## 410. *The Mechanism of the Iodate–Iodide Reaction.*

By K. J. Morgan, M. G. Peard, and C. F. Cullis.

The mechanism of the reaction, $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$, is considered. A reaction scheme is devised, involving the basic dissociation of iodic acid, which yields a kinetic rate expression in agreement with that found experimentally.

The interaction of iodates and iodides in acid solution is one of the best known and most widely used iodometric reactions. The first comprehensive kinetic study was carried out by Dushman (*J. Physical Chem.*, 1904, **8**, 453) who found that the reaction was of the fifth order. The work was extended by Abel (Abel and Stadler, *Z. physikal. Chem.*, 1926, **122**, *A*, 49; Abel and Hilferding, *ibid.*, 1928, **136**, *A*, 186; Abel, *ibid.*, 1931, **154**, *A*, 167), who showed that, although at high iodide concentrations ($>10^{-4}$M.) the kinetic equation is of the form found by Dushman:

$$-d[IO_3^-]/dt = k[IO_3^-][I^-]^2[H^+]^2$$

at low iodide concentrations ($<10^{-8}$M.) it becomes:

$$-d[IO_3^-]/dt = k'[IO_3^-][I^-][H^+]^2$$

Abel suggests that under the latter conditions the initial reaction is:

$$IO_3^- + I^- + 2H^+ \longrightarrow HOI + HIO_2$$

followed by a series of relatively rapid stages; while under the former conditions the rate determining step is believed to be:

$$IO_3^- + 2I^- + 2H^+ \longrightarrow 2HOI + IO^-$$

According to Bray and Liebhafsky (*J. Amer. Chem. Soc.*, 1930, **52**, 3580) the initial reaction is in all circumstances the formation of the compound $H_2I_2O_3$ (or of its anhydride $I_2O_2$), which may either decompose or react with further iodide, the former process predominating at low iodide concentrations:

Rapid equilibrium $\quad IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3 \rightleftharpoons I_2O_2 + H_2O$

followed by either $\quad H_2I_2O_3 \xrightarrow{\text{slow}} HOI + HIO_2$

or $\quad I_2O_2 + I^- \xrightarrow{\text{slow}} I_3O_2^-$

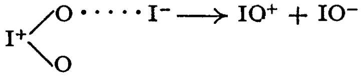
It is becoming apparent that complex reactions can be regarded as the resultants of series of stages, each of which involves a change of a comparatively simple nature (compare Hinshelwood, *J.*, 1947, 694). In this paper an attempt is made to interpret the kinetic data for the iodate-iodide reaction in terms only of steps with a low entropy of activation. The reactions occurring are confined to those in which (i) a single chemical bond is formed or destroyed, the process being accompanied by a redistribution of charge throughout the molecules or ions concerned and (ii) an atom or a charge is transferred from one molecule or ion to another.

The only likely initiating processes in the present case would thus appear to be interactions between: (*a*) $IO_3^-$ and $I^-$, (*b*) $HIO_3$ and $I^-$, and (*c*) $H^+$ and $IO_3^-$. Apart from the fact that (*a*), which involves ions of like charge, is less probable than (*b*) or (*c*), a neutral solution containing iodate and iodide would, if interaction occurred, be expected to exhibit isotopic exchange. There is evidence, however, that such exchange does not occur (Polessitsky, *Compt. rend. U.R.S.S.*, 1939, **24**, 540; Daudel, *Compt. rend.*, 1944, **219**, 129), and this fact renders (*a*) improbable. With regard to (*b*), the dissociation constant of iodic acid is not large ($K_a = 0{\cdot}1686$; Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476), so that in solutions of moderate acidity an appreciable concentration of $HIO_3$ should exist. Nevertheless, it has not been found possible, on the basis of an initial interaction of iodic acid with iodide, to construct a mechanism which will satisfy the observed kinetics.

Finally, therefore, case (*c*), involving interaction of $H^+$ and $IO_3^-$, must be considered as a possible initiating process. The basic dissociation of iodic acid:

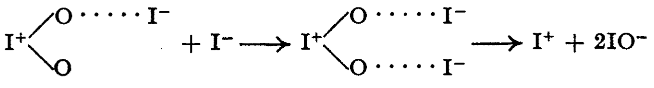
$$H^+ + IO_3^- \rightleftharpoons HIO_3 \rightleftharpoons IO_2^+ + OH^-$$

has recently been postulated to account for the observed kinetics of two reactions of this compound, its exchange with iodine (Myers and Kennedy, *J. Amer. Chem. Soc.*, 1950, **72**, 897), and its interaction with hydrogen peroxide (Peard and Cullis, *Trans. Faraday Soc.*, 1951, **47**, 616). It is here suggested that the ion $IO_2^+$, formed as above, can react with $I^-$ to give a complex: $IO_2^+ \cdots\cdots I^-$ (*A*) which can either decompose:



(*A*)

or react with further iodide:



(*A*) (*B*)

The latter fate of (*A*) is favoured under conditions of high iodide concentration. On the basis of the foregoing, the following reaction scheme may be developed, path (1) involving the reaction of (*A*) with further iodide followed by rapid decomposition of (*B*), and path (2) involving the decomposition of (*A*):

$$H^+ + IO_3^- \overset{K}{\rightleftharpoons} IO_2^+ + OH^-$$

(1)

$$\begin{aligned}
&IO_2^+ + 2I^- \xrightarrow{k_1} I^+ + 2IO^-\\
&2(IO^- + H^+ \xrightarrow{k_2} I^+ + OH^-)\\
&3(I^+ + I^- \xrightarrow{k_3} I_2)\\
&3(OH^- + H^+ \xrightarrow{k_4} H_2O)
\end{aligned}$$

(2)

$$\begin{aligned}
&IO_2^+ + I^- \xrightarrow{k_5} IO^+ + IO^-\\
&IO^+ + I^- \xrightarrow{k_6} I^+ + IO^-\\
&2(IO^- + H^+ \xrightarrow{k_2} I^+ + OH^-)\\
&3(I^+ + I^- \xrightarrow{k_3} I_2)\\
&3(OH^- + H^+ \xrightarrow{k_4} H_2O)
\end{aligned}$$

(It should be pointed out that the representation of a reaction as, *e.g.*, $IO^+ + I^- \xrightarrow{k_6} I^+ + IO^-$ does not imply that it is necessarily irreversible, but that, under conditions where a steady state is set up, the reversible nature of the reaction is not involved.)

Reaction by either path results in the observed stoicheiometric change. On application of the steady-state method to (1), it is found that:

$$\begin{aligned}-d[IO_3^-]/dt = 3d[I_2]/dt &= 3\,k_3[I^+][I^-] \\ &= \frac{3}{2}\,k_1[IO_2^+][I^-]^2 \\ &= \frac{3}{2}\frac{k_1K}{K_w}[IO_3^-][I^-]^2[H^+]^2\end{aligned}$$

since $$[IO_2^+] = K[H^+][IO_3^-]/[OH^-] = K[H^+]^2[IO_3^-]/K_w$$

Similarly for (2),

$$-d[IO_3^-]/dt = 3k_5[IO_2^+][I^-] = 3\frac{k_5K}{K_w}[IO_3^-][I^-][H^+]^2$$

Thus the total rate of reaction is given by an expression of the form:

$$-d[IO_3^-]/dt = k[IO_3^-][I^-]^2[H^+]^2 + k'[IO_3^-][I^-][H^+]^2$$

which is identical with that found experimentally. At high iodide concentrations, the mean life of the complex, $IO_2^+ \cdots\cdots I^-$, is sufficient to enable it to react with further iodide, so that the first term in the rate expression predominates, and the order with respect to $[I^-]$ is approximately two. As the iodide concentration is reduced, the possibility of decomposition of the complex increases, so that the second term in the rate expression becomes appreciable, and in solutions of very low iodide concentration the order with respect to $[I^-]$ tends to a limiting value of one, as Abel and Hilferding (*loc. cit.*) found.

In view of the lack of direct evidence for the basic dissociation of iodic acid, the purely kinetic agreement cannot be regarded as conclusive support for the mechanism outlined. It is significant, however, that the assumption of the initial formation of the species $IO_2^+$, followed by a series of reactions of the simplest nature only, can account for the kinetic features of three different reactions of iodic acid, namely, its interactions with iodides, iodine, and hydrogen peroxide.

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