lium and magnesium do not interfere. The elements lanthanum cerium, praseodymium, neodymium, erbium, yttrium, thorium, zirconium (and probably hafnium) form more soluble double cesium sulfates or form them much more slowly than aluminum.

The authors are indebted to the Maywood Chemical Works for their kind coöperation in this and other work which will be described later.

NEW YORK, N. Y.

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

AN OXIDE OF IODINE, I_2O_2. AN INTERMEDIATE COMPOUND

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The recent experimental proof by Abel and Hilferding[1] that the reaction between iodate and iodide ions in acid solution, long known as a fifth order reaction,[2] is of the fourth order at a low iodide concentration, has led me to reëxamine the series of investigations of Skrabal[3] on the rate of formation of iodate and iodide from iodine and hydroxide ion. Skrabal presented strong evidence that HI_3O and $I_3O_2^-$ exist as intermediate compounds in this reaction, and that HI_3O is a loose addition compound of iodine and hypoiodous acid. He also pictured $I_3O_2^-$ as a similar compound of iodine and iodite ion. The present analysis has led to the conclusion that $H_2I_2O_3$ and I_2O_2 also exist as intermediate compounds, and that $I_3O_2^-$ is really an addition compound of I_2O_2 and iodide ion.

Skrabal succeeded in demonstrating that the results of his rate measurements could be represented by three rate laws, A, B and C, and postulated the following mechanisms

	Relatively rapid equilibrium	$2IOH + I^- \rightleftharpoons I_3OH + OH^-$	(1a)
A	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3IOH + 3OH^- = 2I^- + IO_3^- + 3H_2O$	
	Relatively rapid equilibrium	$2I_3^- + OH^- \rightleftharpoons I_3OH + 3I^-$	(1b)
B	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	
	Relatively rapid equilibrium	$3I_3^- + 4OH^- \rightleftharpoons I_3O_2^- + 6I^- + 2H_2O$	(3b)
C	Rate-determining step	$I_3O_2^- \longrightarrow$	(4)
	4 + rapid steps	$I_3O_2^- + 2OH^- = IO_3^- + 2I^- + H_2O$	(5)
	Main reaction (Sum)	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	(6)

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[1] Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

[2] (a) Dushman, *J. Phys. Chem.*, **8**, 453 (1904); (b) Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924); (c) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

[3] Skrabal, (a) *Monatsh.*, **32**, 815–903 (1911); (b) *Oesterr. Chem.-Ztg*, No. 11 (1913); (a) is the fifth paper of a series of twelve, 1907–1916, on hypohalous acids and hypophalites, and (b) is a general discussion of the stoichiometric reactions of iodine isolated and studied in his investigations.

A and B have the same rate-determining step, (2), the disappearance of I_3OH in a first order reaction; they show differences in the rate laws, in the equilibria that precede the rate-determining step, and in the main reactions, merely because the initial concentrations of OH^-, HIO, I^-, I_3^- and I_2 differ in the two sets of experiments. C involves another rate-determining step, (4), the disappearance of $I_3O_2^-$, which is also a first order reaction. This reaction, termed by Skrabal the "slow" reaction, was detected in the presence of B; and, by suitable variation of the experimental conditions, was studied as a limiting reaction.

Additional evidence for this mechanism was presented by Skrabal by means of rate measurements in the analogous bromine reactions at low concentrations of hydroxide ion.[4] The results furnish for the existence of HBr_3O a proof similar to that for the existence of HI_3O, and show that there is a second independent reaction resembling, but not identical with, that which involves $I_3O_2^-$. Measurements of the rate of formation of chlorate in solutions which contain hypochlorite and hypochlorous acid[5] have given no indication of the existence of either HCl_3O or $Cl_3O_2^-$. There is thus definite evidence that oxyhalogen compounds containing three halogen atoms per molecule exist as intermediate compounds, and that the tendency of such compounds to form decreases rapidly in the order iodine, bromine and chlorine. It will be recalled that the stability of the complex trihalide ions, as I_3^-, Br_3^- and Cl_3^-, decreases in the same order.

The relation of HI_3O and $I_3O_2^-$ to other substances and to each other are shown by the rapidly reversible reactions: 1a, 1b, 3b and the following

$$\begin{aligned}
2I_2 + OH^- &\rightleftharpoons HI_3O + I^- && \text{(1c)}\\
I_2 + HIO &\rightleftharpoons HI_3O && \text{(1d)}\\
3HIO + OH^- &\rightleftharpoons I_3O_2^- + 2H_2O && \text{(3a)}\\
3I_2 + 4OH^- &\rightleftharpoons I_3O_2^- + 3I^- + 2H_2O && \text{(3c)}\\
HI_3O + HIO + 2OH^- &\rightleftharpoons I_3O_2^- + I^- + 2H_2O && \text{(3d)}
\end{aligned}$$

The valence (or polar number) of iodine in $I_3O_2^-$ is, on the average, the same as in hypoiodous acid, and that in HI_3O is lower. It is thus probable that in the spontaneous first order reactions, (2) and (4), at least one of the three atoms of iodine is changed to a higher, and one to a lower, valence stage than that of hypoiodite iodine.

Under the conditions of Skrabal's experiments there are two, and only two, paths which lead, through HI_3O and $I_3O_2^-$, respectively, to the formation of iodate and iodide. These two paths are to be regarded as independent, even though HI_3O and $I_3O_2^-$ are in equilibrium with each other as shown in 3d. Consideration of the equilibria, 1a–d, 3a–d and the hydrolysis of iodine

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[4] Skrabal and Weberitsch, *Monatsh.*, **36**, 237–256 (1915). This is the tenth paper of the series mentioned in the preceding reference.

[5] (a) Skrabal and Weberitsch, Ref. 4, p. 246; (b) Foerster and Dolch, *Z. Elektrochem.*, **23**, 137 (1917).

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (7)$$

leads to the conclusion that the rate of iodate formation must become extremely small in acid solutions which contain iodide, and this is in qualitative agreement with experimental results.[6] It is also to be expected that this spontaneous formation of iodate and iodide from HI_3O or $I_3O_2^-$ is impossible whenever the concentrations of IO_3^-, I^- and H^+ are high enough to enable these substances to react with each other. In this connection, Skrabal proved that the path from $I_3O_2^-$ to iodate and iodide is closely related to, if not identical with, that of the fifth order reaction[2] between IO_3^-, I^- and H^+; he proved this by calculating correctly[7] the value of the equilibrium constant of Reaction 6 from the rate laws and specific reaction rates of "C" and the fifth order reaction. Skrabal, however, did not outline a mechanism for either of the first order reactions, (4) and (2).

Several investigators had commented on the fact that all iodate–halide reactions in acid solution are of the fifth order, while the bromate and chlorate reactions are of the fourth order, and at least one[8] considered a transition to the lower order probable in the case of the IO_3^-–I^-–H^+ reaction. The recent investigation of Abel and Hilferding[1] has demonstrated that this transition is complete at a sufficiently low concentration of iodide ion, about 10^{-8} molal at 25°. They suggest for the mechanism the rate-determining step

$$HIO_3 + HI \text{ (or } IO_3^- + I^- + 2H^+) \longrightarrow HIO + HIO_2 \qquad (8)$$

followed by the rapid reduction of HIO and HIO_2 to iodine; but they do not refer at all to the mechanism of the fifth order reaction, for which Abel and Stadler[2c] had written the rate-determining step

$$IO_3^- + 2I^- + 2H^+ \longrightarrow (IO_3{\cdot}2I{\cdot}2H)' \longrightarrow 2HIO + IO^- \qquad (9)$$

(where the middle term represents a Brönsted "critical complex"). Abel and Hilferding have thus left open the question as to a connection between the fourth and fifth order reactions.

On considering this question, Dr. Liebhafsky and I have concluded that Reaction 8 cannot be the first step in 9, that complete independence is improbable on account of the similarity and high orders of the two reactions, and that they can be brought into close relationship by assuming as an intermediate compound either $H_2I_2O_3$ or I_2O_2. I have now found this assumption to be consistent with Skrabal's reactions. In the following mechanisms, for reasons which will be explained later, both $H_2I_2O_3$ and I_2O_2 are assumed to exist.

Fourth order reaction at low concentration of iodide.

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[6] (a) Skrabal, Ref. 3b, p. 8; (b) Abel, *Nernst Festschrift*, 1 (1912).

[7] Skrabal, Ref. 3a, pp. 878–881.

[8] Skrabal, Ref. 2b, p. 124 (1924); *Monatsh.*, **36**, 230 (1915).

Relatively rapid equilibrium	$IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3$	(10a)
Rate-determining step	$H_2I_2O_3 \longrightarrow HIO_2 + HIO$	(11)
Main reaction	$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$	(12a)

Fifth order reaction, with excess iodide.

Relatively rapid equilibrium	$IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3 \rightleftharpoons I_2O_2 + H_2O$	(10b)
Rate-determining step	$I_2O_2 + I^- \longrightarrow I_3O_2^-$	(13)
Rapid follow reactions	$I_3O_2^- + 6I^- + 4H^+ = 3I_3^- + 2H_2O$	(14)
Main reaction	$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O$	(12b)

There is thus a "forking"[9] at the $H_2I_2O_3$ stage between a first order reaction (11) and a second order reaction which involves iodide ion (13). The rapid follow reactions, of course, take place in steps, which, in (14), are related to the reverse reactions of Nos. 3a–d. One of these, the reverse of (3a)

$$I_3O_2^- + H^+ + H_2O \longrightarrow 3HIO \qquad (14a)$$

is of especial interest, since it leads to three molecules of hypoiodite, as postulated in Reaction 9. A consideration of these reactions leads to the conclusion that $I_3O_2^-$ is extremely unstable in an acid iodide solution.

The complete correspondence between the two series of reactions, 10b–13–14 and 3b–4–5, shows that, in *this path*, there is only one rate-determining step between iodine and iodate–iodide, and that Equation 4 may be completed by writing it as the reverse of (13). The assumption that these two rates are equal at equilibrium leads *directly* to an expression for the equilibrium constant of Reaction 6, closely related to that verified by Skrabal[7]

$$\frac{(IO_3^-)(I^-)^8}{(I_3^-)^3(OH^-)^6} = \frac{k_C}{3k_5k_w^2} \qquad (15)$$

where

$$-d(I_3^-)/dt = 3d(IO_3^-)/dt = k_C(OH^-)^4(I_3^-)^3/(I^-)^6 \qquad (16)$$
$$-d(IO_3^-)/dt = k_5(IO_3^-)(I^-)^2(H^+)^2, \text{ and } K_w = (H^+)(OH^-)$$

In Skrabal's other path from iodine to iodate–iodide there is a single rate-determining step (2), only at a distance from the final equilibrium; a second independent rate-determining step, presumably the reverse of (10), will manifest itself as equilibrium is approached; and the calculation of the equilibrium constant of Reaction 6 from the kinetic data is obviously impossible. The following reactions are suggested to complete (2), and to represent the subsequent relatively rapid steps in the alkaline solution

(Equation 2)	$HI_3O + H_2O \longrightarrow HIO_2 + 2I^- + 2H^+$	(17)
Rapid follow reactions	$2H^+ + 2OH^- = H_2O$	(17a)
	$I_3^- + OH^- = 2HIO + I^-$	(17b)
	$HIO_2 + HIO = H_2I_2O_3$	(17c)
	$H_2I_2O_3 + 2OH^- = IO_3^- + I^- + 2H_2O$	(17d)

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[9] (a) This term was suggested by Luther; Bray, *Z. physik. Chem.*, **54**, 465 (1906); (b) Skrabal, Ref. 3a, p. 880.

It will be noted that the main reaction (6) is the sum of these reactions and (1b); and that (17c), the reverse of (11), appears as one of the rapid follow reactions. In the reverse case in acid solution, it is doubtful whether the rate-determining step (11) will always be followed by the reverse of (2), since this involves the assumption that HIO_2 cannot be reduced by iodide ion in acid solution by any other path than that through HI_3O. The above mechanism requires the presence of I_3^-, HIO_2 and OH^-, and therefore of I_2 and IO_2^- ion, and is thus at variance with the assumption that $I_3O_2^-$ can be formed rapidly from I_2 and IO_2^-.

It has already been mentioned that Skrabal[4] demonstrated two independent paths in the spontaneous formation of bromate and bromide from bromine in weakly alkaline solution, and concluded for one of them that the decomposition of HBr_3O is the rate-determining step. The reverse reaction between bromate and bromide ions in acid solution is well known to be the fourth order.[10] There is thus a complete analogy with the iodine path through HI_3O, and we may postulate a series of intermediate reactions which corresponds exactly with that presented in the preceding paragraph. The other path requires a more detailed consideration.

Skrabal's rate law[4]

$$-d(Br_3^-)/dt = 3d(BrO_3^-)/dt = k_2(OH^-)^4(Br_3^-)^3/(Br^-)^7 \qquad (18)$$

differs from Equation 16 only in the exponent of the halide term, 7 instead of 6. The rate law for the fourth order reaction is

$$-d(BrO_3^-)/dt = k_4(BrO_3^-)(Br^-)(H^+)^2 \qquad (19)$$

Skrabal demonstrated that the equilibrium constant, K, of the main reaction

$$3Br_3^- + 6OH^- = BrO_3^- + 8Br^- + 3H_2O \qquad (20)$$

can be calculated satisfactorily from an expression equivalent to

$$K = k_2/3k_4K_w^2 \qquad (21)$$

which is identical in form with Equation 15.

This evidence proves as conclusively as is possible that there is only one rate-determining reaction in this path, and that Equations 18 and 19 represent its rates in opposite directions far from equilibrium. The formulas of the bromine compounds involved in this rate-determining reaction are limited to the compositions Br_2O_2 and $H_2Br_2O_3$. We have chosen both of these substances, rather than two isomers of one of them. On this basis the mechanism of Skrabal's reaction, 20, by this path, is as follows

Relatively rapid equilibrium	$3Br_3^- + 4OH^- \rightleftharpoons Br_2O_2 + 7Br^- + H_2O$	(22)
Rate-determining step	$Br_2O_2 + H_2O \longrightarrow H_2Br_2O_3$	(23)
Rapid follow reaction	$H_2Br_2O_3 + 2OH^- = BrO_3^- + Br^- + H_2O$	(24)

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[10] (a) Judson and Walker, *J. Chem. Soc.*, **73**, 410 (1898); (b) Skrabal and Weberitsch, *Monatsh.*, **36**, 211–256 (1915); (c) Skrabal, *Z. Elektrochem.*, **30**, 109–124 (1924); (d) Bray and Davis, THIS JOURNAL, **52**, 1427–1435 (1930).

Similarly, the first stage in the fourth order reaction in acid solution is the relatively rapid equilibrium:

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons H_2Br_2O_3 \qquad (25)$$

which is the reverse of (24) and corresponds exactly with the iodine reaction (10a). The rate-determining step in this path is the reverse of (23); but there is a forking at this stage, and some of the $H_2Br_2O_3$ changes to $HBrO_2 + HBrO$ (*cf.* the preceding paragraph and Reaction 11).

This close relationship with the corresponding iodine reactions is a striking result. The only difference is in the path with the single rate-determining step, and is shown, for example, by the presence of one more halide in Equilibrium 22 than in (3b). It seems justifiable to conclude that the same transitions $X_3O_2^- \overset{\alpha}{-} X_2O_2 \overset{\beta}{-} H_2X_2O_3$ actually occur in both cases. In the bromine reactions the β step (23) is the slower, and $Br_3O_2^-$ may be assumed to be included in (22); while in the iodine reactions the α step (13b) is the slower, and the equilibrium $I_2O_2 + H_2O \rightleftharpoons H_2I_2O_3$ may be assumed to be established relatively rapidly.

The rather complicated argument in favor of the existence of both $H_2I_2O_3$ and I_2O_2 may be restated as follows. Reasons were given for assuming an intermediate step in the fourth order iodate reaction. $H_2I_2O_3$ was chosen because it is directly related to both $HIO_3 + HI$ and $HIO_2 + HIO$. Reasoning by analogy, $H_2Br_2O_3$ was assumed in the exactly similar fourth order bromate reaction. The single rate-determining step in the path between bromate–bromide and bromine was shown to involve a second intermediate compound of similar composition, and Br_2O_2 was chosen. By analogy again, I_2O_2 was concluded to exist in the corresponding path between iodate–iodide and iodine. It is of interest to note that, even if $H_2I_2O_3$ and $H_2Br_2O_3$ are considered to be indefinite critical complexes, the reasoning is unchanged, and I_2O_2 and Br_2O_2 are still to be regarded as definite chemical compounds.

A molecule of I_2O_2 (or Br_2O_2) contains 26 valence electrons, and in the simplest electronic formula corresponding to IOOI or OIIO each of the four atoms has eight electrons associated with it. The formation of an addition compound with I^- or H_2O presents no more difficulty than the formation of I_3^- from I_2 and I^-; in all these cases at least one iodine atom must be associated with more than four pairs of valence electrons. $H_2I_2O_3$ is unsymmetrical, and is more closely related to $H^+ + IO_3^-$ and $H^+ + I^-$ than to HIO_2 and HIO (*cf.* the relative rates of Reactions 10a and 11). $I_3O_2^-$ undoubtedly reacts very rapidly in acid solution with H^+ and H_2O to form 3HIO (*cf.* 14a), and there seems to be no evidence that it is directly related to iodine and iodite ion.

The possibility that I_2O_2 might form an addition compound also with iodine was considered. As a result the following mechanism is suggested for the fifth order iodate reaction which is observed in the presence of tri-iodide[2]

Relatively rapid equilibrium $IO_3^- + I_3^- + 2H^+ \rightleftharpoons I_4O_2 + H_2O$ (26)
Rate-determining step $I_4O_2 + I^- \longrightarrow I_3O_2^- + I_2$ (27)

with rapid follow reactions as in (14). This mechanism is in agreement with the observation of Abel and Hilferding[1] that tri-iodide has no effect on their fourth order reaction (at low iodide concentration); but an additional assumption, that equilibrium in (27) is far to the right, seems necessary in order to explain why Skrabal found no trace of the reverse of (27) in his investigations.[11]

The value of any proposed mechanism must be judged by its usefulness, since a rigid proof is impossible. In the present instance Skrabal's proposals, with the extensions here presented, bring into close relationship the complicated reactions of iodine and of bromine with hydroxide ion and the reverse reactions in acid solution. It is hoped that the suggested or related intermediate compounds will prove useful in future work.

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NOTE

The Atomic Weight of Chlorine. The Solubility of Silver Chloride.—We should like to call attention to the fact that Hönigschmid and Chan,[1] in their recent work on the atomic weight of chlorine, have apparently neglected a rather important correction which affects the calculation of the Cl:AgCl ratio. Regarding the silver chloride lost in nephelometric tests, in determining the Cl:Ag ratio, the writers state: "Unter den Fällungsbedingungen enthält die klare eisgekühlte Analysenlösung bei 0° nur etwa 0.05 mg. AgCl pro Liter. Da für jede Nephelometerprobe etwa 50 cm.^{3}, also in ganzen höchstens 150 cm.^{3}, der Lösung entnommen wurden, konnte der durch die Probenahme bedingte Verlust an AgCl kaum mehr als 0.01 mg. betragen, war also bei der folgenden Wägung des Chlorsilbers zu vernachlässigen."

Direct nephelometric measurements of the solubility of flocculent silver chloride in pure nitric acid show that the value accepted by Hönigschmid and Chan as the solubility of silver chloride at 0° in the saturated analytical liquid *at the end-point* is entirely too low. Such measurements, made in this Laboratory in another connection, have yielded the following data.

Temp., °C.	Molarity of nitric acid	AgCl per liter, g.
0.5	0.00	0.00072
.5	.11	.00090
.5	.24	.00100
.5	.49	.00102
.5	.99	.00105

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[11] *Cf.* Skrabal, Ref. 3a, p. 877.

[1] Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 315 (1927).