Daudel,[38] it is evident that 17% L_{II}- and L_{III}-capture is not at all probable here; the inclusion of the data in Table III has been made only for the purposes of comparison.

The L/K-capture ratio is established from this work as being 0.102 ± 0.008 and is in fair agreement with the value of 0.091 calculated from the theoretically-derived formula given by Bouchez, Daudel, Daudel and Muxart.[10] It is, however, significantly different from the results of Brysk and Rose[37] and Hoff and Rasmussen.[39] Further, our experimental results completely verify the use of the Pauli correlation in taking account of the effect of positron–electron correlation, as done recently by Odiot and Daudel[38] in extending the simplified theory of orbital electron-capture previously used. Odiot and Daudel calculated $(L/K)_{true}$ for argon-37 to be equal to 0.100.

2. Occurrence of Double K-Vacancies.—We made two determinations of the occurrence of double K-vacancies. A high-energy "tail" was observed in these spectra, as was also noted by Miskel and Perlman,[20] who showed the peak as occurring over the region of 4.5 to 10 kev. The average result of the two determinations was $(3.7 \pm 0.9) \times 10^{-4}$, which agrees very well with the data of Miskel and Perlman[20,21] and with the theoretical value given by Wolfsberg.[18]

3. Half-life Determinations.—The half-life of argon-37 was determined by integral counting over the region 0.75 to 5.2 kev. The study of the argon-37 decay was continued for seventy days. The results are shown in Fig. 3. From a least squares treatment of the data shown, the half-life is found to be 34.30 ± 0.14 days, the statistics here being given for a 95% confidence level. This result agrees within the quoted errors with the early result of Weimer, Kurbatov and Pool.[5]

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[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE]

The Isotopic Exchange between Hypohalites and Halide Ions. I. The Exchange between Hypobromous Acid and Bromide Ion

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The isotopic exchange of bromine between hypobromite and bromide ions has been studied in concentrated alkaline solutions. The reaction was found to involve a molecule of HOBr and a Br^- ion in the activated complex. The specific rate constant was found as $k = 7.6 \times 10^5$ l. mole^{-1} min.$^{-1}$ at 25°. Contrary to the case of hypobromite–water–oxygen exchange, there is no catalytic effect of chloride ions on the bromine exchange.

Introduction

The reactions of the hypohalous acids and their derivatives with nucleophilic reagents have been studied extensively up to date. The interaction of hypochlorous esters with various anions[1] points to the positive nature of the chlorine in the hypochlorous molecule and suggested the existence of intermediates of the type ACl, wherein chlorine is of a positive character. The study of halogenation of aromatic compounds by hypohalous acids[2] suggested the formation of H_2OX^+ or X^+ as the active species. The reduction of hypochlorous acid by bromide ions[3] provided kinetic information on an irreversible nucleophilic attack on a hypohalous acid; extending this study to hypobromous acid and to iodide ions provided additional information.[4] The last mentioned reactions may be compared to the interaction of hypochlorous with hypobromous acid[5] and with the interaction of hypohalous acids with nitrite ions.[6] The study of the interaction of hypochlorous and hypobromous acids with water by following the rate of oxygen exchange between these species, as well as the catalytic effects of halide ions on this exchange,[6] provided additional basic information on the character of the hypohalite reactions.

The purpose of the present work was to elucidate some points in the halide catalysis of the oxygen exchange reaction and to provide a mechanism for the interaction of hypohalites with the corresponding halide ions. These results will be compared with the reactions of hypohalites with other nucleophilic reagents. In this first paper we shall discuss the hypobromite–bromide reaction. The analogous reactions between hypochlorous acid and chloride ions and between hypochlorous esters and chloride ions will be presented in the following paper.[7]

Experimental

Reagents.—Sodium hypobromite, bromate free, has been prepared by dissolving bromine in ice-cooled 1 molar sodium hydroxide solution, afterwards adding freshly prepared silver oxide, and thereby precipitating the bromide as silver bromide. The silver bromide and the excess of silver oxide were separated by centrifuge as soon as possible. The concentration of the sodium hypobromite solution was determined by reduction with excess of a standardized arsenite solution at *p*H 5, and afterwards the excess arsenite was titrated with a standardized iodine solution. Another aliquot was treated with acid iodide and titrated with a standardized

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[1] M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094 (1954); M. Anbar and D. Ginsburg, *Chem. Revs.*, **54**, 925 (1954).

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[7] M. Anbar, S. Guttmann and R. Rein, *ibid.*, **81**, 1816 (1959).

sodium thiosulfate solution; this gave the total oxidizing capacity of the solution, namely hypobromite plus bromate. The difference between the determinations by the two methods gave the amount of bromate in solution. Bromate concentration in our solutions never exceeded 1% of the total oxidizing power.

TABLE I

$(OBr^-) = 0.01$; $(Br^-) = 0.01$; $(OH^-) = 1.0$

Time, min.	Sp. activity $= A_t$, c./min./ml.	$A_\infty - A_t$	$\log \frac{A_\infty}{A_\infty - A_t}$	p[a]
1	739	9245	0.030	0.069
3	2131	7853	.104	.080
6	3915	6069	.215	.082
9	4608	5376	.267	.068
15	6900	3084	.510	.078
21	7930	2048	.689	.076
	9984			

$p = 0.075 \pm 0.006$;

[a] $p = \frac{2.3}{t} \log \frac{A_\infty}{A_\infty - A_t}$ $t_{1/2} = \frac{0.693}{\bar{p}} = 9.3$ min.

$$R = p\frac{(OBr^-)(Br^-)}{(OBr^-) + (Br^-)};\ R = k'(OBr^-)(Br^-)$$

$$k' = \frac{R}{(OBr^-)(Br^-)} = \frac{p}{(OBr^-) + (Br^-)} = \frac{0.075}{0.02} = 3.75 \pm 0.3 \text{ l. mole}^{-1} \text{ min.}^{1}$$

The hypobromite solutions were further analyzed for bromide content. This time the solution was reduced by addition of hydrogen peroxide in excess and was acidified to *p*H 5. The excess hydrogen peroxide was decomposed by boiling with platinum black. The total bromide was determined by argentometry using an adsorption indicator. The difference between the total bromide concentration and that of the hypobromite gave the bromide concentration. The bromide concentration in the hypobromite stock solutions amounted up to 5%; thus it was necessary to determine the bromide concentration in each reaction mixture separately.

The radioactive bromine, bromine 82, was obtained from Harwell in form of ammonium bromide. This was digested with sodium hydroxide until it was ammonia free and then neutralized and diluted. The specific activity was initially 1 millicurie per gram of sodium bromide, and it was used until the activity dropped to 10 microcuries per gram.

The sodium hydroxide was of analytical grade with no further purification. The hydroxyl content of the reaction mixtures was determined by potentiometric titration with standardized perchloric acid.

The *p*-cresol was purified by distillation under reduced pressure. The reagents for the scintillation solution were of scintillation grade supplied by Tracerlab Company. All other reagents were of analytical grade.

Procedure.—Reaction mixtures containing different concentrations of hypobromite, bromide and hydroxide ions were prepared and diluted to 10 ml. The concentrations of hypobromite, bromide and hydroxide ions were determined for every run by the methods described above. The reaction bottles were placed in a thermostat at 27 ± 0.2° and aliquots of 1 ml. were taken at different intervals. The reaction mixture was added to an equal volume of 0.5% *p*-cresol solution in 1 molar sodium hydroxide, which quenched the reaction. Silver acetate powder then was added and the mixture was shaken to precipitate the bromide ions. The solid silver acetate, silver bromide and oxide were separated by centrifugation. The supernatant solution then was acidified by adding a concentrated acetate buffer and the bromocresol was extracted with 2 ml. of toluene. One ml. of toluene was pipetted off, diluted to 5 ml. and dried over potassium carbonate. An aliquot of this toluene solution was added to a scintillation solution containing 4 g./l. of terphenyl and 0.2 g./l. POPOP in a liquid scintillator vessel. The vessel was measured in a conventional liquid scintillator, using a single channel analyzer to reduce the background. It has been shown that *p*-cresol and its bromo derivatives have no quenching effects on the liquid scintillator in the range of concentrations used in our procedures.

The silver bromide, acetate and oxide mixture was washed with alcohol, and after further centrifugation and drying it was introduced into a sodium iodide well scintillator and its activity was determined. It has been shown that less than 5% of the total activity remained unseparated and could not be measured and accounted for either as *p*-cresol or as silver bromide. Determination of the exchange, both by decrease of the silver bromide activity and by increase in the *p*-bromocresol activity provided a double check on the kinetics. Table I presents a typical run as obtained by following the growth of activity in the bromocresol.

Results and Discussion

The exchange rate has been studied changing the hypobromite concentration ten-fold, the bromide ion concentration fifty-fold and that of hydroxyl ion eight-fold. The results are presented in Table II, each run consists of 4–8 points. The rate coefficients have been calculated by the least mean square method.

TABLE II

THE RATE OF EXCHANGE BETWEEN HYPOBROMITE AND BROMIDE IONS

No.	(OBr^-)	(Br^-)	(OH^-)	$t_{1/2}$, min.	k'[a]	$k'(OH^-) = k''$
1	0.01	0.01	0.5	5.3	6.6	3.3
2	.01	.01	0.5	4.5	7.6	3.8
3	.01	.01	1.0	9.3	3.7	3.7
4	.02	.001	1.0	10.0	3.5	3.5
5	.015	.02	1.5	8.4	2.3	3.5
6	.01	.01	2.0	17.3	1.9	3.8
7	.02	.01	2.0	10.5	2.2	4.4
8	.05	.02	2.0	6.4	1.6	3.2
9	.03	.02	2.0	11.8	1.2	2.4
10	.01	.05	2.0	7.2	1.6	3.2
11	.03	.02	3.0	17.0	1.2	2.4
12	.01	.01	4.0	40.0	1.8	3.6
13	.05	.05	4.0	11.4	1.2	2.4
14	.10	.05	4.0	5.9	1.6	3.2

$k'' = 3.3 \pm 0.6$ min.$^{-1}$

[a] k' is defined in Table I.

It may be seen from Table II that the rate of exchange is directly proportional to hypobromite and to bromide ions concentrations and is inversely proportional to the hydroxyl ion concentration. A mechanism involving hypobromous acid as an active species would show such a dependence on hydroxyl concentrations in the range of *p*H under investigation. The concentration of hypobromous acid may be presented as

$$(HOBr) = 1/K_a(OBr^-)(H^+) = \frac{K_w(OBr^-)}{K_a(OH^-)}$$

where K_a is the dissociation constant of hypobromous acid and K_w the product of (H^+) and (OH^-) in water.

$$R = k''\frac{(BrO^-)(Br^-)}{(OH^-)} = \frac{k''K_a}{K_w}(HOBr)(Br^-) = k(HOBr)(Br^-)$$

Taking the value of 2.4×10^{-9} for K_a at room temperature 25° (*cf.* ref. 6) and 10^{-14} for K_w we obtain for $k = k''K_a/K_w$ the value of $7.6 \pm 1.4 \times 10^5$ l. mole min.$^{-1}$.

Before an attempt is made to postulate a detailed mechanism for the interaction of bromide ion with hypobromous acid, we will compare our results with another study of the reaction of bromide ions with hypobromous acid.[6]

Bromide ion was found to catalyze the rate of oxygen exchange between water and hypobromous acid. Table III presents some results of ref. 6 which did not appear in detail in that paper.

TABLE III

THE CATALYTIC EFFECT OF BROMINE ION ON THE RATE OF OXYGEN EXCHANGE BETWEEN HYPOBROMOUS ACID AND WATER

Run no.	pH	(OBr^-)	(Br^-)	$t_{1/2}$, min.	$k' = \frac{0.693}{t_{1/2}} \frac{1}{(Br^-)(H^+)}$
BA	12.95	0.45	...	27	...
BF	12.95	.45	0.01	7.8	7.9×10^{13}
BG	12.95	.45	.02	4.0	7.7
BH	12.65	.45	.01	4.2	7.4
P	13.60	.13	.01	40	6.9

Mean $\bar{k}' = 7.5 \pm 0.4 \times 10^{13}$ l.^{2} mole^{-2} min.$^{-1}$.

Assuming here again that hypobromous acid is the reactive species we obtain $R = k'(OBr^-)(Br^-)(H^+) = k'K_a(HOBr)(Br^-) = k(HOBr)(Br^-)$ $k = 1.8 \pm 0.1 \times 10^5$ l. mole^{-1} min. In the case of hypobromous acid–water oxygen exchange we find also a large catalytic effect of chloride ion, which is manifested by a rate constant of 5×10^5 l. mole^{-1} min.$^{-1}$ for the (HOBr) (Cl^-) interaction.

Returning to our case of bromide exchange, we have checked the effect of chloride ions; the results appear in Table IV.

TABLE IV

THE EFFECT OF CHLORIDE IONS ON THE RATE OF EXCHANGE OF BROMINE BETWEEN HYPOBROMITE AND BROMINE IONS

No.	($HOBr^-$)	(Br^-)	(HO^-)	(Cl^-)	$t_{1/2}$	k''
13	0.05	0.05	4.0	...	11.4	2.4
15	.05	.05	4.0	0.1	13.6	2.0
16	.08	.04	4.0	0.2	14.7	1.6

We see here a slight retarding effect of chloride ion on the rate of exchange as compared to the large catalytic effect of chloride ion in the oxygen exchange reaction.

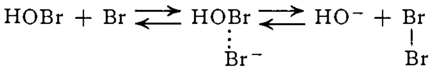
TABLE V

COMPARISON OF THE HALIDE CATALYZED OXYGEN EXCHANGE OF HYPOBROMOUS ACID WITH THE BROMINE EXCHANGE REACTION

	k(HOBr)(Br^-) $\times 10^{-5}$, l. mole^{-1} min.$^{-1}$	Effect of Cl^-
Oxygen exchange	1.8 ± 0.1	*Positive*, stronger than that of Br^-
Bromine exchange	7.6 ± 1.14	Negative

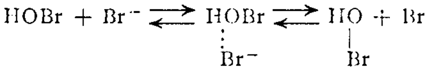
Comparing the results of the two exchange reactions in Table V, we find two reactions involving hypobromous acid and bromide ions with different reaction rate coefficients; this may imply two different mechanisms for these interactions.

A bromide ion may attack the molecule of hypobromous acid in two different ways. (1) It may attack the bromine atom substituting the hydroxyl group



$$\mathrm{HOBr + Br \rightleftharpoons \underset{\underset{Br^-}{\vdots}}{HOBr} \rightleftharpoons HO^- + \underset{\underset{Br}{|}}{Br}} \quad (1)$$

This will result in an exchange of the oxygen of the acid with the solvent simultaneous with a bromine exchange. (2) It may attack the oxygen atom in the acid, substituting the bromine atom of the hypobromous molecule. Consequently the bro-

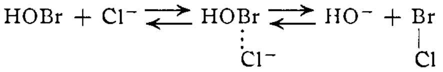


$$\mathrm{HOBr + Br^- \rightleftharpoons \underset{\underset{Br^-}{\vdots}}{HOBr} \rightleftharpoons \underset{\underset{Br}{|}}{HO} + Br^-} \quad (2)$$

mine exchange will not involve an oxygen exchange. As it was stated above, the bromine exchange is faster by a factor of 4 than the oxygen exchange. This result may imply a different mechanism for bromine exchange, namely, mechanism no. 2, where the nucleophilic attack is on the oxygen. Another case in which the oxygen is attacked by a nucleophilic reagent is demonstrated in the HOBr–NO_2^- reaction.[6]

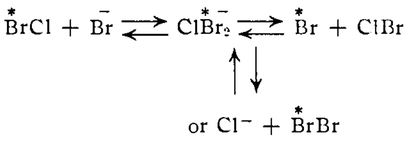
It should be emphasized that the difference in rates of bromine and oxygen exchange is not very large, reaction 2 being only 3 times as fast as reaction 1, as the latter may still contribute 25% of the over-all bromine exchange. This difference may be a result of the difference in experimental conditions in which these two reactions were studied, *e.g.*, ionic strength or temperature. Thus both exchanges may proceed *via* mechanism no. 1.

The positive catalytic effect of chloride ions on the rate of oxygen exchange may be described by reaction 3.



$$\mathrm{HOBr + Cl^- \rightleftharpoons \underset{\underset{Cl^-}{\vdots}}{HOBr} \rightleftharpoons HO^- + \underset{\underset{Cl}{|}}{Br}} \quad (3)$$

The fact that there is no contribution of the Br-Cl formed in reaction 3 to the bromine exchange by reaction 4 is a result of the extremely low sta-



$$\mathrm{\overset{*}{Br}Cl + \overset{-}{Br} \rightleftharpoons Cl\overset{*\,-}{Br_2} \rightleftharpoons \overset{*}{Br} + ClBr} \quad (4a)$$

$$\uparrow\downarrow$$

$$\mathrm{or\ Cl^- + \overset{*}{Br}Br} \quad (4b)$$

tionary concentration of BrCl in the system, which may be calculated[8] for run no. 15 as 6×10^{-13} mole l.$^{-1}$. The rate of Br^-–BrCl interaction should be as high as 10^{13} l. mole^{-1} min.$^{-1}$ in order to contribute to the bromine exchange.[9] Comparing this rate with the upper value of 10^{13} l. mole^{-1} min.$^{-1}$ for the H^+–OH^- interaction,[10] it seems most probable that the Br^-–BrCl reaction would proceed at a lower rate and would thus not contribute to the bromine exchange.

Further implications of these mechanisms as compared to other reactions of the hypohalous acids are presented in the following paper.[7]

REHOVOTH, ISRAEL

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(9) *cf.* R. S. Halford, THIS JOURNAL, **62**, 3233 (1940).

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