26. *The Reaction between Ferric and Iodide Ions. Part II.* The Influence of Ionic Association.*

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Measurements are made of the retardation of the ferric–iodide reaction as perchlorate ions are replaced, at constant ionic strength, by chloride, bromide, nitrate, and sulphate, and as the hydroxyl-ion concentration is allowed to rise.

It is expected theoretically that each of the added anions, X, will associate with the ferric ion to form an inactive complex of the type FeX. This supposition is verified for hydroxyl ions, since the equilibrium constant for the association may be evaluated from the kinetic results in reasonable agreement with independent determinations. The equilibrium constants for the formation of $FeSO_4^+$ and $FeNO_3^{2+}$, which do not appear to have been measured before, are assigned the preliminary values of $1{\cdot}5 \times 10^4$ and 10 respectively at zero ionic strength at 18°.

Neither chloride nor bromide is as strong an inhibitor as predicted from published data on their association with ferric ions. In the presence of chloride the rate of reaction is the same in the dark as in daylight; bromide is a photosensitive catalyst in daylight, but does not appreciably retard the reaction in the dark. These halide complexes must thus be supposed to oxidise iodide ions in the dark as well as in the light.

Large changes may occur in the rate of an ionic reaction if one of the reactants associates specifically with an ion of the opposite sign. This paper describes the important part which such phenomena play in the ferric–iodide reaction when any other anions are present except those with the least tendency towards complex formation.

Although the kinetic significance of ionic association has been appreciated for some time, only recently has a start been made on its experimental study in a systematic way. Some investigations have now been reported in which independent measurements of the

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* Part I, preceding paper.

extent of association are correlated with the kinetic behaviour of the same ion-pair. Wyatt and Davies (*Trans. Faraday Soc.*, 1949, **45**, 774) have shown that CaS_2O_3 and BaS_2O_3 each react at the same rate with bromoacetate ions, but more rapidly than does $S_2O_3^{2-}$. Compared with hydroxyl ions, species of the type $BaOH^+$ do not appreciably catalyse the decomposition of diacetone alcohol or hydrolyse the carbethoxymethyltriethylammonium ion ($^+NEt_3{\cdot}CH_2{\cdot}CO_2Et$); their reactivity is indistinguishable from that of OH^-, however, in the hydrolysis of ethyl acetate (Bell and Prue, *J.*, 1949, 362; Bell and Waind, *J.*, 1950, 1979). All these apparently diverse facts may be interpreted, as indicated by Bell, in terms of the difference of electrical charge, both in magnitude and in distribution, between the transition state and the reactant ion concerned in the association.. The present investigation provides an example of a system of a different charge type. Here the associating reactant, Fe^{3+}, bears a triple positive charge, while the transition state, as shown in Part I, has the composition FeI_2^+. It is to be expected that a given anion, X, will associate much more strongly with the reactant than with the transition state on account of the difference in charge. The ferric complex, FeX, though more stable than the unassociated reactant, will thus be required to pass through essentially the same transition state and so appear to be comparatively unreactive. If the rate of reaction of FeX with I^- is negligible, the equilibrium constant for its formation from Fe^{3+} and X can be calculated from the kinetic results.

FIG. 1. *Effect of hydrogen-ion concentration at* 20°. *I* = 0·066.

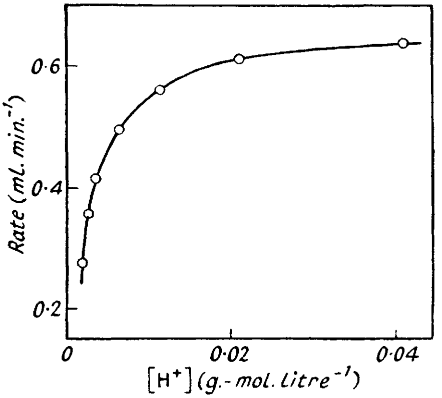
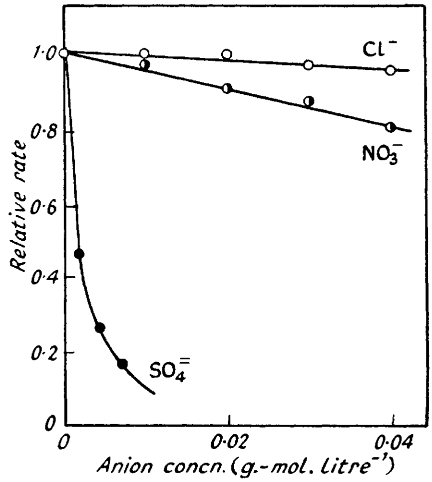


FIG. 2. *Retardation by chloride and nitrate at* 20° *and by sulphate at* 18°. *I* = 0·066.



EXPERIMENTAL

Method.—The change in the rate of reaction is determined as various anions are added at constant ferric and iodide concentrations of 0·00167 and 0·005M., respectively. Since the ferric ion is supplied as ferric nitrate, and nitric acid is used to prevent hydrolysis, all solutions are 0·011M. in hydrogen ion and 0·016M. in nitrate ion unless otherwise stated. The ionic strength is controlled by perchlorate, which, in the absence of evidence to the contrary, is assumed not to associate appreciably with ferric ion. Potassium or sodium perchlorate is used in conjunction with the corresponding salt of the added anion, in order to avoid any change in the cation composition which might influence the effective iodide concentration. All the recorded rates are initial ones determined by method (1) described in Part I; they are expressed as ml. of 0·01M-thiosulphate consumed in one minute by a reaction mixture of total volume 100 ml. (To convert into g.-mol. $l.^{-1}$ $min.^{-1}$, multiply by 10^{-4}.) None of the extrapolations used to calculate the initial rates from the experimental observations is illustrated, since, with the single exception of bromide solution in daylight, they are all of the linear type shown in Fig. 1 of Part I.

Results.—Fig. 1 shows the effect of reducing the nitric acid concentration from 0·041 to 0·001M., *i.e.*, the effect of the corresponding increase of the hydroxyl-ion concentration. The nitrate-ion concentration is held constant at 0·056M. by the addition of potassium nitrate. The initial stoicheiometric hydrogen-ion concentration has been corrected by amounts not exceeding 0·0009, in order to allow for the hydrolysis of the ferric ion in the less acid solutions. It may be seen that the rate of reaction rises rapidly as the hydrogen-ion concentration is first increased, but becomes effectively independent of it above about 0·02M.

Sulphate cannot be added alone, because both the hydrogen-ion and the sulphate-ion concentrations would be seriously altered by the formation of hydrogen sulphate ions. The reaction mixture is thus made only 0·006M. in nitric acid for this particular experiment, and an $SO_4^=$–HSO_4^- buffer of the same acidity is added. On the basis of Sherrill and Noyes's data (*J. Amer. Chem. Soc.*, 1926, **48**, 1861), HSO_4^- is arranged to represent 16·7% of the total sulphate; it is unlikely that HSO_4^-, present only in this relatively small proportion, will compete appreciably with the more highly charged $SO_4^=$ for association with ferric ion. Fig. 2 shows the results obtained in this way for sulphate, together with those for chloride and nitrate at the standard nitric acid concentration of 0·011M. The rates, designated relative, are expressed as fractions of those in perchlorate solution, so that the different effects of the various anions can readily be compared. A striking feature is the exceptionally strong retardation caused by low concentrations of sulphate. The choice of perchlorate as the anion least likely to associate with ferric ion is confirmed by the slower reaction observed in the presence of nitrate. The concentration scale for the latter anion represents the amount present in addition to that originally introduced (0·016M.) as ferric nitrate and nitric acid.

FIG. 3. *Retardation by nitrate at 20° (◑) and by chloride in daylight at 17° (○) and in the dark at 20° (●).* $I = 0{\cdot}426$.

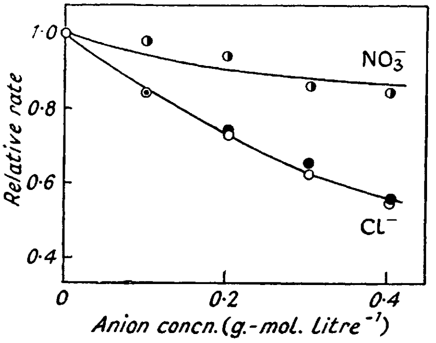
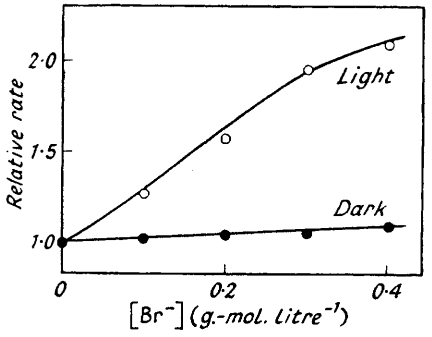


FIG. 4. *Effect of bromide concentration at 18° in daylight and in the dark.* $I = 0{\cdot}426$.



The influence of chloride and nitrate at much higher concentrations and ionic strength is illustrated in Fig. 3. The similar results obtained in the dark (filled circles) and in diffuse daylight (unfilled circles) demonstrate that the chloride solutions, like all the others except the bromide, are not appreciably photosensitive under the present conditions.

Fig. 4 reveals that the reaction is strongly catalysed by bromide ions when the solution is exposed to daylight. By comparison with the results obtained in the dark, it may be seen that the effect is undoubtedly a photochemical one.

DISCUSSION

It is supposed that only unassociated ferric ions react with iodide and that their concentration is governed by equilibria of the type :

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Fe^{3+} + X_i = FeX_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

X_i is any anion present except hydroxyl, the effect of which is allowed for by equation (1), or perchlorate, which is assumed to remain unassociated. Since the initial rate of reaction has been shown in Part I to be proportional to the first power of the ferric concentration, it follows that

$$\text{Rate} = \frac{k}{1 + \sum_i K_i[\mathrm{X}_i] + K_{\mathrm{H}^+}/[\mathrm{H}^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

No iodide term need be included in the summation, as the fraction of the total ferric represented by FeI^{2+} may be neglected. Provided the ferric and the iodide concentration and the ionic strength are all held constant, k should not vary. K_{H^+} and K_i, which are the equilibrium constants expressed in terms of concentrations for equations (1) and (2) respectively, should also be constant at a given ionic strength. Under the present conditions, therefore, equation (3) may be tested graphically, and the equilibrium constants evaluated, by including the appropriate terms in the expression

$$\frac{1}{\text{Rate}} = \frac{1}{k} + \frac{\sum_i K_i[\mathrm{X}_i]}{k} + \frac{K_{\mathrm{H}^+}}{k[\mathrm{H}^+]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The Influence of Hydroxyl Ion.—Since nitrate is the only additional anion present during the experiment in which the hydroxyl-ion concentration is varied, equation (4) may be written

$$\frac{1}{\text{Rate}} = \frac{1}{k} + \frac{K_{\mathrm{NO_3}^-}[\mathrm{NO_3}^-]}{k} + \frac{K_{\mathrm{H}^+}}{k[\mathrm{H}^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In Fig. 5 the reciprocal of the rate is plotted against the reciprocal of the hydrogen-ion concentration; the experimental points represented by unfilled circles are obtained by assuming all the hydrogen ions to be provided by the nitric acid. These points give the required linear relation in the more acid solutions, but deviate progressively as the acid concentration is reduced on account of the increasing formation of H^+ by the hydrolysis of Fe^{3+} according to equation (1).

The acid concentration, $[H^+]$, may be shown to be increased by

$$\Delta\mathrm{H}^+ = \frac{([\mathrm{H}^+]_0 + K')}{2}\{-1 + \sqrt{1 + 4K'[\mathrm{Fe}^{3+}]/([\mathrm{H}^+]_0 + K')^2}\} \quad . \quad . \quad (6)$$

where $[Fe^{3+}]$ is the total ferric concentration and $K' = K_{\mathrm{H}^+}/(1 + K_{\mathrm{NO_3}^-}[\mathrm{NO_3}^-])$. According to equation (5), however, K' is precisely the quantity given by the ratio of slope to intercept in Fig. 5. It is found to be $2{\cdot}16 \times 10^{-3}$ from the straight line drawn through the experimental points obtained from the more acid solutions. On substituting this value into equation (6), the corrected points are found to be those represented by filled circles in Fig. 5. There is no significant change in the higher values of $[H^+]$, and in the middle range the agreement with equation (5) is improved. For the two solutions of least acidity, however, there are now smaller deviations in the opposite sense, but these are probably due to the formation of a small amount of the second association complex, $Fe(OH)_2^+$. The provisional determination of K' is thus confirmed.

K_{H^+} may now be evaluated as $3{\cdot}0 \times 10^{-3}$ for an ionic strength of 0·066 at 20°, since $K_{\mathrm{NO_3}^-}$ is later found to be 6·8 under these conditions, and the nitrate concentration is 0·056M. An independent estimate of K_{H^+} may be obtained from the potentiometric work reviewed by Bray and Hershey (*J. Amer. Chem. Soc.*, 1934, **56**, 1889), whose data give $2{\cdot}65 \times 10^{-3}$ for the same ionic strength at 25°. If the heat content change is taken to be 12·3 kcal. (Rabinowitch and Stockmeyer, *J. Amer. Chem. Soc.*, 1942, **64**, 335), Bray and Hershey's value becomes $1{\cdot}9 \times 10^{-3}$ at 20°. The agreement is reasonably satisfactory in view of the probable errors in the two investigations. Since any significant reactivity of $FeOH^{2+}$ would lower the kinetic value of K_{H^+}, the results appear to warrant the conclusion that $FeOH^{2+}$ does not react appreciably with iodide.

Barb, Baxendale, George, and Hargrave (*Trans. Faraday Soc.*, 1951, **47**, 591) have recently treated in a similar way the effect of hydrogen-ion concentration on the rate at which Fe^{3+} reacts with O_2^- and HO_2^-. By two different experimental methods, they find

K_{H^+} (uncorrected for the presence of nitrate) to be 2·1 and 3·1 × 10^{-3} at 25° and an ionic strength of 0·435, whereas Bray and Hershey's data give 2·1 × 10^{-3} under those conditions. It is noteworthy that the work of these authors thus provides two further examples of $FeOH^{2+}$ being inactive, compared with Fe^{3+}, towards a singly charged negative ion.

The Influence of Sulphate Ion.—For the variation caused by sulphate the appropriate form of equation (4) is

$$\frac{1}{\text{Rate}} = \frac{1}{k} + \frac{K_{NO_3^-}[NO_3^-]}{k} + \frac{K_{H^+}}{k[H^+]} + \frac{K_{SO_4^=}[SO_4^=]}{k} \quad . \; . \; . \; . \; . \quad (7)$$

because some association with both hydroxyl and nitrate must also be taken into account. Fig. 6 shows that the predicted straight line is obtained when the reciprocal of the rate is plotted against the sulphate concentration. Small corrections have been applied for the amount of sulphate required by the observed rate of reaction to be associated with ferric ions. No allowance is made for the association of sulphate with potassium ions, since the effect of this factor will be opposed by any interaction between Fe^{3+} and HSO_4^-. From the ratio of slope to intercept, $K_{SO_4^=}/(1 + K_{NO_3^-}[NO_3^-] + K_{H^+}/[H^+])$ is found to be 688.

FIG. 5. *Test of equation* (5). $[H^+]$ *uncorrected* (○) *and corrected* (●) *for hydrolysis.*

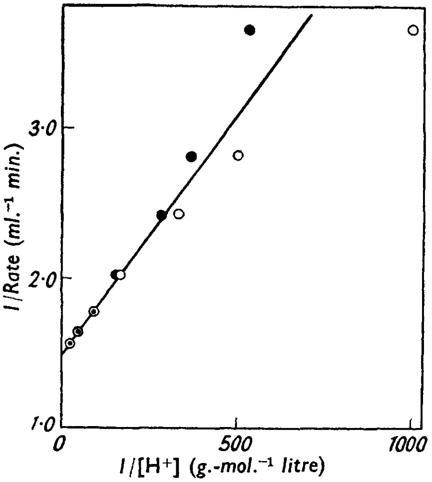
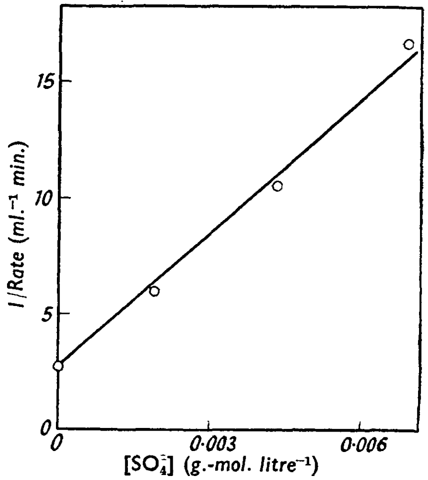


FIG. 6. *Test of equation* (7).



On insertion of the appropriate values of the nitrate and hydrogen-ion equilibrium constants and concentrations, $K_{SO_4^=}$ comes to 1·04 × 10^3 for an ionic strength of 0·066 at 18°.

The association of ferric and sulphate ions does not appear to have been studied previously, so it seems desirable to make a preliminary estimate from the present results of the thermodynamic equilibrium constant expressed in terms of activities. On the basis of the empirical activity coefficient equation introduced by Davies (*J.*, 1938, 2093), *viz.*,

$$-\log_{10} f = 0{\cdot}5z^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I] \quad . \; . \; . \; . \; . \; . \quad (8)$$

the product $f_{FeSO_4^+}/f_{Fe^{3+}} \, . \, f_{SO_4^=}$ is found to be 14·0 at the experimental ionic strength. The thermodynamic equilibrium constant is thus calculated to be approximately 1·5 × 10^4 at 18°.

It appears that lanthanum is the only other triply charged metallic ion of which the association with sulphate has been studied. Davies (*J.*, 1930, 2421) has shown that solubility and conductivity data lead to 0·36 × 10^4 for the equilibrium constant for the formation of $LaSO_4^+$. It is noteworthy that this value is of the same order of magnitude as that now obtained for the corresponding ferric complex by a totally different method.

The Influence of Nitrate Ion.—By calculations similar to those already detailed $K_{NO_3^-}$ is found to be 6·8 for an ionic strength of 0·066, and 0·6 for an ionic strength of 0·426 at 20°. The consistency of these two results may be tested by calculating from each the thermodynamic equilibrium constant, using the activity coefficient function established for reactions of this type by Rabinowitch and Stockmeyer (*loc. cit.*). The values so obtained are 23 and 4, respectively; evidently more accurate experiments are required if reliable values are to be derived from rates of reaction varying by less than 20%.

Whereas the very strong retardation caused by sulphate makes it most unlikely that $FeSO_4^+$ reacts appreciably with iodide, the same cannot be said of $FeNO_3^{2+}$. It cannot be strictly established, therefore, that the results given above for $K_{NO_3^-}$ are other than lower limits. The present investigation does suggest, however, that the thermodynamic equilibrium constant for the association of ferric and nitrate ions is probably of the order of 10 at 20°. No previous estimate of this quantity seems to be available for comparison.

The Influence of Chloride and Bromide Ions.—From the experiments illustrated in Figs. 2 and 3 showing the effect of variation of chloride, K_{Cl^-} at 20° is found to be 1·7 at an ionic strength of 0·066 and 2·5 at an ionic strength of 0·426; Rabinowitch and Stockmeyer's spectroscopic work (*loc. cit.*) gives respectively 6·8 and 3·8 under those conditions. To bring the kinetic into agreement with the spectroscopic results, the decrease in the rate of reaction caused by the chloride would have to be nearly four times larger than that observed at the lower concentration and 20% larger at the higher concentration. Such differences seem to be well outside the present experimental error, so it must be concluded that the reaction between $FeCl^{2+}$ and iodide cannot be neglected, particularly at lower ionic strengths. It will be recalled that the experimental results (Fig. 3) indicate that this reaction is not a photochemical one.

Rabinowitch and Stockmeyer's data lead to a value of 0·54 for K_{Br^-} at 20° and an ionic strength of 0·426. When allowance is made for the effects of hydroxyl and nitrate, it is estimated that the highest concentration of bromide should reduce the rate of reaction by 15%. Fig. 4 shows, however, that even in the dark bromide does not retard the reaction significantly. It thus seems probable that $FeBr^{2+}$ also takes part in the thermal oxidation of iodide.

The photochemical oxidation observed in bromide solutions exposed to daylight may be attributed to the electron-transfer excitation discussed by Evans and Uri (*Nature*, 1949, **164**, 404):

$$Fe^{3+}\,Br^- \overset{h\nu}{\rightleftharpoons} Fe^{2+}\,Br \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Presumably the bromine atom removes an electron from an iodide ion and so initiates an atomic mechanism of iodine formation. A feature of the photochemical experiments is the very rapid decrease in the rate of reaction during the course of a run, a trend which becomes particularly marked at the higher concentrations of bromide. In the dark, however, either bromide or chloride keeps the rate of reaction much more constant than it is in their absence. These observations thus indicate that the photochemical and thermal reactions of iodide with these halide complexes have somewhat different characteristics and so suggest that they might proceed by different mechanisms.

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