25. *The Reaction between Ferric and Iodide Ions. Part I. Kinetics and Mechanism.*

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Previous work on the kinetics of the reaction between ferric and iodide ions has been carried out either at varying ionic strength or in the presence of a high concentration of chloride at which ferric ions are largely converted into various ferric–chloride complexes. Considerable uncertainty arises in the interpretation of such results.

Measurements have now been made at constant ionic strength and with the ferric ion present in its simple hydrated form without appreciable complex formation. The main features of the dependence of the rate of reaction on the various concentrations may be represented by the expression

$$\text{Rate} = \frac{k_1[\text{Fe}^{3+}][\text{I}^-]^2}{1 + k_2[\text{Fe}^{2+}]/[\text{Fe}^{3+}]}$$

It is concluded that the reaction probably occurs through the intermediates FeI^{2+} and I_2^- according to the following sequence of simple stages: $\text{Fe}^{3+} + \text{I}^- = \text{FeI}^{2+}$, $\text{FeI}^{2+} + \text{I}^- = \text{Fe}^{2+} + \text{I}_2^-$, $\text{Fe}^{3+} + \text{I}_2^- = \text{Fe}^{2+} + \text{I}_2$.

THE oxidation of ferric ions by iodide ions,

$$\text{Fe}^{3+} + \text{I}^- = \text{Fe}^{2+} + \tfrac{1}{2}\text{I}_2 \quad \ldots\ldots\ldots \quad (1)$$

presents two main features of fundamental kinetic interest. The simplicity of the stoicheiometric equation suggests that this system might well afford a favourable opportunity of determining the detailed mechanism of an electron-transfer reaction. In view of the tendency of ferric ions to associate and to form complexes with a wide variety of anions, there is also the possibility of investigating the influence of such factors. Although the reaction has been studied on a number of occasions during the last fifty years, neither of these fundamental aspects has yet been fully explored.

The first kinetic measurements were made by Schurakew (*Z. physikal. Chem.*, 1901, **38**, 353), who concluded that the reaction was of the first order with respect to ferric ion and of the second order with respect to iodide ion. There is always some uncertainty, however, about any investigation of a reaction involving multivalent ions which was carried out before the necessity of controlling the ionic strength was appreciated. Sasaki (*Z. anorg. Chem.*, 1924, **137**, 181, 291) studied the reaction extensively in the presence of 2M-sodium chloride. More recent work on the composition of solutions containing ferric and chloride ions (Rabinowitch and Stockmeyer, *J. Amer. Chem. Soc.*, 1942, **64**, 335) shows that in Sasaki's experiments the iodide ion must have been reacting predominantly with various ferric–chloride complexes rather than with the simple ferric ion. Under those conditions the reaction was found to be of the first order with respect to ferric, of between the first and second order with respect to iodide, and to be retarded by ferrous ion. Wagner (*Z. physikal. Chem.*, 1924, **113**, 261), who also worked in the presence of excess of chloride (1·5M-KCl), agreed with Sasaki that the retardation by ferrous ion should be represented by writing the denominator of the rate expression in the form $1 + k[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$. This he explained in terms of competition between ferric and ferrous ions for reaction with I_2^- :

$$\text{I}_2^- + \text{Fe}^{3+} = \text{Fe}^{2+} + \text{I}_2 \quad \ldots\ldots\ldots \quad (2)$$

$$\text{I}_2^- + \text{Fe}^{2+} = \text{Fe}^{3+} + 2\text{I}^- \quad \ldots\ldots\ldots \quad (3)$$

Kiss and Bossanyi (*Z. anorg. Chem.*, 1930, **191**, 289) avoided the complication of a high concentration of chloride, but allowed the hydrogen-ion concentration and the ionic strength to vary during investigation of the order of reaction. They concluded that the relation

$$\text{initial rate} = k[\text{Fe}^{3+}][\text{I}^-]^2 \quad \ldots\ldots \quad (4)$$

was closely obeyed if hydrolysed ferric ion was assumed to be unreactive and allowance was made for the variation of k with the ionic strength (I) by means of the equation

$$\log_{10} k = \log_{10} k_0 - 2{\cdot}0 I^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This procedure, however, does not establish the kinetics of the reaction with any certainty; moreover, a mistake appears to have been made in the derivation of equation (5), for Brönsted's theory of the primary salt effect in dilute solution gives

$$\log_{10} k = \log_{10} k_0 - 5{\cdot}0 I^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This implies that the corrections made to the observed rate by Kiss and Bossanyi, already as much as a factor of 4, were less than half as large as they should have been. Even if equation (6) was used, no quantitative conclusions could be drawn from these data; the ionic strength ranged from 0·01 to 0·12 and was thus too high for the Debye–Hückel limiting law to be obeyed accurately by triply charged ions. Some further papers record observations on the salt effect in more concentrated solutions (Kiss and Bossanyi, *ibid.*, 1931, **198**, 102) and in mixed solvents (Kiss and Vass, *ibid.*, 1932, **206**, 192).

In view of this rather confused situation, it was decided to reinvestigate the kinetics under more favourable conditions; *i.e.*, at constant ionic strength, in the presence of sufficient acid to suppress hydrolysis of ferric ion, and in the absence of anions with any strong tendency towards complex formation. This work is described in the present paper. Part II deals with the effect of complex-forming anions in the light of current theories about the kinetic significance of ionic association. In both these investigations the main object is to make a preliminary survey of the more general aspects of the reaction; it is hoped later to study in more detail those features which are found to be of particular interest. The experimental methods are consequently the simplest which would provide results of sufficient accuracy for the present purpose.

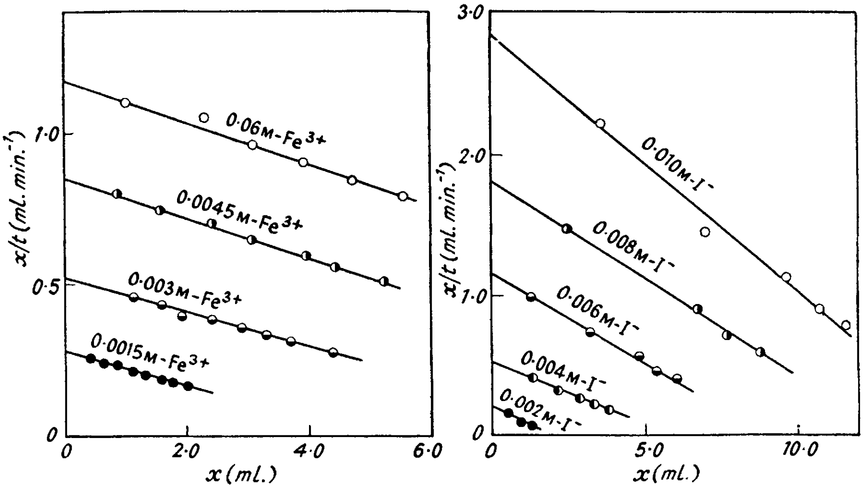
EXPERIMENTAL

Method.—Ferric solutions were prepared from the nitrate, nitric acid being used to control the hydrogen-ion concentration, and potassium nitrate to adjust the ionic strength. Although perchlorate is the anion with the least tendency to form complexes, the more readily available nitrate ion behaves similarly.

In previous work thiosulphate was added initially and the time required for the liberation of iodine was determined. Since under those conditions some thiosulphate may react with ferric ion, two different methods are employed here. In method (1) a slight excess of thiosulphate (x) is quickly added after the reaction has been occurring for a few minutes and the time (t) at which the iodine reappears is noted. After several successive titrations the initial rate (ml. of 0·01M-thiosulphate per min. per 110 ml. of reaction mixture) can be determined as the extrapolated value of x/t when x is zero (Fig. 1*a*). (To convert into g.-mol. l.$^{-1}$ min.$^{-1}$, multiply by $0{\cdot}91 \times 10^{-4}$.) In method (2) samples were withdrawn by pipette and diluted to stop the reaction, and the iodine determined with thiosulphate. The initial rate can be found by a similar method (Fig. 1*b*), but a larger extrapolation must be made because iodide is not being regenerated and the rate of reaction consequently decreases more rapidly Although the accuracy is also reduced by the greater dilution at which the titration is carried out, such experiments provide a useful check on the reliability of method (1). Diffuse daylight, in which all the recorded measurements are made, does not affect the rate of reaction.

Results.—The initial rate is used to investigate the order of reaction, so that interference by the retarding ferrous ion may be avoided. Both methods show that the reaction is of the first order with respect to ferric ion and of the second order with respect to iodide ion (Figs. 2 and 3). At the hydrogen-ion concentrations of 0·009M (Figs. 2*a* and 3*a*) and 0·1M (Figs. 2*b* and 3*b*) 19% and 2%, respectively, of the total ferric ion is present as the unreactive $FeOH^{2+}$ (Part II). Sasaki's observation that in the presence of 2M-sodium chloride the reaction tends to be of first order with respect to iodide at low concentrations of the latter must be attributed to some specific effect of the chloride ion. Since Kiss and Bossanyi found the right order of reaction by the method criticised above, some fortuitous cancellation of errors must have occurred in their correction for the varying ionic strength. Evidently the underestimate of the coefficient of $I^{\frac{1}{2}}$ in equation (5) has been rather closely balanced by the known tendency

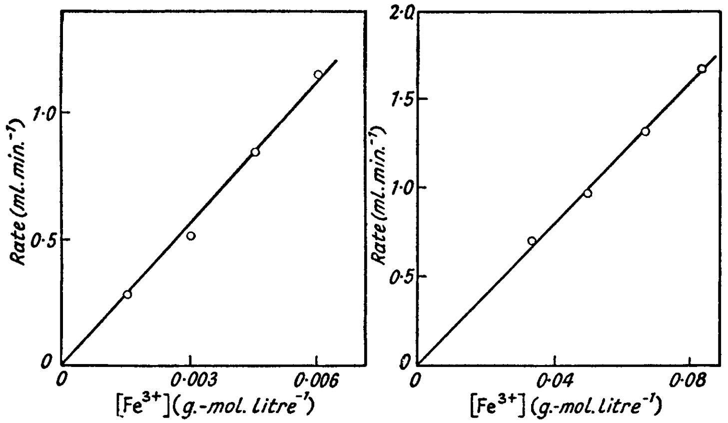
FIG. 1. *Determination of initial rate by extrapolation.*



(a) *Method* (1). *Various ferric concentrations.* 19°.

(b) *Method* (2). *Various iodide concentrations.* 20°.

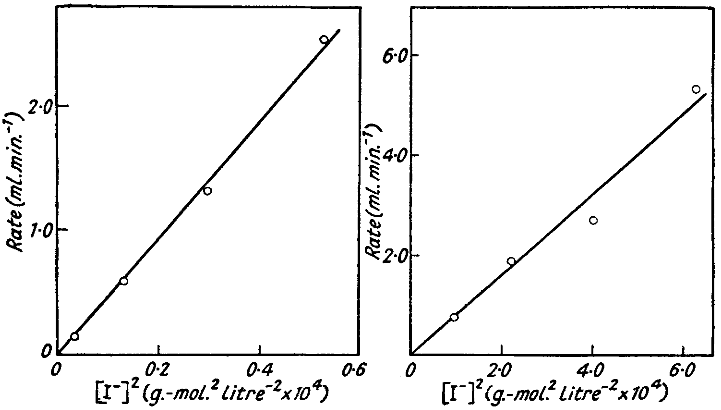
FIG. 2. *Variation of rate with ferric concentration.*



(a) *Method* (1). 0·0036M-I$^-$; I = 0·0673. 19°.

(b) *Method* (2). 0·002M-I$^-$; I = 0·602. 20°.

FIG. 3. *Variation of rate with square of iodide concentration.*



(a) *Method* (1). 0·003M-Fe^{3+}; I = 0·0673. 19°.

(b) *Method* (2). 0·0017M-Fe^{3+}; I = 0·160. 20°.

of the Debye–Hückel limiting law to overestimate the deviation of activity coefficients from unity.

The retarding effect of ferrous ion having been confirmed by the addition of ferrous nitrate, a test is made of the equation

$$\text{Rate} = \frac{k_1[\text{Fe}^{3+}][\text{I}^-]^2}{1 + k_2[\text{Fe}^{2+}]/[\text{Fe}^{3+}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Table 1 analyses a typical experiment made by method (1). The first three columns show the volume of 0·01M-thiosulphate (Δx) added after successive intervals (Δt) to a mixture of volume 110 ml. and the corresponding average rates of reaction ($\Delta x/\Delta t$). The average ferric and iodide concentrations in each interval being known (cols. 4 and 5), it is possible to calculate what the rate of reaction would have been if these concentrations had remained equal to their initial values. The progressive fall of even these corrected rates (col. 7) is a measure of the retardation due to ferrous ion. Reference to the value of the equilibrium constant given by Dawson and Spivey (*J.*, 1932, 1838) proves that the contribution of the reverse reaction may be neglected. The last two columns show the magnitude of the retardation term, R, defined by the equation

$$\text{Rate} = k_1[\text{Fe}^{3+}][\text{I}^-]^2/(1 + R) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and also of k_2.

TABLE 1.

Δx, ml.	Δt, min.	$\Delta x/\Delta t$, ml./min.	$[\text{I}^-]$	$[\text{Fe}^{3+}]$ m.-mol./l.	$[\text{Fe}^{2+}]$	Corr. rate, ml./min.	R	k_2
0·00	0·00	0·283	3·636	1·515	0·000	—	—	—
0·40	1·55	0·258	3·618	1·497	0·018	0·264	0·072	6·0
0·23	1·07	0·215	3·612	1·463	0·047	0·226	0·254	8·0
0·23	1·07	0·215	3·605	1·439	0·067	0·230	0·229	4·9
0·24	1·50	0·160	3·597	1·415	0·088	0·175	0·616	9·9
0·20	1·35	0·148	3·591	1·392	0·108	0·165	0·712	9·2
0·24	1·81	0·133	3·579	1·368	0·128	0·152	0·868	9·3
0·21	1·75	0·120	3·576	1·347	0·147	0·140	1·027	9·4
0·25	2·10	0·119	3·568	1·324	0·168	0·141	1·001	7·9

TABLE 2.

Temp. 19°; I = 0·0673.

$[\text{Fe}^{3+}]$ m.-mol./l.	$[\text{I}^-]$	k_2, mean
1·52	3·64	8·1
3·03	3·64	7·6
4·55	3·64	5·2
6·06	3·64	5·8

Temp. 19°; I = 0·0673.

$[\text{Fe}^{3+}]$ m.-mol./l.	$[\text{I}^-]$	k_2, mean
3·03	3·64	7·7
3·03	5·46	5·2
3·03	7·27	4·2

Temp. 16°; I = 0·160.

$[\text{Fe}^{3+}]$ m.-mol./l.	$[\text{I}^-]$	k_2, mean
1·67	10·0	2·9
1·67	15·0	2·2
1·67	20·0	2·0
1·67	25·0	1·5
1·67	30·0	1·6

Only the first figure of k_2 is significant, because the error produced in k_2 by variations of 0·01 ml. in Δx and of 1 second in Δt is 1·4. Since the average deviation of the eight k_2 values from their mean is, in fact, 1·4 although R changes by a factor of 14, Table 1 establishes the proportionality of the retardation term to the ferrous concentration. The first part of Table 2, which gives average values of k_2 for different initial ferric concentrations, supplies reasonable evidence for the inverse dependence of the retardation term on the ferric concentration.

Equation (7) also requires the retardation term to be independent of the iodide concentration, but the second and the third part of Table 2 indicate that k_2 falls somewhat as the iodide concentration is increased.

These conclusions are confirmed by the results obtained by method (2). If $a - x$, $b - x$, and x are respectively the ferric, iodide, and ferrous concentrations, the integrated form of the rate expression becomes

$$\alpha = k_1 - k_2\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\alpha = \frac{1}{(a-b)^2 t}\left\{\frac{x(a-b)}{b(b-x)} + \ln\frac{a(b-x)}{b(a-x)}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

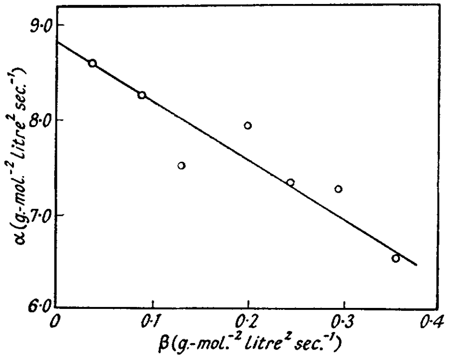
and

$$\beta = \frac{1}{(a-b)^2 t}\left\{\frac{x}{a-x} + \frac{x}{b-x} + \left(\frac{a+b}{a-b}\right)\ln\frac{a(b-x)}{b(a-x)}\right\} \quad . \quad . \quad . \quad (11)$$

Fig. 4 shows that the required linear relation between α and β is well satisfied by a typical run (0·00167M-Fe^{3+} and 0·004M-I^-); the value of 6·3 obtained for k_2 from the slope is also in good agreement with the results given in Table 2. Other k_2 values found in this way at the same iodide concentration, *viz.*, 6·8 at 0·0067M-Fe^{3+} and 4·2 at 0·0083M-Fe^{3+}, confirm the inverse proportionality of the retardation term to the ferric concentration. The iodide variation runs made by method (2) support the view that k_2 decreases as the iodide concentration is raised.

It may be concluded that equation (7), originally derived by Wagner for the reaction in the presence of 1·5M-potassium chloride, is also valid in the absence of chloride, with the exception of the dependence of k_2 upon iodide concentration noted above.

FIG. 4. *Test of equation* (9).



0·00167M-Fe^{3+}; 0·004M-I^-; $I = 0{\cdot}164$. 20°.

DISCUSSION

The most probable mechanism is thought to be

$$Fe^{3+} + I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FeI^{2+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

$$FeI^{2+} + I^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Fe^{2+} + I_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

$$Fe^{3+} + I_2^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Fe^{2+} + I_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

The only fundamentally different possibility is to introduce free iodine atoms. No scheme of that type, however, has been found to explain the observed kinetics without arbitrary assumptions which cannot be justified in terms of general principles.*

The mechanism proposed above differs from the one originally suggested by Wagner in that the rather improbable termolecular process

$$Fe^{3+} + I^- + I^- = Fe^{2+} + I_2^- \quad . \; . \; . \; . \; . \; . \; . \quad (15)$$

is replaced by two bimolecular stages. It is thus brought fully into accord with the general principle of economy of structural change in each elementary process (Hinshelwood, *J.*, 1947, 694). The successive steps now involve nothing more complicated than the association of two oppositely charged ions, the transfer of a single iodine atom, and the transfer of a single electron. Independent evidence supports the introduction of FeI^{2+} as an intermediate. $FeCl^{2+}$ and $FeBr^{2+}$ are well-known species; they have been characterised spectroscopically and the equilibrium constants for their formation determined (Rabinowitch and Stockmeyer, *loc. cit.*). Since the stability decreases on passing from the chloride to the bromide, it is reasonable to suppose that the iodide has the properties expected of a transient entity in a rapid reaction.

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* The only iodine-atom mechanism consistent with equation (7) appears to be: $FeI^{2+} + I^- = FeI^+ + I$; $FeI^+ = Fe^{2+} + I^-$; $FeI^{2+} + I = Fe^{2+} + I_2$. There seems to be no general reason, however, why iodide ion should lose an electron to FeI^{2+} rather than to Fe^{3+}, or why iodine atoms should react with FeI^{2+} rather than combine with each other.

The above mechanism gives for the rate of the forward reaction

$$\text{Rate} = \frac{k_1k_3}{k_2}[\text{Fe}^{3+}][\text{I}^-]^2 \bigg/ \left(1 + \frac{k_4[\text{Fe}^{2+}]}{k_5[\text{Fe}^{3+}]} + \frac{k_3}{k_2}[\text{I}^-]\right) \quad . \quad . \quad . \quad . \quad (16)$$

This is of the same form as the observed rate expression, equation (7), provided that $k_3[\text{I}^-] \ll k_2$; *i.e.*, if the equilibrium between FeI^{2+} and its constituents is not appreciably disturbed by the further reaction of FeI^{2+} with I^-. Since ion-pair complexes are probably formed and dissociated very rapidly, the required condition is likely to be satisfied.

The variation of the ferrous retardation with the iodide concentration cannot be attributed to the last term in the denominator of equation (16), because the initial rate remains strictly proportional to the square of the iodide concentration up to the highest values investigated. If it is assumed that the mechanism is essentially unchanged, the results imply that, as the iodide concentration is raised, I_2^- reacts either more rapidly with ferric or more slowly with ferrous ions. Any such change could be due only to the association of either Fe^{3+} or Fe^{2+} with I^-. If FeI^{2+} is sufficiently more reactive than Fe^{3+}, it need not represent any large proportion of the total ferric concentration in order to make the major contribution to the oxidation of I_2^-. However unreactive FeI^+ might be compared with Fe^{2+}, the retardation would not be much affected unless half or more of the ferrous ions were associated. Since the general tendency is for ferrous ions to be less associated than ferric ions, the first explanation appears to be the more probable.

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