 2 \times 10^9$.[14] Correspondingly $Hg(CN)_3^-$ and $Hg(CN)_4^=$ appear to be labile complexes; when Hg^{++} is added to them it is immediately cyanide complexed, as is evidenced by the disappearance of the Hg^{++} absorption at 220 mμ and the failure of the solution to give a precipitate with $NaIO_3$.

[13] This constant approximately evaluated from data on Hg^{++}(aq)CN^-(aq) and $Hg(CN)_2$(crystalline) in Latimer ["Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 176] and from the solubility of $Hg(CN)_2$.

[14] This constant approximately evaluated from data referred to in footnotes 4 and 12.

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The Decomposition of Hypobromite and Bromite Solutions

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The kinetics of the decomposition of hypobromite solutions were investigated in a limited range of *p*H and initial concentrations by measuring the change of concentration of both hypobromite and bromite. The results can be satisfactorily explained on the basis of two second-order consecutive reactions, the first involving the formation of bromite, and the second a comparatively fast reaction between bromite and hypobromite. The decomposition of the intermediate, bromite, was investigated separately and was found in the main to follow an analogous mechanism, hypobromite now taking the role of intermediate. In the *p*H range considered, the assumption that the reactions take place exclusively between an undissociated acid molecule and an anion does not give satisfactory agreement with experiment; much better agreement is obtained by assuming, in addition, reactions involving either free bromine or two uncharged molecules of acid.

Alkali hypobromite solutions are known to decompose to give a mixture of bromide and bromate. The kinetics and mechanism of this decomposition have been the object of several investigations.[2-7] However, the mechanism is still not fully understood.

Bromous acid and the bromite anion have been assumed by several authors as intermediates in the decomposition of hypobromite,[5,8,9] in the back reaction in acid solution, *i.e.*, the formation of bromine from bromate and bromide,[10] and in the acid reduction of bromate by hydrogen peroxide.[11] Some experiments have also been reported on the reaction between bromite and hypobromite.[5,8] However, the reactions involved in the formation of bromate from bromite have not yet been investigated in detail. An understanding of this reaction can be expected to throw some further light on the mechanism of the decomposition of hypobromite solutions.

The object of the present work was to clarify further, in a limited range of *p*H, the mechanism of the processes by isolating the single steps as far as possible.

Experimental

Hypobromite solutions were prepared by adding an appropriate amount of bromine to a cooled solution of sodium hydroxide. The solutions thus prepared were kept in a refrigerator for not more than 24 hours before use.

Bromite solutions were prepared by the method described by Chapin[5] and brought to the desired *p*H by adding solid boric acid and shaking vigorously. The bromide content of these solutions was regulated by the addition of either potassium bromide solution, or of silver nitrate solution, followed by rapid filtration.

The analyses of bromite, hypobromite and bromate were carried out by the methods used by Chapin,[5] the temperature being kept below 20° during the titration of bromite with iodine in the presence of phenol[12] and those of bromide by adding hydrogen peroxide to an alkaline solution in order to reduce the hypobromite and bromite to bromide, boiling off the excess of hydrogen peroxide, acidifying with acetic acid and titrating with silver nitrate. The difference between this titration and that of hypobromite and bromite gives the bromide concentration.[12]

The *p*H was ≥ 8.0. (At lower values of *p*H, free bromine appears in appreciable quantities and would complicate both the analytical methods and the experimental procedure.) The experiments were carried out in buffered solutions, using borax–boric acid mixtures, or sodium phosphate.

The *p*H was measured with a glass electrode, using a

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(1) To whom inquiries should be addressed.

(2) H. Kretzschmar, *Z. Elektrochem.*, **10**, 789 (1904).

(3) A. Skrabal and S. R. Weberitsch, *Monatsh.*, **36**, 237 (1915).

(4) H. A. Liebhafsky and B. Makower, *J. Phys. Chem.*, **37**, 1037 (1933).

(5) R. M. Chapin, THIS JOURNAL, **56**, 2211 (1934).

(6) C. F. Prutton and S. H. Maron, *ibid.*, **57**, 1652 (1935).

(7) A. Skrabal, *Z. Elektrochem.*, **40**, 232 (1934); **48**, 314 (1942); *Monatsh.*, **71**, 251 (1938).

(8) J. Clarens, *Compt. rend.*, **157**, 216 (1913).

(9) R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 655, 666 (1951).

(10) C. N. Hinshelwood, *J. Chem. Soc.*, 694 (1947).

(11) H. A. Young, THIS JOURNAL, **72**, 3310 (1950).

(12) M. Lewin, Ph.D. Thesis, Jerusalem, 1947.

Beckman Model G *p*H meter. All the experiments were carried out at 25 ± 0.1°.

Ordinary glass vessels were used since two experiments, carried out under otherwise identical conditions, one in an ordinary vessel and one in a blackened vessel, gave identical results. Direct sunlight was avoided.

The influence of *p*H, ionic strength, concentration of bromide and initial concentration of reactants was investigated.

Results

A. Hypobromite Solutions.—The total oxidizing capacity was found to remain constant during all experiments. The concentration of hypobromite decreased as the reaction proceeded, and some bromite was formed, its concentration reaching a maximum and then slowly decreasing as the reaction proceeded (see Fig. 1).

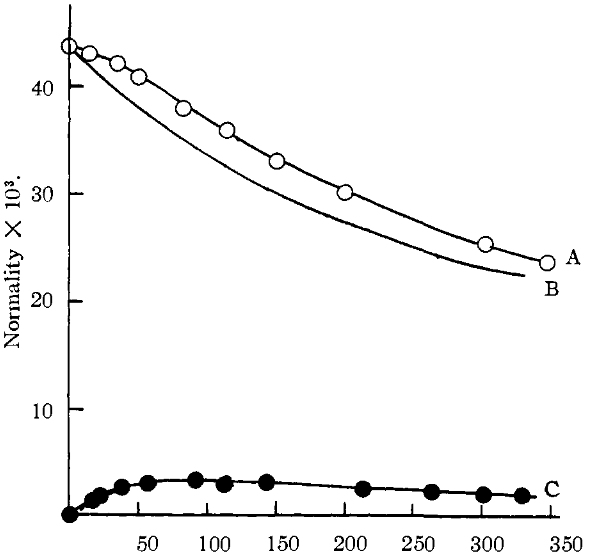

Fig. 1.—The dependence of the normalities of hypobromite plus bromite (A, ○), of hypobromite (B, —) and of bromite (C, ●) on time. The *p*H is 7.84.

Experiments were carried out at *p*H 8.84 and with initial concentrations varying between 0.017 and 0.027 *M*. The reaction follows a second-order course, plots of the reciprocal of the concentration *vs.* time giving straight lines (see Fig. 2).

The apparent rate constant, k_a, was found to be 0.134 min.$^{-1}$ mole^{-1} l. with a maximum deviation of ±0.004 in the range of initial concentration of between 0.017 and 0.024 *M*. At higher concentrations, k_a is somewhat higher, indicating an apparent order slightly greater than 2.

Experiments were carried out at an initial concentration of about 0.02 *M* in the range of *p*H between 8.0 and 9.15 The reaction rate decreased strongly with increasing *p*H. An inspection of Fig. 3 shows the rate to be approximately proportional to the hydrogen ion concentration.

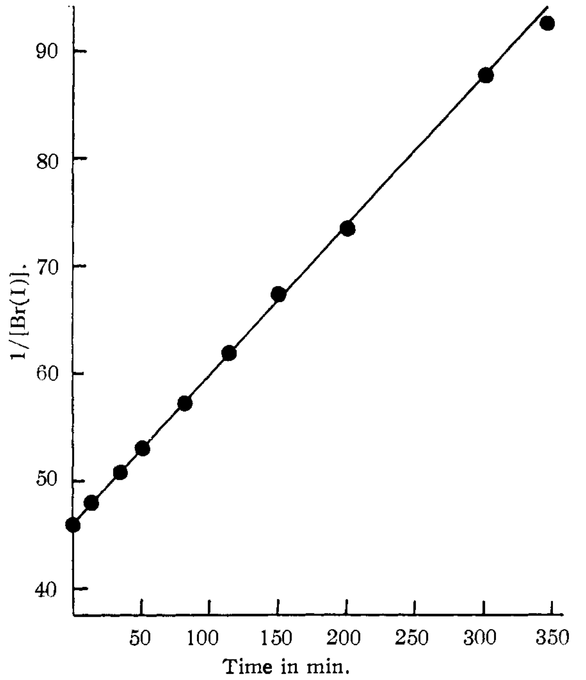

Fig. 2.—The reciprocal of the hypobromite molarity *vs.* time, for the experiment given in Fig. 1.

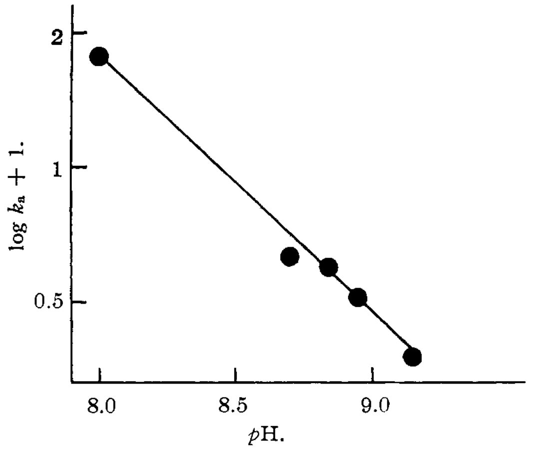

Fig. 3.—The dependence of the apparent rate constant on *p*H, for the decomposition of hypobromite solutions. The initial concentration of both hypobromite and bromide is approximately 0.020 *M*. (Semi-quantitative relation.)

The influence of bromide on k_a was investigated by varying the initial bromide concentration between 0.019 and 0.087 *M*. The value of k_a was found to increase slightly with increasing bromide concentration, as shown in Fig. 4, where the same scale is used as in Fig. 3. On the other hand, increasing the ionic strength from about 0.29 to values up to 0.7 by the addition of sodium sulfate had no detectable influence on k_a.

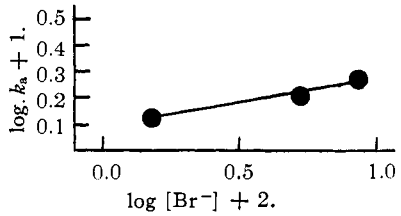

Fig. 4.—The dependence of the apparent rate constant on bromide concentration, for the decomposition of hypobromite solutions. The *p*H is 8.84 and the initial concentration 0.020 *M*. (Semi-quantitative relation.)

B. Bromite Solutions.—In all the experiments the total oxidizing capacity was found to remain constant; bromite decreased, and some hypobromite was formed. The results of a typical experiment are shown in Fig. 5.

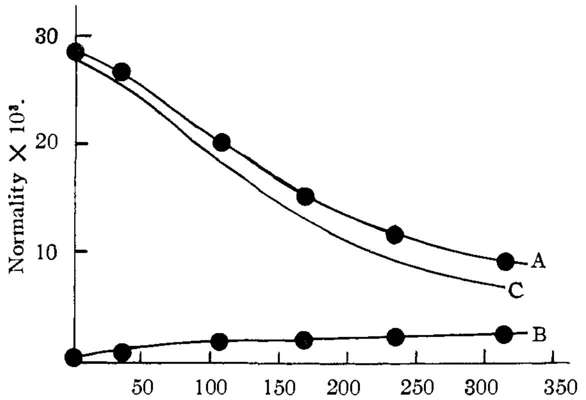

Fig. 5.—The dependence of the normalities of hypobromite plus bromite (A), of hypobromite (B) and of bromite (C) on time. The *p*H is 8.5 and the initial bromide concentration 0.186 *M*.

Experiments were carried out at *p*H 8.5 and an initial bromite concentration of 0.0075 *M*, and the ionic strength was varied between 0.29 and 0.58 by the addition of sodium sulfate. The ionic strength was again found to have no influence on the velocity of the reaction within the limit of experimental accuracy.

Experiments were carried out at an initial bromite concentration of approximately 0.01 *M*, initial bromide concentration of approximately 0.4 *M* and at values of *p*H of 8.5, 9.7 and 13.0; the rate decreased by a factor of approximately 3 for every unit increase of *p*H (see Fig. 6).

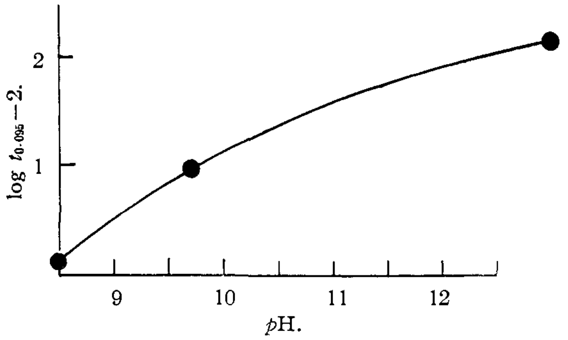

Fig. 6.—The dependence of the rate of reaction on *p*H for the decomposition of bromite solutions. The logarithm of the time for 9.5% decomposition, corrected for equal bromide concentrations, is plotted *vs.* *p*H. (Semi-quantitative relation.)

When the initial bromide concentration was equal to zero, and the initial bromite concentration was comparatively high (~0.04 *M*), the reaction was found to be of the second order with respect to bromite during its initial stage, while the bromide concentration was still low. The velocity constant was approximately 0.008 min.$^{-1}$ mole^{-1} l. No hypobromite was formed.

The presence of bromide was found to increase the rate of reaction considerably. Two series of experiments were carried out in this connection, both at *p*H 8.5. In the first series, the initial bromite concentration was 0.0075 *M*, whereas the initial bromide concentration was varied from 0.024 to 0.35 *M*. The rate was found to be roughly proportional to the bromide concentration. Furthermore, the concentration of the hypobromite formed during the reaction was found to increase with increasing bromide concentration.

In the second series, the initial bromide concentration was kept constant at 0.09 *M*, while the initial bromite concentration was varied from 0.0065 to 0.017 *M*.

When the logarithm of the bromite concentration was plotted against time, curves similar to that shown in Fig. 7 were obtained. After the first 10% of reaction this plot is seen to become a straight line, indicating that at this stage the reaction is of the first order with respect to bromite. The extent of reaction after which the plots became straight lines decreased with decreasing bromide concentration, but increased with decreasing initial bromite concentration.

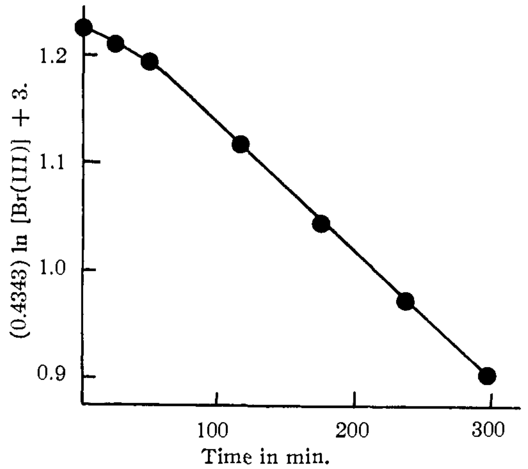

Fig. 7.—The dependence of the logarithm of the molarity of bromite on time. The initial bromide concentration is 0.098 *M*.

Discussion

A. Hypobromite Solutions.—Whilst the over-all course of the reactions in a system containing bromine, bromide, hypobromite, bromite and bromate will be very complicated, one can to some extent separate the individual steps. Thus, in the case of a solution containing initially only hypobromite, Br(I), our results can best be interpreted by assuming that the first reaction is

$$2\mathrm{Br(I)} \xrightarrow{k_1} \mathrm{Br(III)} + \mathrm{Br}^- \qquad \text{(I)}$$

This reaction is followed immediately by a second reaction, involving the bromite formed in reaction I

$$\mathrm{Br(III)} + \mathrm{Br(I)} \xrightarrow{k_2} \mathrm{Br(V)} + \mathrm{Br}^- \qquad \text{(II)}$$

These reactions lead to the rate equations

$$-\,\mathrm{d}[\mathrm{Br(I)}]/\mathrm{d}t = 2k_1[\mathrm{Br(I)}]^2 + k_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \quad (1)$$

$$\mathrm{d}[\mathrm{Br(III)}]/\mathrm{d}t = k_1[\mathrm{Br(I)}]^2 - k_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \quad (2)$$

Evaluation of Rate Constants.—In order to calculate the rate constant k_2, expression 2 was multiplied by two and subtracted from expression 1 to give

$$-\mathrm{d}([\mathrm{Br(I)}] + 2[\mathrm{Br(III)}])/\mathrm{d}t = 3k_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \quad (3)$$

(The value of [Br(I)] + 2[Br(III)] is easily obtained experimentally, since it is just half the normality of the solution with respect to arsenite.)

At *p*H 8.84 and in the range of initial concentrations considered (0.017 to 0.027 *M*), k_2 was found from this expression to be 1.10 ± 0.20 min.$^{-1}$ mole^{-1} l., independent of the initial concentrations of hypobromite and bromide.

The rate constant k_1 was calculated from the following considerations: at the point where the bromite concentration reaches its maximum, expression 2 becomes

$$[\mathrm{Br(III)}]_{\max}/[\mathrm{Br(I)}] = k_1/k_2 \equiv R \quad (4)$$

When no bromide was added to the reaction mixture, the value of R was found to be 0.046 ± 0.003 under the above conditions of *p*H and initial concentration. This leads to $k_1 = k_2 \times R = 1.10 \times 0.046 = 0.05$ min.$^{-1}$ mole^{-1} l.

A combination of equations 1 and 2 yields

$$-\mathrm{d}[\mathrm{Br(I)}]/\mathrm{d}t = 3k_1[\mathrm{Br(I)}]^2 - \mathrm{d}[\mathrm{Br(III)}]/\mathrm{d}t \quad (5)$$

Thus, if bromite were an unstable intermediate, *i.e.*, if we could neglect its rate of change of concentration in comparison with that of hypobromite, we could write

$$k_a = 3k_1 \quad (6)$$

As shown in the experimental part, k_a is equal to 0.134 min.$^{-1}$ mole^{-1} l., *i.e.*, only slightly less than the value of 0.15 obtained by this simplification. Our present experimental results are insufficient to elucidate the reason for the slight upward trend which k_a exhibits when the initial hypobromite concentration is increased above 0.024 *M*.

Influence of Bromide Concentration.—The value of R was found to increase by about 34% when the initial bromide concentration was increased from 0.019 to 0.087 *M*. Since, as we have seen, k_2 is unaffected by the addition of bromide, expression 4 shows that this increase in R causes a corresponding increase in k_1. In the experimental part it has been shown that k_a increases to just this extent with increasing bromide concentration, which is in accordance with the approximate equation 6.

The increase in the rate of reaction I with increasing bromide concentration is not explicitly included in the proposed reaction scheme. The effect may be explained by assuming that in addition to reaction I there also exists the reaction

$$\mathrm{HBrO} + \mathrm{Br_2} + \mathrm{H_2O} \longrightarrow \mathrm{HBrO_2} + 2\mathrm{Br^-} + 2\mathrm{H^+} \quad (\mathrm{Ia})$$

$$\text{or } \mathrm{BrO^-} + \mathrm{Br_2} + \mathrm{H_2O} \longrightarrow \mathrm{BrO_2^-} + 2\mathrm{Br^-} + 2\mathrm{H^+} \quad (\mathrm{Ib})$$

A reaction between halogen and hypohalous acid appears in Skrabal's reaction scheme[13] as one of several consecutive reactions and thus leads to the prediction of a stronger dependence of the rate on halide concentration than that actually found in the case of hypobromite.

Since the bromine concentration is very low, such a reaction would have to have a high rate constant in order to make an appreciable contribution to the over-all reaction. The observed increase in the reaction rate on the addition of bromide would then be due to the increased bromine concentration in accordance with the equilibrium

$$\mathrm{Br^-} + \mathrm{H^+} + \mathrm{HBrO} \rightleftarrows \mathrm{Br_2} + \mathrm{H_2O}$$

Influence of *p*H.—An increase in *p*H was found to increase the value of R (by 33% for an increase of 0.45 unit of *p*H); on the other hand, k_a was shown in the experimental part to decrease strongly with increasing *p*H (see Fig. 3). Thus it may be concluded that both reactions I and II are slowed down by an increase in *p*H, reaction II being somewhat more strongly affected.

This decrease in the rate of reaction with increasing *p*H together with the fact that the ionic strength has no influence on the apparent rate constant precludes the possibility that either of the two consecutive reactions takes place between two anions. If reaction I were to take place in the form

$$\mathrm{HBrO} + \mathrm{BrO^-} \longrightarrow \mathrm{BrO_2^-} + \mathrm{H^+} + \mathrm{Br^-} \quad (\mathrm{Ic})$$

the reaction rate should be at a maximum at $p\mathrm{H} = pK_\mathrm{D} = 8.7$,[14,15] where K_D is the dissociation constant of hypobromous acid. Since this is not in accordance with our experimental results we must assume either that reaction Ia makes a considerable contribution to the over-all decomposition, or that the chief reaction takes place between two undissociated hypobromous acid molecules

$$2\mathrm{HBrO} \longrightarrow \mathrm{HBrO_2} + \mathrm{H^+} + \mathrm{Br^-} \quad (\mathrm{Id})$$

with Ia, Ib and Ic as possible concomitant reactions.[16] The range of *p*H and bromide concentrations investigated is too limited to permit a quantitative statement to be made on this point.

Similarly, the *p*H-dependence of the second of the two consecutive reactions can be explained by assuming a reaction between hypobromous acid and the bromite anion to take place simultaneously with a reaction involving two undissociated acid molecules.

The Apparent Order of the Reaction.—Our mechanism differs from that of previous authors who suggested that the reaction was kinetically of the third order and could be represented by

$$2\mathrm{HBrO} + \mathrm{BrO^-} \longrightarrow \mathrm{BrO_3^-} + \mathrm{H^+} + 2\mathrm{Br^-} \quad (\mathrm{III})$$

This reaction seems to have been suggested for the first time by Kretzschmar[2]; Liebhafsky and Makower[4] carried out experiments at very low bromide concentrations and showed that their results, though not actually supporting the third order with respect to Br(I), definitely favor this re-

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(13) A. Skrabal, *Monatsh.*, **72**, 200 (1938).

(14) E. A. Shilov, THIS JOURNAL, **60**, 490 (1938).

(15) L. Farkas and M. Lewin, *ibid.*, **72**, 5766 (1950).

(16) It can easily be seen that in the range of bromide and hydrogen ion concentrations considered the rate of reaction Ic is, to a good approximation, proportional to $[\mathrm{H^+}]/(K_\mathrm{D} + [\mathrm{H^+}])^2$, and thus passes through a maximum at $[\mathrm{H^+}] = K_\mathrm{D}$; on the other hand, the rate of reaction Ia is proportional to $[\mathrm{H^+}]^3/(K_\mathrm{D} + [\mathrm{H^+}])^2$, *i.e.*, it increases strongly with increasing hydrogen ion concentration in the whole range considered, while that of reaction Id (and also that of reaction Ib) is proportional to $[\mathrm{H^+}]^2/(K_\mathrm{D} + [\mathrm{H^+}])^2$, which in turn can be shown to be proportional to the hydrogen ion concentration around *p*H 8.7, as required by our experimental data. It must be added, however, that this proportionality extends to *p*H 8—the lowest *p*H employed by us—only to a very rough approximation.

action rather than the reaction scheme of earlier authors[3] which predicted a rate inversely proportional to the bromide concentration. Chapin[5] investigated the decomposition of Br(I) solutions over a wide range of *p*H and found the reaction order to lie between 2 and 3 at *p*H 9.4. By tentatively assuming reaction III to be predominant in neutral solution, he derived from the *p*H dependence of the reaction rate the value of 2.5×10^{-8} for the dissociation constant of hypobromous acid. The value subsequently obtained by direct potentiometric titration,[14] and confirmed in our laboratory by an indirect method[15] is 2.06×10^{-9}. Chapin's value for the dissociation constant was used by Prutton and Maron[6] who investigated both the order with respect to Br(I) and the *p*H dependence, and found their results to be in accordance with reaction III. However, their rate constant shows a considerable scattering (see last column of their Table I), and when their results are recalculated, using the 7th column of their table and the correct value for the dissociation constant, this lack of constancy becomes still more marked. Also, their assumption that under their experimental conditions the bromine concentration is negligible, does not seem justified. We repeated some of their experiments and failed to confirm them; our results agreed much better with a second than with a third-order mechanism.

As recognized by Liebhafsky and Makower, Chapin, and especially by Skrabal,[7] the difficulty of establishing the order of the reaction, and the discrepancies between the results of different authors may be due to the fact that the reaction consists of a mixture of concurrent reactions, the relative contributions of which vary strongly with the experimental conditions. Furthermore, the fact that the over-all reaction consists of consecutive reactions may also give an apparent order changing considerably with the experimental conditions. Whilst authors other than Chapin measured only the sum of hypobromite plus bromite, the separate determination of these yields fuller information on the mechanism.

B. Bromite Solutions.—On the basis of our experiments we suggest that in the absence of bromide and hypobromite a solution of bromite decomposes according to

$$2\mathrm{Br(III)} \longrightarrow \mathrm{Br(V)} + \mathrm{Br(I)} \qquad \text{(IV)}$$

The rate of this reaction is very small, and it can be shown that in all our experiments carried out in the presence of bromide it may be neglected to a first approximation in comparison with that of the reaction

$$\mathrm{Br(III)} + \mathrm{Br}^- \xrightarrow{k_1'} 2\mathrm{Br(I)} \qquad \text{(I')}$$

Reactions IV and I′ are immediately followed by the reaction

$$\mathrm{Br(I)} + \mathrm{Br(III)} \longrightarrow \mathrm{Br(V)} + \mathrm{Br}^- \qquad \text{(II)}$$

Reaction I′[9,11] is the back reaction of reaction I, the rate of which is now small owing to the low concentration of hypobromite present, and is neglected in the following treatment.[17]

From reactions I′ and II we obtain the rate equations

$$-\mathrm{d}[\mathrm{Br(III)}]/\mathrm{d}t = k_1'[\mathrm{Br(III)}][\mathrm{Br}^-] + k_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \qquad (7)$$

$$\mathrm{d}[\mathrm{Br(I)}]/\mathrm{d}t = 2k_1'[\mathrm{Br(III)}][\mathrm{Br}^-] - k_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \qquad (8)$$

The above reaction scheme is formally very similar to (though not identical with) that proposed in our previous paper[18] for the oxidation of ethanol by bromine *via* acetaldehyde, and treated more recently by Benson ("Case 3"),[19] and by Lautout, Wyllie and Magat[20] (in the case where $v_{\mathrm{III}} = 0$). The concentration of the intermediate (hypobromite) approaches a constant maximum value. At this stage, expression 8 is equal to zero, or

$$[\mathrm{Br(I)}]_s = (2k_1'/k_2) \times [\mathrm{Br}^-] \qquad (9)$$

Although theoretically this steady state concentration is never fully reached, our experiments show that in most cases it is very closely approached.

Introducing 9 into 7, we get

$$-\mathrm{d}[\mathrm{Br(III)}]/\mathrm{d}t = 3k_1'[\mathrm{Br}^-][\mathrm{Br(III)}] \qquad (10)$$

Thus, the slope of the ln [Br(III)] *vs.* time plots which we found in our experiments to be constant in the later stages of the reaction must be equal to $3k_1'[\mathrm{Br}^-]$.[21] From six experiments, we found: $k_1' = 0.86 \times 10^{-2}$ min.$^{-1}$ mole^{-1} l. with a maximum deviation of $\pm 0.18 \times 10^{-2}$.

The value of $[\mathrm{Br(I)}]_s$ was plotted *vs.* bromide concentration. From the slope of the line, we obtained: $2k_1'/k_2 = 0.84$, so that $k_2 \approx 2$ min.$^{-1}$ mole^{-1} l. at *p*H 8.5, in reasonable agreement with the value of 1.1 min.$^{-1}$ mole^{-1} l. obtained from the decomposition of hypobromite at *p*H 8.8.

In order to show that the mechanism proposed is consistent with the results, the following calculations were carried out, using our previous nomenclature.[18]

Dividing expression 8 by expression 7 we get

$$\frac{\mathrm{d}[\mathrm{Br(I)}]}{\mathrm{d}[\mathrm{Br(III)}]} = \frac{[\mathrm{Br(I)}] - (2k_1'/k_2)[\mathrm{Br}^-]}{[\mathrm{Br(I)}] + (k_1'/k_2)[\mathrm{Br}^-]} \qquad (11)$$

Defining $(k_1'/k_2)[\mathrm{Br}^-] \equiv K$[21] and integrating (remembering that at the beginning of the reaction $[\mathrm{Br(I)}] = 0$ and $[\mathrm{Br(III)}] = [\mathrm{Br(III)}]_0$) we get

$$-2q - 3 \ln (1 - q) = p \qquad (12)$$

where $p \equiv ([\mathrm{Br(III)}]_0 - [\mathrm{Br(III)}])/K$ and $q \equiv [\mathrm{Br(I)}]/2K$ = fraction of steady state concentration reached by hypobromite after time *t*.[22]

$$\text{As } [\mathrm{Br(I)}] \longrightarrow [\mathrm{Br(I)}]_s,\ q \longrightarrow 1$$

We calculated the values of *p* for $q = 0.90$ and $q = 0.99$.

TABLE I

$[\mathrm{Br(III)}]_0/K$	$(1 - q_\infty)$	Extent of reaction for $q = 0.9$	Extent of reaction for $q = 0.99$
1	0.48	...	..
4	.14	...	..
7.6	.05	0.67	..
10	.02	.51	..
13	7×10^{-3}	.39	0.91
50	3×10^{-8}	.102	.24
58	8×10^{-9}	.088	.21
100	6×10^{-15}	.051	.12

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(17) Similarly, in the decomposition of hypobromite, where the bromite concentration is low, reaction I′ can be shown to be slow in comparison with reaction I.

(18) L. Farkas, B. Perlmutter and O. Schächter, THIS JOURNAL, **71**, 2829 (1949).

(19) S. W. Benson, *J. Chem. Phys.*, **20**, 1605 (1952).

(20) M. Lautout, G. Wyllie and M. Magat, *J. chim. phys.*, **50**, 199 (1953).

(21) The value of [Br$^-$] was treated as constant during each experiment, its average value being used.

(22) Termed *R* in Benson's paper.

The extent of reaction, $([Br(III)]_0 - [Br(III)])/[Br(III)]_0$, is given by $p(K/[Br(III)]_0)$ and was calculated for several values of $[Br(III)]_0/K$. Furthermore, we calculated $(1 - q_\infty)$, *i.e.*, that fraction of the steady state concentration which is not reached when $t = \infty$, for the same values of $[Br(III)]_0/K$.[23] The results are shown in Table I (*cf.* Table III of Benson's paper[19]). Our values of $[Br(III)]_0/K$ lie between 4 (for the highest bromide concentration) and 58 (for low bromide or high initial bromite concentration). An inspection of the table shows, therefore, that the steady-state concentration of hypobromite is practically reached in all the experiments, except that having the highest bromide concentration; for this experiment, expression 10 is not applicable. Furthermore, the steady state is seen to be approached earlier the higher the initial concentration and the lower the bromide concentration, as borne out by our experiments.

We are indebted to Dr. G. Stein for helpful discussion.

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[23] The calculation was based on the assumption that the rate of reaction I can be neglected in comparison with that of reaction I′, even when $[Br(III)] \rightarrow 0$. This assumption is clearly not justified; nevertheless, the values of $(1 - q_\infty)$ can serve to decide to what extent the steady state concentration is approached in a given case.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. III. The Catalyzed Sulfur Exchange between Thionyl Bromide and Sulfur Dioxide[1]

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In sharp contrast to previously reported results on the almost utter absence of isotopic exchange in the systems SO_2–$SOCl_2$ and SO_2–$SOBr_2$ (excess SO_2), it has now been found that the addition of a number of ionic halides to the SO_2–$SOBr_2$ system produces a strong catalysis of the exchange. The catalysis is homogeneous, with exchange rates apparently first order in catalyst concentration and zero order in thionyl bromide concentration. Tetramethylammonium bromide, rubidium bromide, rubidium chloride, cesium bromide, potassium bromide and potassium chloride act as catalysts, although the last two are limited by low solubility. Roughly comparable k values, based on the expression, rate = k(catalyst concn.), are obtained at a given temperature, irrespective of which of the first four catalysts are employed, average values for tetramethylammonium bromide being (1) 5.8×10^{-2} min.$^{-1}$ at 25°, and (2) 6.2×10^{-3} min.$^{-1}$ at 0°; a representative exchange half-time for this catalyst is 80 minutes at 25° (0.163 mmole in 9.9 and 1.24 mmoles each of SO_2 and $SOBr_2$). The reaction is interpreted as involving basic catalysis by halide ions. Pyrex glass powder also shows a weak catalysis (half-time 307 hours at 25°).

In an earlier communication[3] it was reported that, using S^{35} as tracer, neither thionyl chloride nor thionyl bromide, dissolved in liquid sulfur dioxide, showed a significant rate of sulfur exchange. The bromide, at a mole fraction of *ca.* 0.090 gave an exchange half-time of about 1.9 years at 25°. In the same paper were recorded some observations of anomalous exchange effects obtained when potassium bromide (relatively insoluble) was added to thionyl chloride dissolved in sulfur dioxide (thionyl bromide and potassium chloride being obtained by double decomposition). Further investigation has now shown that there is here involved a striking catalysis of the thionyl compound–sulfur dioxide exchange. In this paper we report the results of an investigation of the catalysis by several halide salts of the thionyl bromide–sulfur dioxide exchange.

Experimental

Techniques used were in general similar to those in previous work.[3] Radiosulfur was obtained from the Atomic Energy Commission. All samples were counted as thin layers of barium sulfate under an end window counter, all appropriate corrections being applied.

Preparation of Reactants.—Sulfur dioxide from a cylinder was purified by successive passage through concentrated sulfuric acid and phosphorus pentoxide. Freezing with liquid air and pumping to a high vacuum ensured the absence of permanent gases.

Potassium chloride (Mallinckrodt Analytical Reagent) was pulverized and dried at 140°. The powder was sieved through standard mesh screens, that portion passing a 250 micron, but retained by a 177 micron screen being collected for use.

Potassium bromide (J. T. Baker Reagent) was treated in the same manner as the chloride. **Rubidium and cesium halides** (99% purity, from A. D. Mackay, Inc.) were pulverized and dried at 140° for an hour. **Tetramethylammonium bromide** (Eastman Kodak Co., White Label) was dried at 140° for 20 minutes. **Thionyl bromide** was prepared essentially by the method of Hibbert and Pullman[4] and was fractionally distilled under reduced pressure in an all-glass, ground joint-free system at room temperature. The middle 60% of the distillate was collected in glass tubes, which were sealed off and stored in a refrigerator until ready for use.

Anal. Calcd. for $SOBr_2$: S, 15.42; density expected (25°) 2.672.[5] Found: S, 15.43; density, 2.67 (24°).

Pyrex glass powder was prepared from tubing which had been carefully cleaned with chromic acid cleaning solution, washed with distilled water and dried. Thin glass "balloons," blown from the tubing, were crushed and ground up. The powder so obtained was sieved in the same manner as the potassium bromide and chloride.

Labeled sulfur dioxide was prepared either by the method of Johnson and Huston[6] or, more recently, Masters and Norris.[7]

Labeled thionyl bromide was prepared by a method based on the results of the present work. In a typical preparation 10 millimoles of active sulfur dioxide, 5 millimoles of thionyl

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[2] Taken from the thesis of Rolfe H. Herber, submitted in partial fulfillment of the requirements for the Ph.D. degree, at Oregon State College, September, 1952.

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[4] H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 113.

[5] H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, 2594 (1926).

[6] Rowland E. Johnson and J. L. Huston, THIS JOURNAL, **72**, 1841 (1950).

[7] B. J. Masters and T. H. Norris, *ibid.*, **74**, 2395 (1952).