## SOME REACTIONS OF INORGANIC IODINE COMPOUNDS

By K. J. MORGAN, B.A., B.Sc.

(BRASENOSE COLLEGE, OXFORD)

To obtain a fuller understanding of the fundamental properties of chemical bonds, as shown by stability and reactivity, the study of the kinetics and mechanism of chemical reactions is of vital importance. The physico-chemical investigation of reactions has in the course of a century yielded much information and from the data so obtained it is possible to deduce evidence for the mechanism of a chemical reaction. However, attempts to do this in the past have frequently been unsuccessful and occasionally even misleading. The reason for this lies in the comparatively recent realisation of the factors which control reactions.[1] Every reaction must be capable of being analysed into a series of steps, simultaneous or not, each of which is simple : the making or breaking of a single bond, transfer of a single charge or atom. The energy conditions for such changes are in the normal state unfavourable. This is usually expressed by saying that an energy barrier exists between the initial and the final state. To overcome this barrier the system must fulfil one or both of two conditions : (a) an abnormal amount of energy must be accumulated by one or more of the reacting molecules ; (b) there must be a suitable arrangement of the molecules. Fulfilment of these conditions results in the lowering of the energy barrier but produces simultaneously a lowering in the entropy of activation. The balance struck between these two factors determines the course of the reaction.

Insufficient is known about the strength of bonds under reaction conditions to enable a complete generalisation of the effect of energy and entropy on the course of a reaction to be formulated. It is, however, possible to establish certain guiding principles of a qualitative nature. Since only in the most exceptional cases will a very large entropy of activation be available to counterbalance a very large energy of activation (and *vice versa*) we may say that reactions involving extremes of entropy and energy are highly improbable. From this it follows that :

(i) Only bimolecular and, very occasionally, termolecular collisions are important. (It may be noted that reactions showing third-order kinetics for the rate-determining step are usually best explained :

$$A + B \rightleftharpoons AB; \quad AB + C \longrightarrow \text{product(s)}$$
$$\text{Rate} \propto [A][B][C]$$
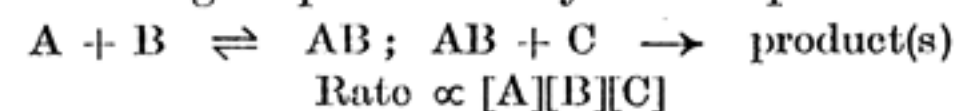
[1] Hinshelwood, *J.*, 1947, 694.

In a true termolecular collision the species AB is regarded as existing only for the duration of the bimolecular collision.)

(ii) Reactions between uncharged molecules, between an uncharged molecule and an ion, or between ions of opposite charge occur preferentially to reactions involving ions of like charge.

(iii) The intermolecular changes are simple and may be classified as (a) internal rearrangements involving electronic shifts; (b) transfer of charge from one molecule to another; (c) transfer of an atom or radical from one molecule to another.

The application of these principles has long been implicit in the discussion of organic reactions, but only to a lesser extent and much more recently have they been applied to inorganic problems. From such discussions it often appears that the formulation of a rational reaction mechanism entails postulating one or more intermediate molecular species. Then confirmatory evidence for a mechanism can be given in two major ways: by the study of the kinetics of the reaction and by obtaining experimental evidence for the presence of the intermediates. Alternatively, if the kinetic evidence will permit only one mechanism, the mechanism itself provides evidence for the existence of the intermediates; or if the presence of sufficient intermediates is shown or inferred we can deduce, from the mechanism, the kinetics of the reaction. Most reactions are sufficiently complicated to make the usual process by which a complete picture is obtained a cumulative one involving both kinetic and mechanistic evidence.

The chemistry of iodine presents an apparently bewildering complexity of reactions of every type. However, intensive investigations during the past half-century, notably by Abel and his collaborators, have achieved such success that an immense store of information is now available. By analysing a selection of the data on the more important reactions it is possible to suggest the structure which must run through them all.

Reactions of Iodine

(1) The Hydrolysis of Iodine.—Iodine is hydrolysed in solution to a small extent to produce hydrogen ions, iodide ions, and hypoiodous acid according to the equation

$$I_2 + H_2O = H^+ + I^- + HIO$$
$$K = [H^+][I^-][HIO]/[I_2] = 3 \times 10^{-13}$$
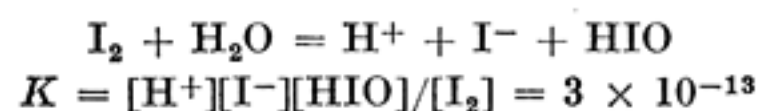
It will be apparent that such a reaction cannot occur by one simple change and so it must be regarded as involving several stages. No kinetic studies of this hydrolysis have been reported; it has been assumed that the speed with which equilibrium is established precludes any adequate investigation, but this view probably requires modification since the corresponding reaction with chlorine has been successfully investigated by the constant-flow method [2] and the results, confirming the deductions of earlier investigators,[3]

[2] Shilov and Solodushenkov, *Doklady Akad. Nauk S.S.S.R.*, 1936, **3**, 15.
[3] Soper and Smith, *J.*, 1926, 1588.

show that the rate of hydrolysis of chlorine is not particularly fast:

$$-d[Cl_2]/dt = k[Cl_2] - k'[HClO][H^+]/[Cl^-]$$
$$k = 7 \times 10^2 \text{ (min.}^{-1}) \text{ (at } 18°)$$

Whether the rate of hydrolysis of iodine is faster or slower than that of chlorine is not immediately obvious.

A considerable body of evidence shows that a probable intermediate, the iodine cation, is capable of existence under the conditions of hydrolysis. Conductivity studies [4] indicate that iodine can dissociate heterolytically, and Finkelstein [5] showed that during the electrolysis of iodine chloride and iodine bromide some of the iodine migrated to the cathode though the concentration of the iodinium ion must be small.[6] The iodination of aromatic compounds has been shown to be due to the action of iodinium ions under most conditions.[7] By replacing hydrogen ions on an ion-exchange resin with iodinium ions obtained from an ethanolic solution of iodine it has been possible to prepare a variety of iodinium salts.[8] Finally, Bell and Gelles [9] have shown on the basis of thermodynamic calculations that, although the value of the equilibrium constant, $K = [I^+][I^-]/[I_2]$, is of the order 10^{-40}, yet the hydrated iodinium ion, H_2OI^+, is considerably more stable: K' ($= [H_2OI^+][I^-]/I_2]$) is approximately 10^{-10}. Using an electrometric method, they were able to confirm this value experimentally; the observed value of K' is $1 \cdot 2 \times 10^{-11}$.

Accordingly, we may write for the hydrolysis of iodine:

$$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^-$$
$$H_2OI^+ \rightleftharpoons HIO + H^+$$
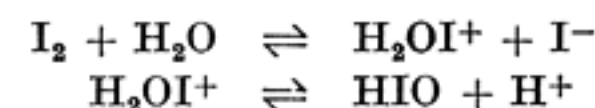
(It may be noted that for hypoiodous acid, HIO, the basic dissociation constant, $K_b = 3 \times 10^{-13}$, is of the same order of magnitude as the acid dissociation constant, $K_a = 4 \cdot 5 \times 10^{-13}$.)[10]

(2) The Oxidation of Formic and Oxalic Acids by Iodine.—Formic acid and oxalic acid are both quantitatively oxidised by iodine with the production of carbon dioxide:

$$I_2 + H \cdot CO_2H = CO_2 + 2I^- + 2H^+$$
$$I_2 + (CO_2H)_2 = 2CO_2 + 2I^- + 2H^+$$
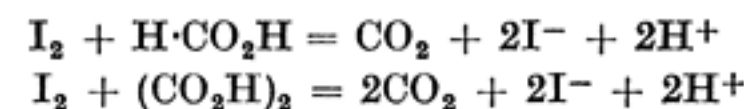
An analogous reaction, the oxidation of oxalic acid by bromine, was shown by Griffith and his collaborators [11] to have, for the rate-determining step, the kinetics

$$-d[Oxalate]/dt = k[HOOC \cdot COO^-][HBrO]$$

and they suggested that the reaction was to be regarded as occurring

[4] Oddo, *Gazzetta*, 1901, **31**, ii, 151.
[5] Finkelstein, *Z. physikal. Chem.*, 1926, **124**, 285.
[6] Noyes, *J. Amer. Chem. Soc.*, 1934, **56**, 1819; Philbrick, *ibid.*, p. 1257; Faull and Baeckström, *ibid.*, 1932, **54**, 620.
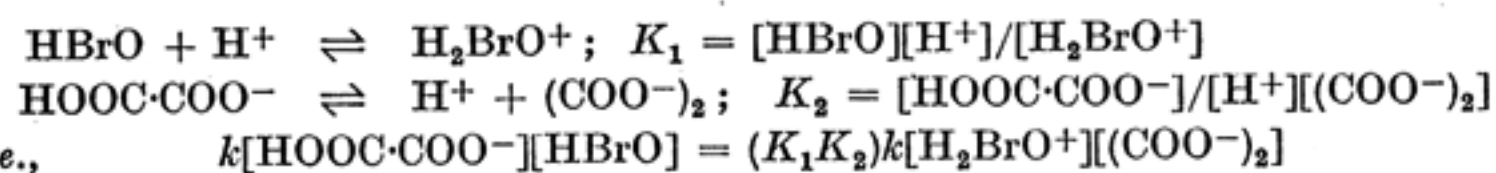[7] Derbyshire and Waters, *J.*, 1950, 564, 3694.
[8] Kikindai and Cassel, *Compt. rend.*, 1951, **232**, 1110.
[9] Bell and Gelles, *J.*, 1951, 2734.   [10] Skrabal, *Ber.*, 1942, **75**, 1570.
[11] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 107.

between the hydrogen oxalate ion and hypobromous acid. An alternative and kinetically equivalent mechanism has been proposed by Hinshelwood [1] which involves the interaction of a positive bromine ion and an oxalate ion :

$$HBrO + H^+ \rightleftharpoons H_2BrO^+; \quad K_1 = [HBrO][H^+]/[H_2BrO^+]$$

$$HOOC \cdot COO^- \rightleftharpoons H^+ + (COO^-)_2; \quad K_2 = [HOOC \cdot COO^-]/[H^+][(COO^-)_2]$$

$$i.e., \quad k[HOOC \cdot COO^-][HBrO] = (K_1K_2)k[H_2BrO^+][(COO^-)_2]$$

The reaction may then be pictured as the withdrawal of electrons from the C–C bond :
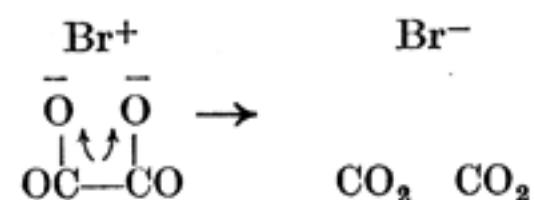
It now seems doubtful whether a concentration of bromine cations sufficient to effect the reaction can exist.[9] A possible solution would appear to lie in the production of the bromine cation *in situ* from hypobromous acid and the proton of the acid oxalate ion :
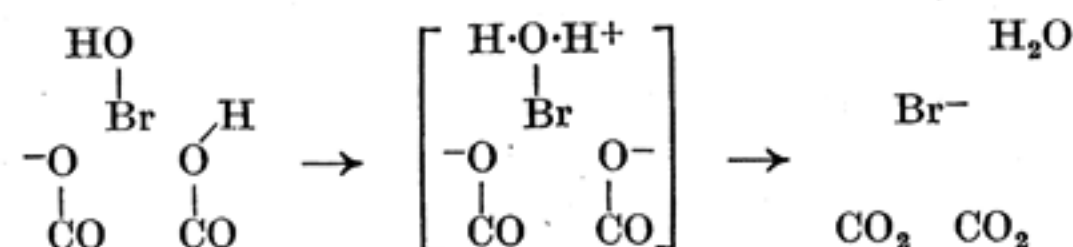

Such a rearrangement is envisaged as occurring during the lifetime of the bimolecular collision and thus does not necessitate the postulation of any other intermediates.

The reaction between iodine and oxalic acid has been shown by Abel *et al.*[12] to involve two reactions. One appears to be identical with the bromine–oxalate reaction, though here the simple Hinshelwood mechanism can apply and it is no longer necessary that the cationic species should be produced in the reaction complex. The other reaction shows kinetics :

$$- d[I_2]/dt = k[(COO^-)_2][I_2]^{\frac{1}{2}}$$

suggesting that the mechanism of this second reaction is [12b, 13]

$$(COO^-)_2 + I \cdot \rightarrow (COO)_2^- + I^-$$
$$(COO)_2^- + I \cdot \rightarrow 2CO_2 + I^-$$
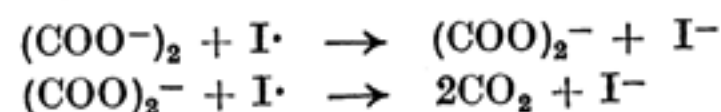
The reaction is found to be photosensitive.[14]

Besides the direct oxidation of oxalic acid by iodine there is a better known reaction, oxidation by iodic acid. This reaction is marked by an induction period during which the rate is very low, followed by a fast reaction which goes rapidly to completion. The reaction is autocatalytic and the rate of the fast reaction is identical with that found for the iodine–

oxalic acid oxidation. Hence it was suggested [12] that it proceeds :

(i) $IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$

(ii) $I_2 + (CO_2H)_2 = 2H^+ + 2I^- + 2CO_2$
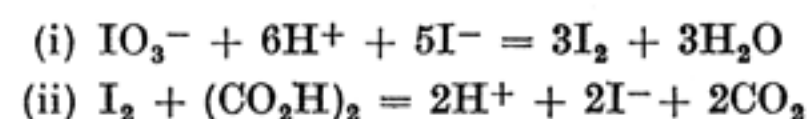
It appears probable that the iodate–iodide reaction generates iodinium ions (see p. 138) and it is likely that these will attack the oxalate directly.

Precisely similar is the reaction between iodine and formic acid. In the presence of excess of iodide ions the reaction is bimolecular,[15] and its kinetics may be written as $v \propto [H \cdot CO_2^-][I_2]/[I^-]$, leading to the mechanism :

$$I_2 + H_2O \rightleftharpoons H_2IO^+ + I^-$$
$$H_2IO^+ + H \cdot CO_2^- \rightarrow H^+ + CO_2 + I^- + H_2O$$
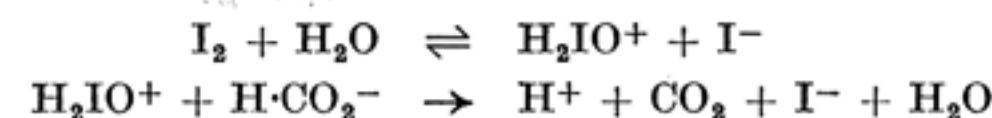
The inhibitory action of iodide ions is supposed to be due to the suppression of the iodine hydrolysis and not, as was originally suggested, to the reversibility of the second stage. The iodic acid oxidation of formic acid is, like the corresponding oxalic acid oxidation, induced by iodine [16] and is probably similar to it in mechanism.

(3) **The Iodine–Thiosulphate and Related Reactions.**—The speed of this reaction, producing tetrathionate and iodide ions, is sufficiently great to render useless the normal methods of following a chemical change. It is, however, not so great that it must be regarded as instantaneous. Two groups of workers have succeeded in overcoming this difficulty ; Griffith and his co-workers,[17, 18] by studying the stoicheiometry of the reaction under a wide variety of conditions, have obtained information about the component reactions ; Awtrey and Connick [19] have applied the constant-flow technique to obtain the kinetics directly. The latter found that, under certain conditions, when the iodine and thiosulphate are mixed the colour of the tri-iodide ion is first removed, only to appear again in the observation tube. Raschig [20] had shown that in the iodine–azide reaction induced by thiosulphate there exists a catalyst whose life under certain conditions can be of the order of minutes. This he suggested is $S_2O_3I^-$. This same intermediate was used by Kolthoff [21] to explain the reappearance of the starch colour near the end of an iodine–thiosulphate titration. Griffith,[17, 18] from his own work, suggests that the reaction occurring here is

$$2S_2O_3I^- \rightarrow S_4O_6^{2-} + I_2$$

The rate of formation of $S_2O_3I^-$ is extremely great and this makes it probable that the reaction is between thiosulphate ions and iodine or iodinium ions rather than tri-iodide ions. Tetrathionate corresponding to one-third to one-half of the thiosulphate is always formed in the initial stage and since, in order to give a colourless solution at the point of mixing, the ratio

[12] (a) Abel, *Z. physikal. Chem.*, 1931, *A*, **154**, 167 ; (b) Abel and Hilferding, *ibid.*, 1935, *A*, **172**, 353 ; (c) Abel, Hilferding, and Smetana, *ibid.*, 1936, *B*, **32**, 85.

[13] Abel, *Sitzungsber. Akad. Wiss. Wien*, 1948, **157**, (2), 178.

[14] Dhar, *J.*, 1923, **123**, 1856 ; Mukerji and Dhar, *J. Indian Chem. Soc.*, 1925, **2**, 277 ; Bhattacharya and Dhar, *ibid.*, 1929, **6**, 451.

[15] Dhar, *J.*, 1917, **111**, 690 ; Hammick and Zvegintzov, *J.*, 1926, 1105.

[16] Abel and Bilderman, *Sitzungsber. Akad. Wiss. Wien*, 1936, **145**, 435.

[17] Griffith and Irving, *Trans. Faraday Soc.*, 1949, **45**, 305.

[18] Dodd and Griffith, *ibid.*, p. 546.

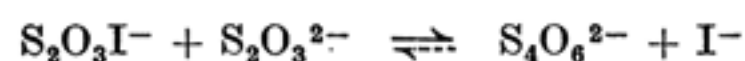[19] Awtrey and Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1341.

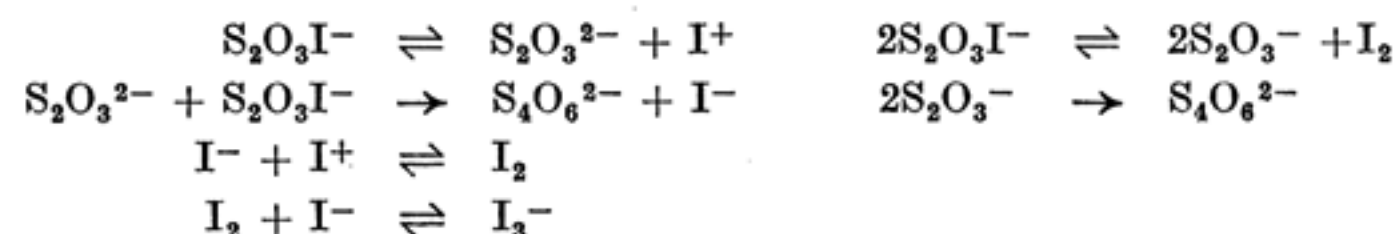[20] Raschig, *Ber.*, 1915, **48**, 2088. [21] Kolthoff, *Z. anal. Chem.*, 1921, **60**, 341.

of thiosulphate to iodine must be greater than unity, a second reaction, a very slowly established equilibrium, is suggested : [19]

$$S_2O_3I^- + S_2O_3{}^{2-} \rightleftharpoons S_4O_6{}^{2-} + I^-$$

The existence of this equilibrium is supported by investigations of the azide–iodine–thiosulphate reaction.[18] The kinetics of the main reaction are [19]

$$-d[I_2]/dt = k_1[S_2O_3I^-]^2[I^-]^2/[I_3^-] + k_2[S_2O_3I^-]^2[I^-]/[I_3^-]$$

corresponding to the mechanisms : [22]

$$S_2O_3I^- \rightleftharpoons S_2O_3{}^{2-} + I^+ \qquad 2S_2O_3I^- \rightleftharpoons 2S_2O_3{}^- + I_2$$
$$S_2O_3{}^{2-} + S_2O_3I^- \rightarrow S_4O_6{}^{2-} + I^- \qquad 2S_2O_3{}^- \rightarrow S_4O_6{}^{2-}$$
$$I^- + I^+ \rightleftharpoons I_2$$
$$I_2 + I^- \rightleftharpoons I_3{}^-$$

The postulation of the coexistence of these two mechanisms is eminently reasonable ; they correspond to the two rational ways of producing tetra-thionate ions and iodine. At very low iodide concentrations some of the iodine oxidises some thiosulphate to sulphate. The rate of this reaction is proportional to $[S_2O_3I^-]$ and possibly to some fractional inverse power of the iodide concentration [19] (the difficulties of investigating this side reaction made the results obtained only approximate). It has been suggested that the analogous ion $S_2O_3N_3{}^-$ can decompose to $N_3{}^-$, SO, and SO_2 [18] or to $N_3{}^-$ and S_2O_3 ; the reaction corresponding to this would be

$$S_2O_3I^- \rightleftharpoons I^- + SO + SO_2 \quad (\text{or } I^- + S_2O_3)$$
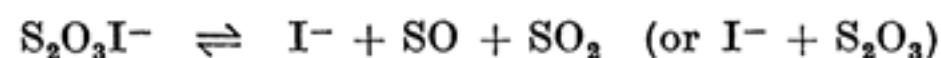
which could be followed by oxidation of the sulphur compounds to sulphate. An alternative course would appear to lie in disturbing the hydrolysis equilibrium of the thiosulphate :

$$S_2O_3I^- \rightleftharpoons S_2O_3{}^{2-} + I^+$$
$$S_2O_3{}^{2-} + H_2O \rightleftharpoons HSO_4{}^- + HS^-$$
$$HS^- \xrightarrow{I^+}$$
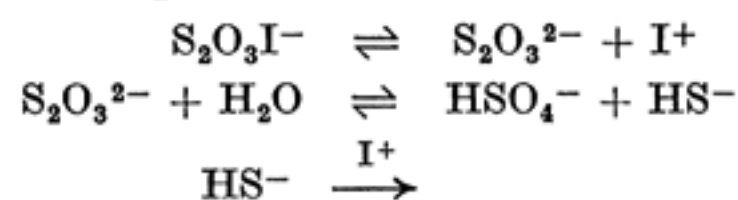
for it has been shown that neutral iodine will very slowly oxidise thiosulphate to sulphate. The kinetics calculated from this mechanism do not correspond to a simple dependence on the $S_2O_3I^-$ ion but show instead that sulphate ions exert a retarding influence. This effect is not reported in the observed kinetics though it might well be masked by the undetermined iodide effect.

The reactions between iodine and nitrite ions [17] and azide ions [18, 23] induced by thiosulphate have been shown to follow a path essentially similar to the iodine–thiosulphate reaction in their earlier stages and the alternative mechanisms suggested by Abel [24, 25] appear to be less probable.
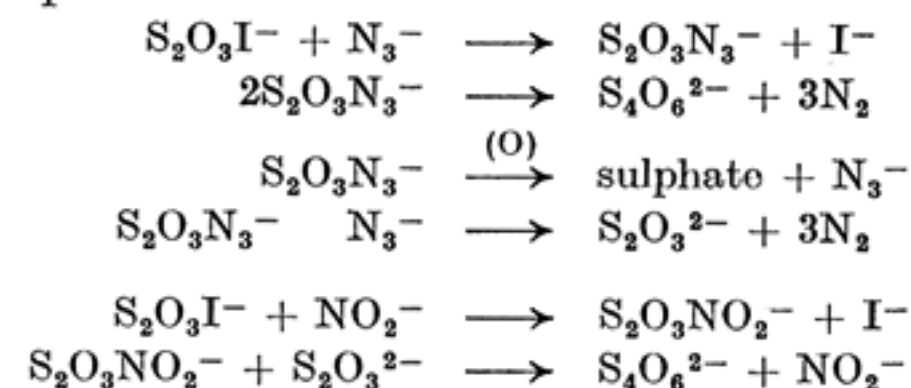
[22] Evans and Baxendale, *Trans. Faraday Soc.*, 1946, **42**, 197.
[23] Hofman-Bang, *Acta Chem. Scand.*, 1949, **3**, 872 ; 1950, **4**, 456, 856, 1005 ; Hofman-Bang and Szybalski, *ibid.*, 1949, **3**, 1418.
[24] Abel, *Z. anorg. Chem.*, 1912, **74**, 395.
[25] Idem, *Sitzungsber. Akad. Wiss. Wien*, 1950, **159**, 346.

The essential steps are :

$$S_2O_3I^- + N_3{}^- \longrightarrow S_2O_3N_3{}^- + I^-$$
$$2S_2O_3N_3{}^- \longrightarrow S_4O_6{}^{2-} + 3N_2$$
$$S_2O_3N_3{}^- \xrightarrow{(O)} \text{sulphate} + N_3{}^-$$
$$S_2O_3N_3{}^- \quad N_3{}^- \longrightarrow S_2O_3{}^{2-} + 3N_2$$
$$S_2O_3I^- + NO_2{}^- \longrightarrow S_2O_3NO_2{}^- + I^-$$
$$S_2O_3NO_2{}^- + S_2O_3{}^{2-} \longrightarrow S_4O_6{}^{2-} + NO_2{}^-$$

Many side reactions occur which cause the complete reaction scheme to be complicated.

Reactions of Iodide Ions

(Several of the better known reactions of iodide ions, notably the iodate–iodide reaction, the periodate–iodide reaction, and the hypoiodite disproportionation reaction are discussed in subsequent sections.)
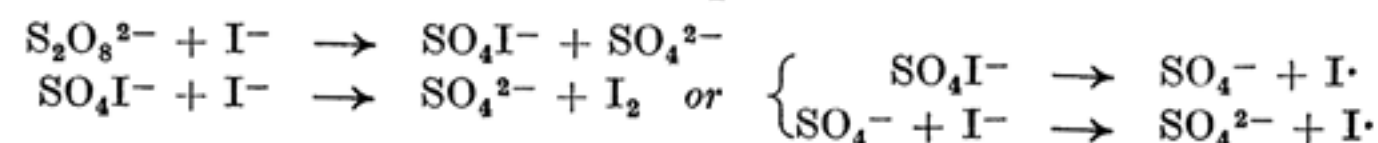
(1) **The Iodide–Persulphate Reaction.**—This reaction resulting in the production of iodine and sulphate ions has second-order kinetics : [26]

$$d[SO_4{}^{2-}]/dt = k[S_2O_8{}^{2-}][I^-]$$

and it has been shown that the rate-determining step does in fact involve the interaction of two such ions since a plot of $\log k$ against $\sqrt{\mu}$, where μ is the ionic strength of the solution, has a slope of $+2$.[27, 28] Brönsted postulated a complex, $S_2O_8I^{3-}$, formed in the rate-determining step, which subsequently reacted with iodide ion.[28] Dhar has shown that the reaction is photosensitive,[29] and recently Kolthoff and Miller [30] have found that the decomposition of persulphate ions in aqueous solution proceeds with fission of the peroxide bond to give $SO_4{}^-$ radical ions ; accordingly it is possible that the reaction is similar to the iodide–hydrogen peroxide reaction (see p. 130) :

$$S_2O_8{}^{2-} \rightarrow 2SO_4{}^-$$
$$SO_4{}^- + I^- \rightarrow SO_4{}^{2-} + I\cdot$$
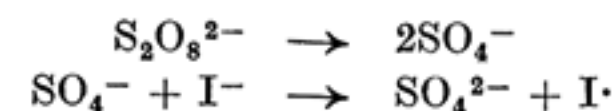
However, it is difficult to reconcile such a mechanism with the kinetic data. A more probable route may be found in the simultaneous attack by the iodide ion and fission of the peroxide bond : [22]

$$S_2O_8{}^{2-} + I^- \rightarrow SO_4I^- + SO_4{}^{2-}$$
$$SO_4I^- + I^- \rightarrow SO_4{}^{2-} + I_2 \quad or \quad \begin{cases} SO_4I^- \rightarrow SO_4{}^- + I\cdot \\ SO_4{}^- + I^- \rightarrow SO_4{}^{2-} + I\cdot \end{cases}$$

The mechanism of the catalytic effect exhibited by a great number of metallic salts is not apparent.

[26] Price, *Z. physikal. Chem.*, 1898, **27**, 474 ; Kiss, *ibid.*, 1928, **134**, 26 ; Jette and King, *J. Amer. Chem. Soc.*, 1929, **51**, 1034.
[27] Kiss and Zombory, *Rec. Trav. chim.*, 1927, **46**, 225 ; Kiss and Bruckner, *Z. physikal. Chem.*, 1927, **129**, 71 ; King and Jacobs, *J. Amer. Chem. Soc.*, 1931, **53**, 1704 ; Knudsen and King, *ibid.*, 1938, **60**, 687.
[28] Brönsted, *Z. physikal. Chem.*, 1922, **102**, 169.
[29] Mukerji and Dhar, *J. Indian Chem. Soc.*, 1925, **2**, 277 ; Bhattacharya and Dhar, *ibid.*, 1929, **6**, 451.
[30] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.

(2) The Iodide–Hydrogen Peroxide Reaction.—The extreme complexity of the reactions between iodine and hydrogen peroxide is largely due to the coexistence of several chemical changes (Table 1). Iodine may be oxidised to hypoiodite and iodate or reduced to iodide; iodide may be

TABLE 1. *Reactions between iodine and hydrogen peroxide* *

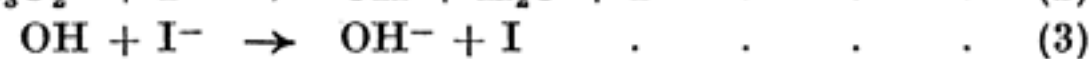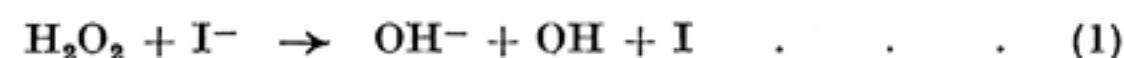| pH	Reaction of H_2O_2 with:			
	I^-	I_2	$I_2 + IO_3^-$	IO_3^-
13	(a) —	(d) $I_2 \rightarrow I^-$ (fast)	(g) $I_2 \rightarrow I^-$ (fast)	(j) —
5	(b) $I^- \rightarrow I_2$	(e) $I_2 \rightarrow I^-$ (moderate)	(h) —	(k) $IO_3^- \rightarrow I_2 + I^-$ (very slow)
1	(c) $I^- \rightarrow I_2$ (faster than e)	(f) —	(i) $I_2 \rightarrow IO_3^-$ (fast)	(l) $IO_3^- \rightarrow I_2$ (faster than k)

* Taken from Bray and Liebhafsky, *J. Amer. Chem. Soc.*, 1931, **53**, 38.

oxidised to hypoiodite or iodine; iodic acid may be reduced to hypoiodite or iodine. Discussion of those reactions involving iodic acid will be deferred to a later section; the remainder comprise the iodide-catalysed decomposition of hydrogen peroxide and will be dealt with here.

The reaction between iodide ions and hydrogen peroxide in acid solution has the distinction of being the first reaction to be successfully investigated kinetically.[31] It is complex;[32] the coexistence of two reactions is indicated by the kinetics:[33]

$$-d[I^-]/dt = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+]$$

The direct formation of hypoiodite and hypoiodous acid respectively as suggested by Bray[34] would not appear compatible with the linear H–O–O–H structure of hydrogen peroxide. An alternative mechanism has been proposed by Weiss.[35] This involves attack on the hydrogen peroxide or the protonated $H_3O_2^+$ (H_2O^+–OH) molecule by iodide ion:

$$H_2O_2 + I^- \rightarrow OH^- + OH + I \quad . \quad . \quad . \quad (1)$$
$$H_3O_2^+ + I^- \rightarrow OH + H_2O + I \quad . \quad . \quad . \quad (2)$$
$$OH + I^- \rightarrow OH^- + I \quad . \quad . \quad . \quad (3)$$
$$2I \rightleftharpoons I_2 \quad . \quad . \quad . \quad . \quad (4)$$

The kinetic expression derived from this scheme is identical with that obtained experimentally.

When the concentration of acid is reduced so that the ion HO_2^- can be present, a second reaction occurs. This is the reduction of iodine to iodide with the simultaneous liberation of oxygen. Weiss[35] has suggested the following mechanism:

$$HO_2^- + I^+ \rightarrow HO_2 + I \quad . \quad . \quad . \quad (5)$$
$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH \quad . \quad . \quad (6)$$
$$I^- + I^+ \rightleftharpoons I_2 \quad . \quad . \quad . \quad . \quad (7)$$

When these two reaction sequences are combined they constitute a system for the catalytic decomposition of hydrogen peroxide. In a brilliant series of investigations Abel[36] succeeded in showing that the kinetics of oxygen evolution could be written:

$$d[O_2]/dt = [I_2][H_2O_2](k + k'/[H^+])/[I^-][H^+]$$

From Weiss's mechanism we get:

$$\frac{d[O_2]}{dt} = \frac{k_7 k_5[I_2][HO_2^-]}{k_7[I^-]} = \frac{k_7 k_5 K[I_2][H_2O_2]}{k_7[I^-][H^+]}$$

This is identical with the first term of the equation determined experimentally. The existence of the second term in Abel's equation shows that the final reaction (6) must involve the ion O_2^- as well as HO_2. It was pointed out by Brode[37] that the rate of oxygen evolution is twice the rate at which iodide is oxidised to iodine in the acid reaction. Weiss's mechanism reflects this:

$$d[I_2]/dt = k_1[H_2O_2][I^-] - \tfrac{1}{2}d[O_2]/dt$$

In neutral solution when the reaction is catalytic $d[I_2]/dt$ is zero and so:

$$d[O_2]/dt = 2k_1[H_2O_2][I^-]$$

It may be noted that further confirmation of this mechanism is found in the fact that both oxygen atoms in the evolved oxygen originate as peroxide.[38]

The iodine–iodide catalytic reaction sets up a steady state the position of which depends on the concentrations of acid, of iodide, and of iodine; with alkaline peroxide all the iodine is converted into iodide. The slow reaction between iodine and hydrogen peroxide in neutral solution is effectively the iodide-catalysed reaction. At concentrations of acid greater than those that permit the iodide catalysis, an induction period is followed by a reaction involving iodate. This is discussed on p. 142.

(3) The Reaction between Ferric and Iodide Ions.—The reduction of ferric ions to ferrous ions by iodide ions was first investigated by Schurakew,[39] who showed that the rate of reaction was proportional to the ferric-ion concentration and to the square of the iodide-ion concentration. Subsequent workers,[40] by keeping the ionic strength of the solution constant,

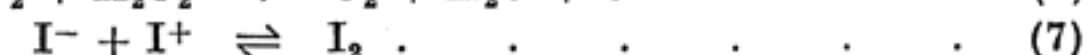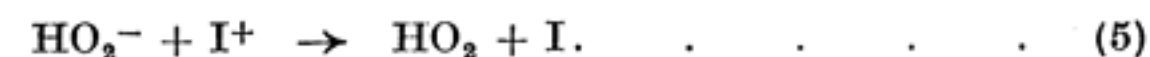[31] Harcourt, *J.*, 1867, **20**, 460; Harcourt and Esson, *Phil. Trans.*, 1867, **157**, 117.

[32] Magnanini, *Gazzetta*, 1891, **21**, 476.

[33] Noyes and Scott, *Z. physikal. Chem.*, 1895, **18**, 118.

[34] Bray, *ibid.*, 1906, **54**, 463.   [35] Weiss, *Ann. Reports*, 1947, **44**, 60.

[36] Abel, *Z. Elektrochem.*, 1908, **14**, 598; *Sitzungsber. Akad. Wiss. Wien*, 1919, **128**, 401; *Z. physikal. Chem.*, 1920, **96**, 1; 1928, **136**, 161.

[37] Brode, *ibid.*, 1904, **49**, 208.

[38] Bunton and Llewellyn, *Research*, 1952, **5**, 142; Cahill and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312; cf. Edwards, *J. Phys. Chem.*, 1952, **56**, 279.
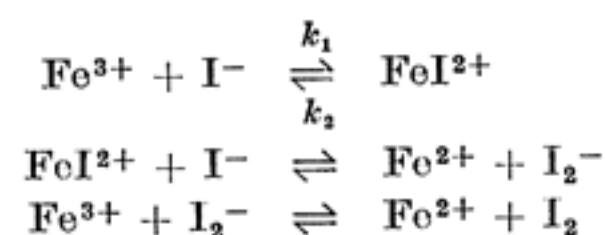
[39] Schurakew, *Z. physikal. Chem.*, 1901, **38**, 353.

[40] Sasaki, *Z. anorg. Chem.*, 1924, **137**, 181, 291; Wagner, *Z. physikal. Chem.*, 1924, **113**, 261.

with excess of chloride ion, showed that the form of the retarding influence exerted by ferrous ion was $1/(1 + k[Fe^{2+}]/[Fe^{3+}])$. However, the work of Rabinowitch and Stockmeyer[41] shows that under such conditions the effective reaction must have been between iodide ions and various ferric chloride complexes. Kiss and Bossanyi[42] investigated the reaction at low salt concentrations but allowed the hydrogen-ion concentration to vary, and it is only recently that an adequate investigation has been reported, namely, that by Fudge and Sykes.[43] They show that the kinetics of the reaction may be written :

$$\frac{d[I_2]}{dt} = \frac{k_1[Fe^{3+}][I^-]^2}{1 + k_2[Fe^{2+}]/[Fe^{3+}]}$$

These authors suggest the following mechanism :

$$Fe^{3+} + I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FeI^{2+}$$
$$FeI^{2+} + I^- \rightleftharpoons Fe^{2+} + I_2^-$$
$$Fe^{3+} + I_2^- \rightleftharpoons Fe^{2+} + I_2$$

using the I_2^- radical originally suggested by Wagner.[40] The only alternative scheme appears to be :

$$Fe^{3+} + I^- \rightleftharpoons FeI^{2+} \qquad\qquad FeI^+ \rightleftharpoons Fe^{2+} + I^-$$
$$FeI^{2+} + I^- \rightleftharpoons FeI^+ + I \qquad FeI^{2+} + I \rightleftharpoons Fe^{2+} + I_2$$

Although the species FeI^{2+} has not been recognised before, the analogous ions $FeCl^{2+}$ and $FeBr^{2+}$ are fully authenticated and have been characterised spectroscopically and the equilibrium constants for their formation have been measured.[41]

Reactions of Hypoiodites

The Disproportionation of Hypoiodite to Iodate.—This reaction has been the subject of many investigations. The first experiments were carried out by Balard[44] on the analogous hypochlorite reaction. The earliest reported study of the iodine system is that of Schönbein,[45] who showed that the reaction between iodine and sodium hydroxide, involving loss of active iodine, is similar to the chlorine and bromine reactions. More precise measurements showed that the rate is proportional to the concentration of iodine, that it is retarded by alkali in excess of that required for the stoicheiometric equation[46]

$$I_2 + OH^- = HIO + I^-$$
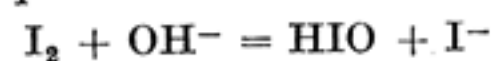
and that the reaction is catalysed by iodide ion.[47, 48] The first kinetic expression was established by Förster[49] to be, in strongly alkaline solution :

$$-d[IO^-]/dt = k[I^-][IO^-][HIO]$$

Then followed the extensive series of papers by Skrabal.[50] For the main reaction he wrote the kinetics :

$$-d[XO^-]/dt = k[HXO]^2[X^-][H^+] \quad (X = I \text{ or } Br)$$

but the evidence for this was subsequently shown to be better interpreted by :

$$-d[BrO^-]/dt = k[HBrO]^2[BrO^-]$$

in the hypobromite reaction.[51] This expression has been suggested by many authors[52] for the hypobromite and hypochlorite reactions ; others have proposed second-order kinetics[51, 53]

$$-d[XO^-]/dt = k[XO^-]^2 \quad \text{or} \quad -d[XO^-]/dt = k[HXO][XO^-]$$

This apparent anomaly was resolved by A. and R. Skrabal,[54] who showed that, as the pH is reduced from strongly to weakly alkaline, the order of the reaction changes from third to second. A similar change of order in the hypoiodite reaction has been reported by Josien and her collaborators ;[55] using silver acetate in iodine solutions to produce hypoiodous acid (via H_2IO^+), they found that the disproportionation was of third order only in buffered solution and was rapidly replaced by a second-order reaction in unbuffered solutions. In agreement with this, Skrabal[50g] had found that at low concentrations of iodide the rate becomes

$$-d[IO^-]/dt = k[IO^-][HIO]$$

Yet even these expressions do not seem sufficient. Although it has been shown that the hypobromite reaction under conditions of low hydroxyl- and bromide-ion concentration is independent of the bromide-ion concentration,[51] yet the decomposition of hypochlorite, like the hypoiodite reaction, appears to be autocatalytic.[56] The most recent determination of the kinetics of the iodine reaction[57] leads to the equation

$$-d[IO^-]/dt = k_1[IO^-]^2 + k_2[IO^-]^2[I^-]/[OH^-]$$
$$k_1 = 2\cdot9 ; \quad k_2 = 109 \text{ (l. mole}^{-1} \text{ min.}^{-1})$$

[41] Rabinowitch and Stockmeyer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.
[42] Kiss and Bossanyi, *Z. anorg. Chem.*, 1930, **191**, 289.
[43] Fudge and Sykes, *J.*, 1952, 119.
[44] Balard, *Ann. Chim. Phys.*, 1834, **57**, 225 ; *Annalen*, 1835, **14**, 167, 298.
[45] Schönbein, *J. pr. Chem.*, 1861, **84**, 384.
[46] Schwicker, *Z. physikal. Chem.*, 1895, **16**, 303.
[47] Lonnes, *Z. anal. Chem.*, 1894, **33**, 409.
[48] Förster and Gyr, *Z. Elektrochem.*, 1903, **9**, 1.

[49] Förster, *J. Phys. Chem.*, 1903, **7**, 640.
[50] Those of special interest are : (a) Skrabal, *Sitzungsber. Akad. Wiss. Wien*, 1907, **116**, 215 ; (b) idem, ibid., 1908, **117**, 827 ; (c) idem, ibid., 1911, **120**, 27 ; (d) idem, ibid., p. 47 ; (e) idem, ibid., p. 609 (review) ; (f) Skrabal and Webertitsch, ibid., 1914, **123**, 1205 ; (g) Skrabal and Hohlbaum, ibid., 1916, **125**, 3 ; (h) Skrabal, *Z. Elektrochem.*, 1934, **40**, 232 (review).
[51] Liebhafsky and Makower, *J. Phys. Chem.*, 1933, **37**, 1037.
[52] E.g. Kretzschmar, *Z. Elektrochem.*, 1904, **10**, 789 ; Kauffman, *Z. angew. Chem.*, 1924, **37**, 364 ; Gallart, *Anal. Fis. Quím.*, 1933, **31**, 422 ; Prutton and Maron, *J. Amer. Chem. Soc.*, 1935, **57**, 1652.
[53] Clarens, *Compt. rend.*, 1913, **157**, 216 ; Förster and Dolch, *Z. Elektrochem.*, 1917, **23**, 137 ; Weiss, *Z. anorg. Chem.*, 1930, **192**, 97 ; Chapin, *J. Amer. Chem. Soc.*, 1934, **56**, 2211 ; Ramsetter and Hantke, *Z. physikal. Chem.*, 1941, A, **189**, 122.
[54] Skrabal and Skrabal, *Sitzungsber. Akad. Wiss. Wien*, 1937, **146**, 697.
[55] Josien, *Compt. rend.*, 1948, **226**, 1607 ; *Bull. Soc. chim.*, 1948, 814 ; *Compt. rend.*, 1949, **228**, 1862 ; Josien and Williams, *Bull. Soc. chim.*, 1949, 551.
[56] Barredo, *Rev. Acad. Cienc. Madrid*, 1941, **35**, 387.
[57] Li and White, *J. Amer. Chem. Soc.*, 1943, **65**, 335.

in highly alkaline solution; the second term is identical with that suggested by Förster.[49]

Thus five distinct kinetic expressions have been proposed for this reaction:

$$\text{(i)} \quad -d[XO^-]/dt = k_1[X^-][XO^-]^2/[OH^-]$$
$$\text{(ii)} \quad -d[XO^-]/dt = k_2[HXO]^2[X^-]/[OH^-]$$
$$\text{(iii)} \quad -d[XO^-]/dt = k_3[HXO]^2[XO^-]$$
$$\text{(iv)} \quad -d[XO^-]/dt = k_4[HXO][XO^-]$$
$$\text{(v)} \quad -d[XO^-]/dt = k_5[XO^-]^2$$

and of these only (ii) seems to be discredited. Skrabal[58] has derived an expression which incorporates all these equations but the complexity of this does not help us to arrive at the operative mechanism which is obviously composite.

Few suggestions for the mechanisms have been made. Skrabal,[50a] noticing that chloroform added to an alkaline solution of iodine gradually became coloured owing to the absorption of iodine, the colour disappearing on shaking, suggested that the reaction
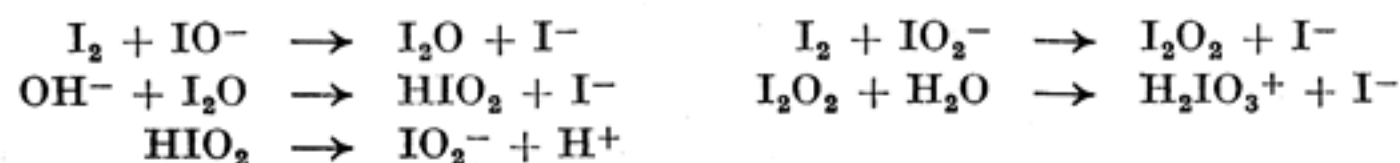
$$2HIO + I^- \rightleftharpoons HI_3O + OH^-$$
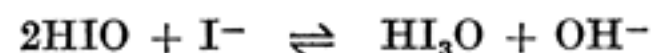
was the rate-determining step; he obtained some evidence for the existence of HI_3O.[59] Since this reaction is shown by the kinetics not to be the rate-determining step, Bray[60] suggested that an analogous ion $I_3O_2^-$, previously postulated by Skrabal,[50e] was the key intermediate:

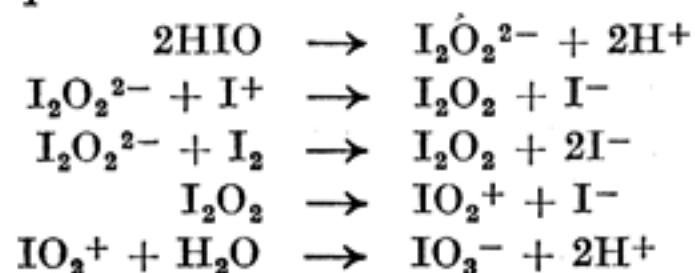$$3HIO + OH^- \rightarrow I_3O_2^- + 2H_2O$$
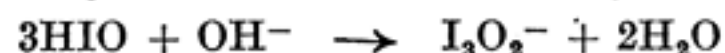
Although as written this reaction is not probable, it may be noted that this ion, $I_3O_2^-$, has recently been suggested as a collisional complex in the iodide–iodate reaction.[61] Li and White[57] suggested an intermediate, $HI_3O_2^-$, formed by the reaction
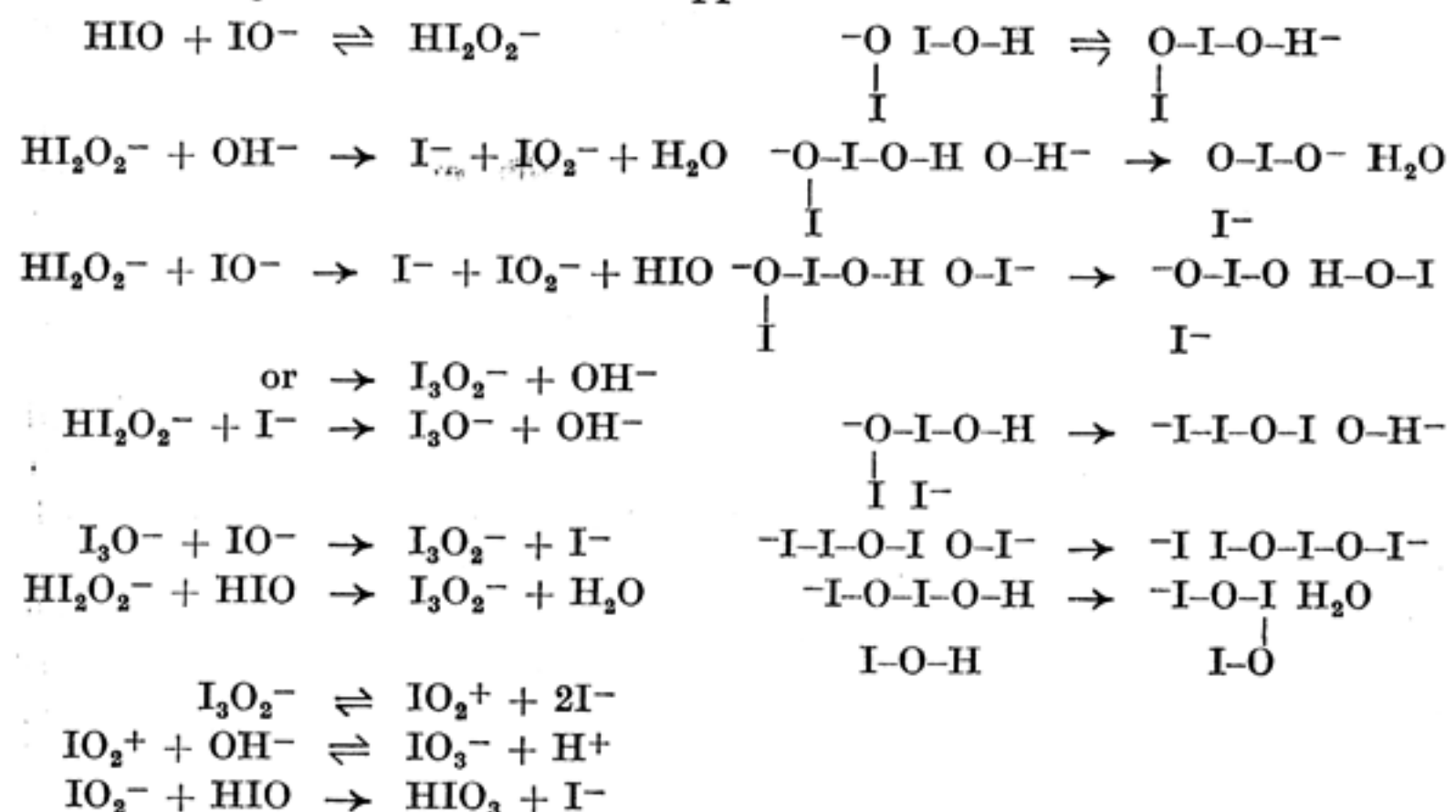
$$2IO^- + I^- + H_2O \rightleftharpoons HO_2I_3^- + OH^-$$
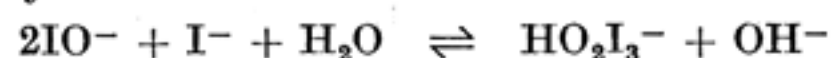
and recently Edwards[62] has suggested an intermediate I_2O:

$$I_2 + IO^- \rightarrow I_2O + I^- \qquad I_2 + IO_2^- \rightarrow I_2O_2 + I^-$$
$$OH^- + I_2O \rightarrow HIO_2 + I^- \qquad I_2O_2 + H_2O \rightarrow H_2IO_3^+ + I^-$$
$$HIO_2 \rightarrow IO_2^- + H^+$$

but this mechanism can only give rise to second-order kinetics. Abel[63] has suggested the sequence:

$$2HIO \rightarrow I_2O_2^{2-} + 2H^+$$
$$I_2O_2^{2-} + I^+ \rightarrow I_2O_2 + I^-$$
$$I_2O_2^{2-} + I_2 \rightarrow I_2O_2 + 2I^-$$
$$I_2O_2 \rightarrow IO_2^+ + I^-$$
$$IO_2^+ + H_2O \rightarrow IO_3^- + 2H^+$$

[58] Skrabal, *Sitzungsber. Akad. Wiss. Wien*, 1938, **147**, 276, 299.
[59] See also Lennsen and Löwenthall, *J. pr. Chem.*, 1862, **86**, 216.
[60] Bray, *J. Amer. Chem. Soc.*, 1930, **52**, 3580.
[61] Morgan, Peard, and Cullis, *J.*, 1951, 1865.
[62] Edwards, *Chem. Reviews*, 1952, **50**, 455.
[63] Abel, *Sitzungsber. Akad. Wiss. Wien*, 1951, **160**, 751, 1028.

and while this as it stands is not fully satisfactory it may be developed to give a comprehensive reaction scheme. From a consideration of the kinetic expressions certain facts emerge. It will be seen that equations (iv) and (v) differ only in the hydrogen-ion term, while equation (iii) contains a second term in HIO in place of the iodide ion term. Accordingly, the following mechanisms would appear feasible:

$$HIO + IO^- \rightleftharpoons HI_2O_2^-$$
$$HI_2O_2^- + OH^- \rightarrow I^- + IO_2^- + H_2O$$
$$HI_2O_2^- + IO^- \rightarrow I^- + IO_2^- + HIO$$
$$\text{or} \rightarrow I_3O_2^- + OH^-$$
$$HI_2O_2^- + I^- \rightarrow I_3O^- + OH^-$$
$$I_3O^- + IO^- \rightarrow I_3O_2^- + I^-$$
$$HI_2O_2^- + HIO \rightarrow I_3O_2^- + H_2O$$
$$I_3O_2^- \rightleftharpoons IO_2^+ + 2I^-$$
$$IO_2^+ + OH^- \rightleftharpoons IO_3^- + H^+$$
$$IO_2^- + HIO \rightarrow HIO_3 + I^-$$

($I_3O_2^-$ is regarded as existing only for the duration of a collision; $HI_2O_2^-$ is supposed to have a longer life). The key intermediate is seen to be $HI_2O_2^-$; this is supposed to be able to react with every other species present, i.e., OH^-, IO^-, I^-, HIO, to give either the transient collision complex, $I_3O_2^-$, or IO_2^- by a simple replacement reaction. Essentially this mechanism is a synthesis of those proposed by Abel, Bray, and Skrabal. It leads directly to the kinetic expressions (i), (iii), (iv), and (v).

Mention may be made of the iodite oxidation state. Its occurrence in this disproportionation reaction is essential and without it the reaction would be incomprehensible. Li and White[57] noted that in the earliest stages of the hypoiodite reaction the rate as shown by titration with phenol was greater than that shown by arsenite titration though the difference soon vanishes. They suggest that this is due to the formation of an intermediate which oxidises arsenite but does not react with phenol; this could well be iodite. Differential analysis of hypoiodite solutions supports this[64] and although iodite salts cannot be prepared there seems little reason to doubt that the ion is capable of formation and existence in solution.

Reactions of Iodates

Before discussing these reactions, some consideration must be given to the mass of conflicting evidence concerning the structure of iodic acid. It would be expected to be, by analogy with chloric acid, a simple, fairly

[64] Josien, *Ann. Chim.*, 1936, **5**, 147; *Compt. rend.*, 1945, **216**, 842.

TABLE 2. *Oxygenated cations*

Group	Typical elements	A Sub-group	B Sub-group	Type found
III		ScO^+; $ScOHSO_4$ LaO^+; $LaONO_3$,aq.		MO^+
IV		TiO^{2+}; $TiOSO_4$,aq. ZrO^{2+}; $ZrOSO_4$,aq. ThO^{2+}; $ThO(NO_3)_2$		MO^{2+}
V	NO^+; $NOHSO_4$ NO_2^+; NO_2ClO_4	VO^{3+}; $VOCl_3$ VO^{2+}; $VOSO_4$ VO^+; $VOCl$ NbO^{3+}; $NbOF_3$ TaO^{3+}; $TaOBr_3$	AsO^+ (?) SbO^+; $K(SbO)C_4H_4O_6$ BiO^+; $BiOCl$	MO^+ MO^{2+} MO^{3+} MO_2^+
VI		MoO_2^{2+}; MoO_2Cl_2 UO^{2+}; $UO(NO_3)_2$ UO_2^{2+}; $UO_2(NO_3)_2$	SeO (?) TeO (?)	MO^{2+} MO_2^{2+}
VII		ReO_2^{2+}; ReO_2F_2	BrO_2^+ (?) IO^+; $(IO)_2SO_4$ IO_2^+; I_2O_5	MO^+ MO_2^+ MO_2^{2+}
VIII		FeO_2^{2+} (?) OsO_2^{2+}; $2KCl,OsO_2Cl_2$ PtO_2^{2+}; PtO_2SO_3,aq. RuO^{2+}; $RuOCl_2,2CsCl$ RhO^{2+}; $RhOBr_2$,aq.		MO^{2+} MO_2^{2+}

pentoxide, are in marked contrast to those of the other halogen oxides except I_2O_4 and I_4O_9 which are known to be ionic, and suggest an ionic structure. This is further supported by magnetic-susceptibility data; the magnetic susceptibility calculated for the structure $IO_2^+IO_3^-$ is:

$$IO^+ + I-O + IO_3^{-\ [86,\ 87]} = (-24.88 - 4.3 - 51.4) \times 10^{-6} = -80.58 \times 10^{-6}$$

for the structure IO_2-O-IO_2 we have:

$$IO^+ + 2I-O + IO_3^- = (-24.88 - 8.6 - 51.4) \times 10^{-6} = -84.88 \times 10^{-6}$$

The experimentally determined value [88] is $(79.4 \pm 0.89) \times 10^{-6}$.

Clearly, it is important that decisive experimental evidence be obtained of the structures that iodic acid can adopt. Work is at present in progress with this end in view.

(1) The Iodide–Iodate Reaction.—This reaction, often called after either Andrews or Dushman, was investigated by the former as an analytical procedure.[89] Early attempts 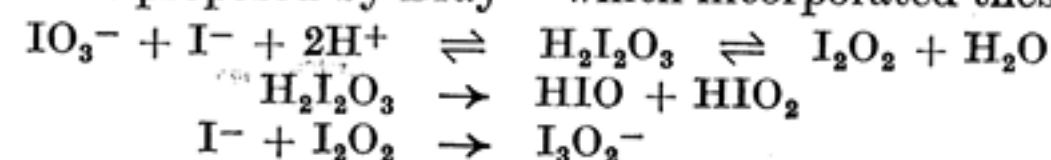to measure the kinetics had failed [90] and the first important kinetic study was carried out by Dushman, who derived the kinetics [91]

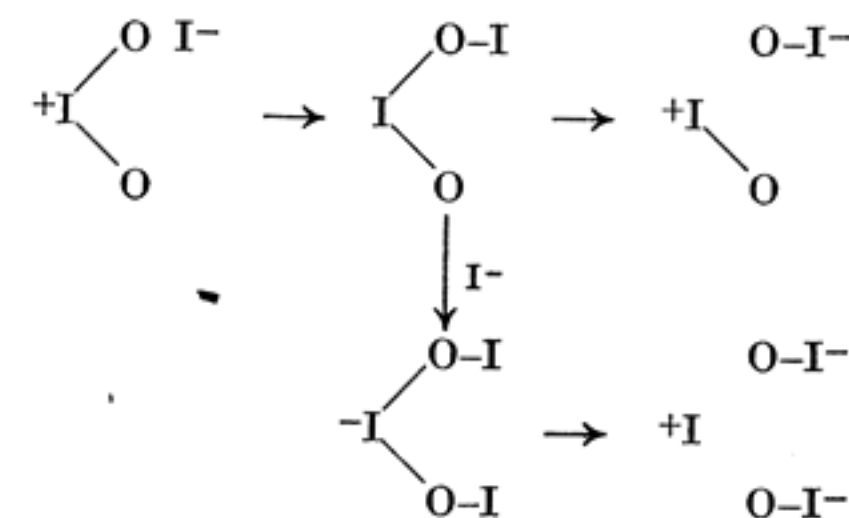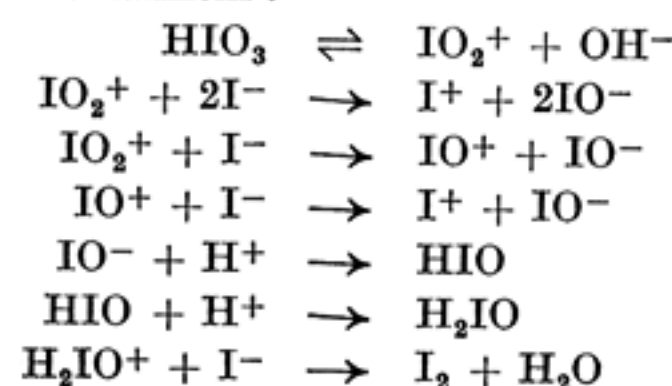$$-\mathrm{d}[IO_3^-]/\mathrm{d}t = k[IO_3^-][I^-]^2[H^+]^2$$

Abel and his collaborators [92] extended the work and showed that in addition to Dushman's expression there is a second term, important at low iodide concentrations ($< 10^{-8}$M):

$$-\mathrm{d}[IO_3^-]/\mathrm{d}t = k[IO_3^-][I^-][H^+]^2$$

A mechanism was proposed by Bray [60] which incorporated these two terms:

$$IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3 \rightleftharpoons I_2O_2 + H_2O$$
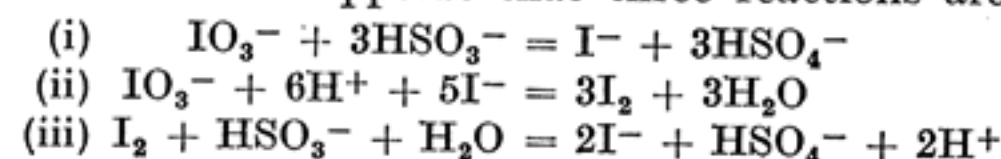$$H_2I_2O_3 \rightarrow HIO + HIO_2$$
$$I^- + I_2O_2 \rightarrow I_3O_2^-$$

(see also Skrabal [50e]). The actual reaction must be simpler than this; Abel suggested that the key lay in the basic dissociation of iodic acid [13, 93] and it has since been shown that from this it is possible to develop a rational mechanism: [61]

$$HIO_3 \rightleftharpoons IO_2^+ + OH^-$$
$$IO_2^+ + 2I^- \rightarrow I^+ + 2IO^-$$
$$IO_2^+ + I^- \rightarrow IO^+ + IO^-$$
$$IO^+ + I^- \rightarrow I^+ + IO^-$$
$$IO^- + H^+ \rightarrow HIO$$
$$HIO + H^+ \rightarrow H_2IO$$
$$H_2IO^+ + I^- \rightarrow I_2 + H_2O$$

A similar mechanism has been suggested by Edwards.[62] This mechanism involves the intermediates suggested by Bray but they are now regarded as existing only for the duration of a collision. These same intermediates have already been met in the hypoiodite disproportionation reaction. (It should perhaps be pointed out that the representation of a reaction as, e.g., $IO^+ + I^- \rightarrow I^+ + IO^-$ does not imply that it is necessarily irreversible but that under such conditions as are operative when a steady state is set up the reversible nature of the reaction is not invoked.)

A reaction bearing some relation to this, the iodine–iodate isotopic exchange reaction, has been shown to be best interpreted as a reaction involving IO_2^+.[84]

(2) The Reaction between Iodic Acid and Sulphurous Acid : Landolt's Reaction.—This reaction, well known as a chemical " clock ", was first investigated in 1885.[94] It appears that three reactions are involved :

$$\text{(i)} \quad IO_3^- + 3HSO_3^- = I^- + 3HSO_4^-$$
$$\text{(ii)} \quad IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$$
$$\text{(iii)} \quad I_2 + HSO_3^- + H_2O = 2I^- + HSO_4^- + 2H^+$$

[86] Trew, *Trans. Faraday Soc.*, 1941, **37**, 476.
[87] Wilmarth and Dharmatti, *J. Amer. Chem. Soc.*, 1950, **72**, 5789.
[88] Gray and Farquharson, *Phil. Mag.*, 1930, **10**, 191.
[89] Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756.
[90] Burchard, *Z. physikal. Chem.*, 1888, **2**, 796; Judson and Walker, *J.*, 1898, **73**, 410.

[91] Dushman, *J. Phys. Chem.*, 1904, **8**, 453.
[92] Abel and Stadler, *Z. physikal. Chem.*, 1926, **122**, 49; Abel and Hilferding, *ibid.*, 1928, **136**, 186; Abel, *ibid.*, 1931, *A*, **154**, 167.
[93] Abel, *Helv. Chim. Acta*, 1950, **33**, 785.
[94] Landolt, *Ber.*, 1886, **19**, 1317; 1887, **20**, 745.

The last is well known as the basis for Karl Fischer's method for the determination of moisture.[95]

Reaction (i) is the sum of reactions (ii) and (iii) and so, until the appearance of free iodine, the net reaction is represented by equation (i). The iodide–iodate reaction may be suppressed by keeping the concentration of iodide ions very low, e.g., by adding a silver salt. Under such conditions the kinetics have been studied; although the first investigations [96, 97] suggested that the rate was proportional to the first power of the hydrogen-ion concentration, Skrabal [98] found the results were better interpreted as:

$$- d[IO_3^-]/dt = k_1[IO_3^-][SO_3^{2-}][H^+]^2 + k_2[IO_3^-][HSO_3^-][H^+]$$
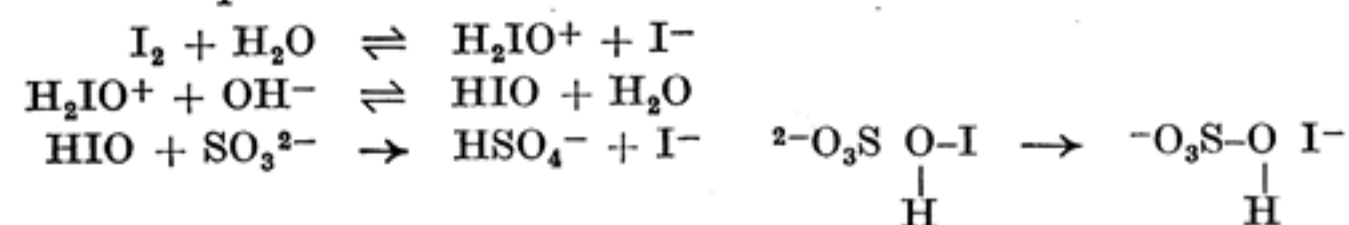$$k_1 = 10^{17} \text{ mole}^{-3} \text{ l.}^3 \text{ min.}^{-1}; \quad k_2 = 10^6 \text{ mole}^{-2} \text{ l.}^2 \text{ min.}^{-1}$$

At hydrogen-ion concentrations greater than 10^{-5} the fast SO_3^{2-} reaction is of negligible importance, and if to a solution of this acidity additional iodide ion is added the time for the end-point to be reached is [96]

$$t = k[SO_3^{2-}]/[IO_3^-][I^-]^2[H^+]^2$$

(SO_3^{2-} should here be taken as implying total "sulphite" concentration rather than the concentration of sulphite ions) where the denominator is composed of the terms found in the kinetic expression for the iodide–iodate reaction. The two reactions (i) and (ii) will accordingly be competitive. Under normal conditions equation (ii) will represent the main route, but it needs only a change in the hydrogen-ion concentration or in the specific rates of the two reactions to make (i) the important change. Replacement of iodate ions by chlorate ions effectively alters the specific rate; it is known that the halogenate reactions with chlorine are slower than the corresponding iodine reactions [97, 98] and it has been shown, by using ^{18}O-labelled chlorate, that direct oxygen transfer from chlorate to sulphite provides the path for the reaction under these conditions [99] (see p. 141).

Reaction (iii) has been assumed to be instantaneous on the grounds that iodine does not appear until all the sulphite is consumed. It seems more reasonable to suppose that it is not iodine but some precursor which is the effective oxidising agent. The isolated reaction between iodine and sulphite ions is very susceptible to changes of pH, the reaction being catalysed by hydroxyl ions.[100] This immediately suggests that hypoiodite is the active species:

$$I_2 + H_2O \rightleftharpoons H_2IO^+ + I^-$$
$$H_2IO^+ + OH^- \rightleftharpoons HIO + H_2O$$
$$HIO + SO_3^{2-} \rightarrow HSO_4^- + I^-$$

$$^{2-}O_3S{-}O{-}I \rightarrow {}^-O_3S{-}O{-}I$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad |$$
$$\quad\quad\quad H \quad\quad\quad\quad\quad H$$

The mechanism of the direct oxidation has been discussed by Abel,[101]

[95] Bunsen, Annalen, 1853, 86, 265; Fischer, Angew. Chem., 1935, 48, 394.
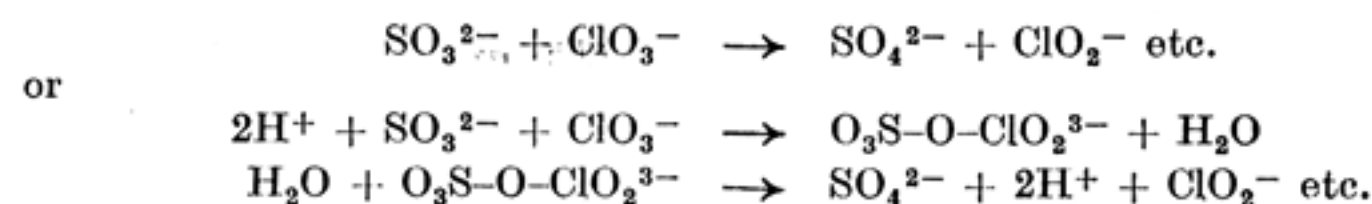[96] Skrabal, Z. Elektrochem., 1922, 28, 224.
[97] Idem, ibid., 1924, 30, 109.
[98] Skrabal and Zahorka, ibid., 1927, 33, 42.
[99] Halperin and Taube, J. Amer. Chem. Soc., 1950, 72, 3319.
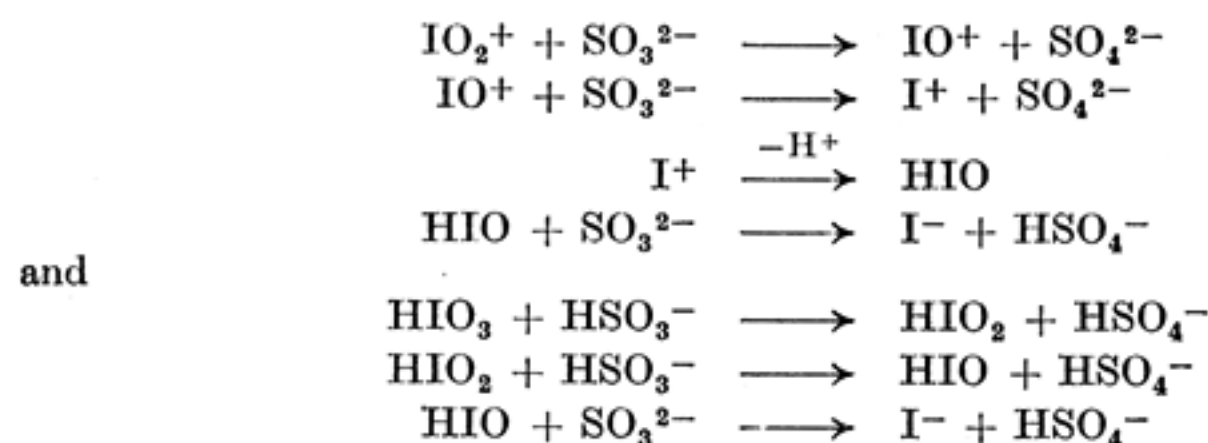[100] Thiel and Meyer, Z. anorg. Chem., 1924, 137, 125.
[101] Abel, Sitzungsber. Akad. Wiss. Wien, 1950, 159, 1029.

who suggests that the reaction proceeds through charge exchange between IO_2^+, IO^+, I^+, and SO_3^{2-} to give IO_2^-, IO^-, I^-, and SO_3. In an investigation of the corresponding reaction between chlorate and sulphite ions, Halperin and Taube [99] showed, by using oxygen-labelled chlorate, that direct oxygen transfer from chlorate to sulphite does occur (though the data also indicate a side reaction in which some labelled oxygen is lost). Assuming that the reduction of chlorate is stepwise, they suggest as a possible mechanism: [102]

or

$$SO_3^{2-} + ClO_3^- \rightarrow SO_4^{2-} + ClO_2^- \text{ etc.}$$

$$2H^+ + SO_3^{2-} + ClO_3^- \rightarrow O_3S{-}O{-}ClO_2^{3-} + H_2O$$
$$H_2O + O_3S{-}O{-}ClO_2^{3-} \rightarrow SO_4^{2-} + 2H^+ + ClO_2^- \text{ etc.}$$

It seems probable that the reaction between iodate ions and sulphite ions will be similar to the chlorate reaction. If this is so, a possible mechanism which conforms to the kinetic limitations is:

and

$$IO_2^+ + SO_3^{2-} \longrightarrow IO^+ + SO_4^{2-}$$
$$IO^+ + SO_3^{2-} \longrightarrow I^+ + SO_4^{2-}$$
$$I^+ \xrightarrow{-H^+} HIO$$
$$HIO + SO_3^{2-} \longrightarrow I^- + HSO_4^-$$

$$HIO_3 + HSO_3^- \longrightarrow HIO_2 + HSO_4^-$$
$$HIO_2 + HSO_3^- \longrightarrow HIO + HSO_4^-$$
$$HIO + SO_3^{2-} \longrightarrow I^- + HSO_4^-$$

(this suggests that the SO_3^{2-} reaction is strictly analogous to the fourth-order iodide–iodate reaction).

(3) **The Reactions between Iodic Acid and Hydrogen Peroxide.**—The reactions occurring in hydrogen peroxide solutions leading to the production or decomposition of iodic acid are as complex as those occurring in solutions containing the iodide–iodine system (see Table 1). Unfortunately, the literature is neither so comprehensive nor so conclusive here as it is for the reactions described earlier. Essentially two reactions are involved in this system: the decomposition of iodate yielding iodine and oxygen:

$$5H_2O_2 + 2HIO_3 = 5O_2 + I_2 + 6H_2O$$

and the oxidation of iodine to iodate:

$$5H_2O_2 + I_2 = 2HIO_3 + 4H_2O$$
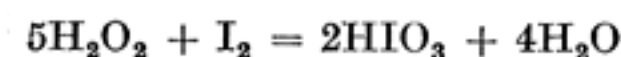
producing no oxygen (though the secondary reaction, the iodine–iodide catalytic reaction which is set up and is of importance, does). These reactions are mutually inductive and under normal working conditions combine to give another catalytic decomposition of hydrogen peroxide. However, factors other than the mere balancing of these two reactions seem to be involved in the catalysis, for the rate of evolution of oxygen is found to be a periodic function.

The reduction of iodate to iodine by hydrogen peroxide was demonstrated

[102] Halperin and Taube, J. Amer. Chem. Soc., 1952, 74, 375.

by Auger[103] and first investigated as an isolated reaction by Liebhafsky.[104] The latter extracted the iodine as it was formed into chloroform and thus prevented the reverse reaction. The kinetics derived by this procedure are:

$$-d[IO_3^-]/dt = k_1[H_2O_2][IO_3^-] + k_2[H_2O_2][IO_3^-][H^+]$$
$$k_1 = 2.6 \times 10^{-4} \text{ (l. mole}^{-1} \text{ min.}^{-1}); \quad k_2 = 1.29 \times 10^{-2} \text{ (l.}^2 \text{ mole}^{-2} \text{ min.}^{-1})$$

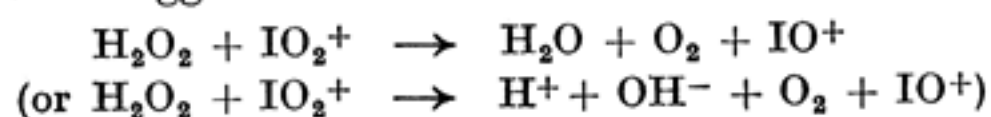Recently, however, from a study of the catalytic reaction, Peard and Cullis[105] derived the rate expression:

$$-d[IO_3^-]/dt = k_3[H_2O_2][IO_3^-][H^+]^2$$

There is no reason to suppose that the iodate–peroxide reaction which exists as part of the catalytic decomposition is different from the isolated reaction and so it appears that three parallel courses are open to this reaction. An explanation of the failure of the two sets of workers to obtain terms in common may be found in the different hydrogen-ion concentrations at which they worked. Peard and Cullis used acid solutions approximately 0.09N and their results are too imprecise to allow an accurate evaluation of the order with respect to hydrogen ion to be made, though from their data an apparent order of 2 seems possible; Liebhafsky used solutions whose acid strength ranged from 0.007 to 0.7N but it is noteworthy that the experimental values for $d[I_2]/dt$ obtained by him lie on a smooth curve only below an acid strength of 0.07N and it is possible that above this concentration the rate of the reverse reaction becomes sufficiently great to invalidate the extraction procedure.
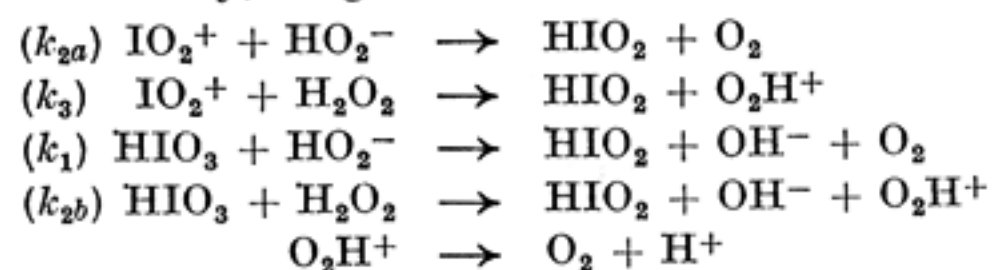
It is highly probable that the three parallel reactions will be closely related mechanistically, and some clue to the route followed would be given by identifying an intermediate common to all three. Abel[106] suggested that the obvious route lies through the ion IO_2^+ reacting with O_2^{2-}, HO_2^-, and (presumably) hydrogen peroxide itself:

e.g.
$$IO_2^+ + HO_2^- \rightarrow IO_2 + HO_2$$
$$IO_2 + HO_2 \rightarrow IO_2^- + O_2 + H^+ \text{ etc.}$$
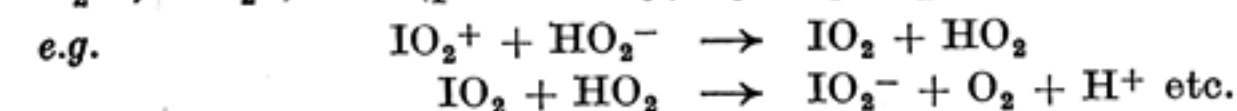
Peard and Cullis suggest a similar scheme:

$$H_2O_2 + IO_2^+ \rightarrow H_2O + O_2 + IO^+$$
$$(\text{or } H_2O_2 + IO_2^+ \rightarrow H^+ + OH^- + O_2 + IO^+)$$

These two mechanisms may be combined, together with that suggested originally by Liebhafsky, to give a unified scheme:

$$(k_{2a}) \quad IO_2^+ + HO_2^- \rightarrow HIO_2 + O_2$$
$$(k_3) \quad IO_2^+ + H_2O_2 \rightarrow HIO_2 + O_2H^+$$
$$(k_1) \quad HIO_3 + HO_2^- \rightarrow HIO_2 + OH^- + O_2$$
$$(k_{2b}) \quad HIO_3 + H_2O_2 \rightarrow HIO_2 + OH^- + O_2H^+$$
$$O_2H^+ \rightarrow O_2 + H^+$$

The iodous acid may then ionise to IO^+ and by a similar series of reactions

[103] Auger, *Compt. rend.*, 1911, **153**, 1005.
[104] Liebhafsky, *J. Amer. Chem. Soc.*, 1931, **53**, 896.
[105] Peard and Cullis, *Trans. Faraday Soc.*, 1951, **47**, 616.
[106] Abel, *Sitzungsber. Akad. Wiss. Wien*, 1948, **157**, (2), 178.

produce hypoiodous acid which can then react to give iodine with iodide ions or to set up the iodine–iodide catalytic decomposition system. The driving force for these reactions is provided by the formation of oxygen.

About the formation of iodic acid from iodine by the action of hydrogen peroxide little is known. It was first studied by Skrabal,[107] and the stoicheiometry investigated by Auger.[103] The reaction shows an induction period which is shortened by the addition of acid and reduced to negligible proportions if iodate ion is added.[108] Bray and Caulkins[109] give the kinetics as

$$-d[I_2]/dt = k[I_2]$$

for concentrations of iodine of 1×10^{-3} to 3×10^{-4}; this expression was rewritten by Liebhafsky[108] as:

$$-d[I_2]/dt = k_1[I_2] - k_2[H^+][I^-][HIO]$$

indicating that the hydrolysis of iodine is the first step; this accounts for the action of iodate ion. The mechanism of the reaction remains obscure. Liebhafsky suggests that it is an intermediate in the iodide–iodate reaction that is oxidised; Abel[106] suggests a chain of reactions:

$$I^+ + H_2O_2 \rightarrow I^{2+} + OH + OH^-$$
$$I^{2+} + OH \rightarrow I^{3+} + OH^-$$
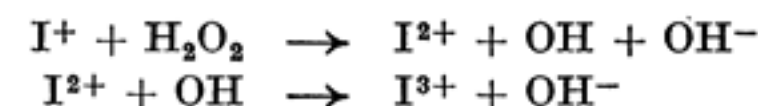
but neither of these conforms to the reported kinetic expression; it is indeed difficult to visualise any mechanism that can lead to such kinetics.

Unless special precautions are observed, the reaction found to occur in solutions of hydrogen peroxide containing iodate ions and iodine will be the catalytic production of oxygen. It was Bray[110] who noted that between hydrogen-ion concentrations of 0.073 and 0.0916N the evolution of oxygen is periodic. A more recent study[105] has confirmed this, giving the limiting hydrogen-ion concentrations as 0.074 and 0.113N and showing that in addition the concentrations of iodine and iodate ion are important. The explanation of this periodicity appears to lie in two factors. Besides the catalytic decomposition given by the iodine–iodate–iodine sequence, iodine causes the decomposition of hydrogen peroxide through the iodine–iodide system and so, as the reaction proceeds, building up the concentration of iodine, the rate of evolution of oxygen increases. When this has reached a sufficiently high value iodine is, for a short time, carried out of the solution by the oxygen (at 60°, the usual reaction temperature, iodine is appreciably volatile) faster than it is formed. This decreases the concentration of iodine and hence the rate of evolution of oxygen. It is the repetition of this process that gives the reaction its periodic nature.

Reactions of Periodates

Investigations involving periodates are fogged by a lack of precise information about the molecules which may be present in solutions of

[107] Skrabal, *Chem.-Ztg.*, 1905, **29**, 554.
[108] Leibhafsky, *J. Amer. Chem. Soc.*, 1931, **53**, 2074.
[109] Bray and Caulkins, *ibid.*, p. 44.   [110] Bray, *ibid.*, 1921, **43**, 1262.

periodic acid and periodates. Although alkali-metal salts MIO_4 are known and analogy with perchloric acid would suggest the formula HIO_4 for the free acid, there are many indications that this is not so and that periodic acid is instead to be regarded as analogous to telluric acid, H_6TeO_6.[111] The acid corresponding to the formula HIO_4 is obtained only with difficulty,[112, 113] the normal crystalline solid being H_5IO_6. Heating this gives ozone,[114] but cautious treatment leads to a solid, $H_4I_2O_9$;[115] no indication of the existence of H_3IO_5 is obtained.[113] In solution periodic acid behaves as a polybasic acid:[113, 116]

$$K_1 = 2\cdot30 \times 10^{-2}; \quad K_2 = 4\cdot35 \times 10^{-9}; \quad K = 1\cdot05 \times 10^{-15} \text{ [117]}$$

and although it is usually thought that H_5IO_6 is the only periodic acid capable of existing in equilibrium with an aqueous solution and it has been shown that equilibria such as

$$2H_3IO_6{}^{2-} \rightleftharpoons I_2O_9{}^{4-} + 3H_2O$$
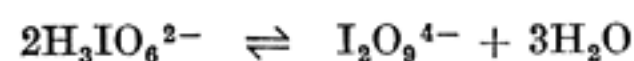
do not occur since the solutions obey Beer's law,[117] yet it is reported that $H_4I_2O_9$ may be titrated and behaves as a dibasic acid.[115] The several magnetic studies [118] of periodic acid(s) and periodates do not elucidate the problem; indeed, the results suggest that periodic acid both as solid and in solution is to be represented as $HIO_4, 2H_2O$.[119] Finally, a recent solubility study indicates a transition point at $29\cdot5°$ showing the presence of two forms of the acid possibly differing in water content.[120]

With this evidence it is clearly impossible to arrive at any conclusions concerning the nature of the solutions. It is equally impossible to place any degree of confidence in mechanisms proposed for the reactions of periodates.

(1) **The Periodate–Iodide Reaction.**—This reaction was investigated by Müller [121] and later by Abel and his collaborators,[122] who showed that the kinetics are:

$$- d[IO_4{}^-]/dt = k_1[IO_4{}^-][I^-] + k_2[IO_4{}^-][I^-][H^+]^2$$

[111] Rosenheim and Löwenthal, *Kolloid Z.*, 1919, **25**, 53.

[112] Lamb, *Amer. Chem. J.*, 1902, **27**, 134.

[113] Partington and Bahl, *J.*, 1934, 1086, 1088.

[114] Rammelsberg, *Ber.*, 1868, **1**, 70.

[115] See, *e.g.*, Rippan and Duca, *Anal. Acad. Rep. Populare Romane*, Sect. Stiinte Mat., Fiz. Chim., 1949, Ser. A2, Mem. 11; *Chem. Abs.*, 1951, **45**, 7906.

[116] Ostwald, *J. pr. Chem.*, 1885, **32**, 300; Dubrisay, *Compt. rend.*, 1913, **157**, 1150; Malaprade, *Ann. Chim.*, 1929, **11**, 104; Rae, *J.*, 1931, 876; Hill, *J. Amer. Chem. Soc.*, 1943, **65**, 1564.

[117] Crouthamel, Meek, Martin, and Banks, *ibid.*, 1949, **71**, 3031.

[118] *E.g.*, Sahney, Aggarwal, and Singh, *J. Indian Chem. Soc.*, 1946, **23**, 177; 1947, **24**, 193.
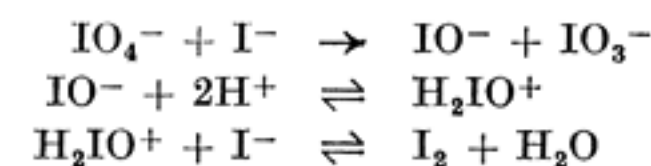
[119] Aggarwal and Singh, *ibid.*, 1945, **22**, 158.
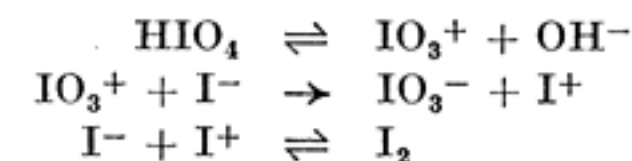
[120] Gyani and Gyani, *ibid.*, 1949, **26**, 239.

[121] Müller and Friedberger, *Ber.*, 1902, **35**, 2652; Müller and Vogelin, *Z. anal. Chem.*, 1913, **52**, 755.

[122] Abel, *Rec. Trav. chim.*, 1922, **41**, 610; Abel and Fürth, *Z. physikal. Chem.*, 1923, **107**, 313; Abel and Siebenschein, *ibid.*, 1927, **130**, 631.

Abel suggests that the mechanism is:

$$IO_4{}^- + I^- \rightarrow IO^- + IO_3{}^-$$
$$IO^- + 2H^+ \rightleftharpoons H_2IO^+$$
$$H_2IO^+ + I^- \rightleftharpoons I_2 + H_2O$$

and [13]

$$HIO_4 \rightleftharpoons IO_3{}^+ + OH^-$$
$$IO_3{}^+ + I^- \rightarrow IO_3{}^- + I^+$$
$$I^- + I^+ \rightleftharpoons I_2$$

(2) **Other Reactions of Periodates.**—The reaction with arsenites has been studied and may be represented as [123]

$$- d[IO_4{}^-]/dt = k[IO_4{}^-][AsO_2{}^-]$$

and the catalytic effect of iodide ions is supposed to be due to the hypoiodite oxidation of arsenite.

The reaction between periodates and hydrogen peroxide [103] is extremely complicated.[124] The rate is proportional to $[IO_4{}^-][H_2O_2]$; it shows an induction period and is autocatalytic.

The periodate oxidation of α-glycols is dependent on the concentration of periodate and of glycol and on an undetermined power of the hydrogen-ion concentration.[125] Again, a mechanism cannot be specified.

Conclusions

The reactions discussed above are some of those of the greatest importance in iodine chemistry. There are in addition many reactions of considerable interest, if not of equivalent importance. To attempt to discuss them in detail would be neither possible nor profitable, for investigation of many of them has been restricted to a qualitative examination or a preliminary quantitative determination. It is possible to suggest suitable reaction routes for many of these, but such mechanisms are of course far more tentative even than those suggested above. Although we now appear to be in a position to say that a reaction can proceed by one or more of several routes, we are still far from being able to decide, merely by consideration of reagent and conditions, the path a given reaction will follow.

In many cases we can extend discussions of the reactions of iodine compounds to include the reactions of the corresponding bromine and chlorine compounds. Throughout this Review little stress has been placed on the relationship of iodine to the other halogens, but an examination of the literature shows that there is, in general, extreme similarity between the kinetics of the three halogens. However, much caution must be exercised in pursuing this relationship. The results of Bell and Gelles [9] show that, while the participation of iodine cations in reactions is possible, the similar action of cations derived from bromine and chlorine is highly improbable. Yet this does not necessarily mean that the mechanisms are fundamentally different. The concept of the ion pair enables us to visualise

[123] Abel and Fürth, *Z. physikal. Chem.*, 1923, **107**, 305.

[124] Abel (and Ziffer), *Sitzungsber. Akad. Wiss. Wien*, 1949, **158**, 585.

[125] See, *e.g.*, Price and Knell, *J. Amer. Chem. Soc.*, 1942, **64**, 552.

a kinetically equivalent process which does not involve the free cation. Such a view can be extended, not only to other intermediates containing chlorine and bromine in place of iodine, but also to some of the iodine intermediates themselves if it is found that a belief in their separate existence is no longer tenable. One then adopts the view that the highly unstable intermediate exists only for the duration of a collision.