# Kinetics of Oxidation of Aquairon(2+) by Iodate in Dilute Perchloric Acid Solution

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The kinetics of oxidation of aquairon(2+) by iodate in dilute perchloric acid have been studied at 35 °C in the presence of allyl alcohol, thus avoiding catalysis by the molecular iodine normally formed in this reaction. Overall, the reaction is $4Fe^{2+} + IO_3^- \longrightarrow 4Fe^{3+} + I^I$, followed by rapid removal of $I^I$ by its reaction with allyl alcohol. The kinetic equation is $-d[Fe^{2+}]/dt = 4k_1(k_2 + k_3[Fe^{2+}])[Fe^{2+}][IO_3^-]/(k_{-1} + k_2 + k_3[Fe^{2+}])$. Aspects of the reaction mechanism are discussed.

THE reaction between aquairon(2+) and iodate in aqueous acid is shown in (1), the kinetics of which have

$$10Fe^{2+} + 2IO_3^- + 12H^+ \longrightarrow 10Fe^{3+} + I_2 + 6H_2O \quad (1)$$

been studied previously by Mitzner *et al.*[1] These authors observed an autocatalytic effect by the molecular iodine produced and suggested mechanisms both for the uncatalysed reaction and for that catalysed by iodine. In our initial studies with this system we sought evidence for active free radicals in the reacting system by observing the effect of appropriate organic substrates such as aliphatic alcohols in decreasing the stoicheiometry of the reaction. Following an earlier suggestion,[2] this approach was successful in demonstrating the intermediate formation of ·ClO and ·Cl in the reaction between aquairon(2+) and chlorate.[3] Propan-2-ol was found to be highly effective in decreasing the stoicheiometries of the reactions of aquairon(2+) with chlorate, and with bromate,[3] but this alcohol was ineffective in the system aquairon(2+) plus iodate. However, a very small concentration of allyl alcohol, a substrate of similar efficacy to propan-2-ol in the system aquairon(2+) plus chlorate, caused a change in consumption ratio $\Delta[Fe^{2+}] : \Delta[IO_3^-]$ from the normal 5.0 : 1 for the system aquairon(2+) plus iodate to 4.0 : 1. We have therefore concluded that the allyl alcohol reacts rapidly and quantitatively with iodine(I) produced in this system, possibly in the form of hypoiodous acid. The overall reaction is probably that shown in equation (2). Although molecular iodine also

$$4Fe^{2+} + IO_3^- + 5H^+ + C_3H_5OH \longrightarrow 4Fe^{3+} + C_3H_5I(OH)_2 + 2H_2O \quad (2)$$

adds readily to allyl alcohol, this reaction would not affect the consumption ratio of 5.0 : 1 in accordance with equation (1). A few kinetic measurements in the presence of allyl alcohol showed behaviour markedly different from that observed by Mitzner *et al.*[1] Accordingly we have investigated this reaction in more detail because it seemed possible that the autocatalysis by iodine might vitiate the earlier conclusions.

## EXPERIMENTAL

Reagents were of AnalaR quality and were used without purification with the exceptions noted below. Allyl alcohol was allowed to stand for several days over iron powder and was then distilled in a current of nitrogen. The peroxide-free product and its aqueous solutions were kept under nitrogen; samples were extracted by syringe through rubber serum caps. Iron(2+) perchlorate stock solutions were obtained by dissolving Specpure iron sponge from Johnson Matthey & Co. Ltd. in *ca.* 1.5 mol dm$^{-3}$ perchloric acid and diluting to a final concentration of 0.20 mol dm$^{-3}$ $Fe^{2+}$ and 1.0 mol dm$^{-3}$ $H^+$. The concentration of iron(2+) was found by titration against standard cerium(IV) sulphate solution (ferroin), and iron(3+) was determined by measuring the optical density of a suitably diluted sample in the presence of 0.20 mol dm$^{-3}$ perchloric acid and 0.20 mol dm$^{-3}$ ammonium thiocyanate at 480 nm ($\varepsilon = 8\,900$ dm$^3$ mol$^{-1}$ cm$^{-1}$). The concentration of sodium perchlorate stock solutions was found by dilution to *ca.* 0.1 mol dm$^{-3}$ and cation exchange on Amberlite IR-120(H) resin; the acidic eluate was titrated with standard sodium hydroxide (screen methyl orange). AnalaR potassium iodate was dried at 130 °C for 2 h and solutions of it were made up by weight. All solutions were made with doubly distilled water. Stock solutions of ' iodine(I) ' were made in 1.0 mol dm$^{-3}$ perchloric acid by mixing an acid solution of mercury(2+) perchlorate (18.0 cm$^3$) with a solution containing an equivalent amount of iodine in methanol (2.0 cm$^3$) and filtering off the precipitate of mercury(2+) iodide. The oxidising strength of the solution was obtained by adding potassium iodide and water, and titrating the iodine produced. About 12% of this oxidising strength was shown spectrophotometrically to be due to molecular iodine (*ca* 0.8 mmol dm$^{-3}$) and the remainder was ascribed to ' iodine(I) '. Such solutions, typically 6.5 mmol dm$^{-3}$ $I^I$, were used immediately after standardisation.

In making up reaction solutions, stock solutions, mixed in appropriate proportions if required, were evacuated (water-pump vacuum) in small vessels, each fitted with a rubber serum cap, for *ca.* 1 min. Argon was then introduced to give atmospheric pressure. The evacuation and introduction of argon was then repeated. An appropriate volume of each solution was removed by a glass syringe fitted with a stainless-steel needle and introduced into a small reaction tube of volume 3.0 cm$^3$ and length *ca.* 6 cm which had previously been flushed for *ca.* 5 min by argon entering through a stainless-steel needle and leaving by a similar needle. The stopper through which these needles and the syringe needles were passed was of silicone rubber and was discarded after each experiment. When the reaction mixture had been made up in a tube, it was placed in a water thermostat and shielded from light. Samples for the determination of iron(3+) were removed by syringe at appropriate intervals of time, argon being introduced by needle in place of each sample. In preliminary experiments adverse effects of light and of the presence of oxygen were noted; consequently for most experiments at least two reaction tubes were prepared and inconsistent results were rejected. The volume of the reaction solution was 2.6 cm$^3$ and the normal sample size was 0.1 cm$^3$. For most kinetic experiments 15 to 20 samples were taken from a given tube and the extent of reaction measured was 85 to 95%. A third tube containing a mixture similar to the others, but with water replacing potassium iodate, was made up to provide samples for the determination of the initial concentration of iron(3+).

Samples were diluted from 20 to 400 times; solutions after dilution were always 0.20 mol dm$^{-3}$ in each of perchloric acid and ammonium thiocyanate, and their optical density was measured at 480 nm. This method was satisfactory for determining iron(3+) in reaction mixtures with iron(2+) present in excess, the concentration of unreacted iodate after dilution being usually *ca.* $10^{-5}$ mol dm$^{-3}$ or less. With iodate in excess, concentrations after dilution of $6 \times 10^{-5}$ mol dm$^{-3}$ or more were obtained and under these conditions a reaction occurred involving iron(3+), iodate, and thiocyanate giving a yellow product which absorbed light at 480 nm. An empirical correction for this unwanted absorption was devised, enabling the iron(3+) concentrations in reaction mixtures to be obtained. The correction to any value of optical density measured at an intermediate time was obtained by linear interpolation from a plot of the corrections found at $t = 0$ and $t = \infty$ against the appropriate value of the measured optical density. From the iron(3+) concentrations in reaction mixtures the corresponding values for iron(2+) and iodate were evaluated, and hence plots of the appropriate functions of reactant concentrations against time could be constructed.

Methods similar to those described above were used for preparing reaction mixtures for the spectrophotometric investigation of complex formation between iron(2+) and iodate; allyl alcohol was present to prevent the appearance of molecular iodine. No evidence for such complex formation was obtained; a characteristic absorption observed below 360 nm was ascribed to complex formation between iron(3+) and iodate. Quantitative measurements were made of this absorption for solutions containing $1.94 \times 10^{-4}$ mol dm$^{-3}$ $Fe^{3+}$ and 0—$9.39 \times 10^{-2}$ mol dm$^{-3}$ $IO_3^-$ in 0.494 mol dm$^{-3}$ $HClO_4$ (ionic strength *ca.* 0.55 mol dm$^{-3}$) at 16 °C. The measurements were consistent with the equilibrium $Fe^{3+} + IO_3^- \rightleftharpoons [Fe(IO_3)]^{2+}$ with $K = 4.0 \pm 0.6$ dm$^3$ mol$^{-1}$ and $\varepsilon$ = *ca.* 13 000 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 310 nm. No allowance has been made here for the substantial proportion of iodate present in the form of its conjugate acid.

Sets of experiments to determine the stoicheiometry of reaction were carried out by using the procedures described above for kinetic experiments. Initial concentrations were 7.5 and 15.6 mmol dm$^{-3}$ $Fe^{2+}$, 0.95 mmol dm$^{-3}$ $IO_3^-$, and 0.99 and 1.99 mol dm$^{-3}$ $H^+$. The mean consumption ratio $\Delta[Fe^{2+}] : [IO_3^-]_0$ obtained from measurements of $[Fe^{3+}]$ when reaction had ceased was $4.002 \pm 0.077 : 1$ for experiments at 0.99 mol dm$^{-3}$ $H^+$ in the presence of 0.001 23—1.923 mol dm$^{-3}$ allyl alcohol. The ratio was 4.51 : 1 in an experiment with 0.62 mmol dm$^{-3}$ allyl alcohol, a concentration less than that of iodate, but sufficient to react with all the molecular iodine which might have been formed. Other experiments in the absence of allyl alcohol confirmed the stoicheiometry of 5.0 reported by Mitzner *et al.*[1] At 1.99 mol dm$^{-3}$ $H^+$ and 15.6 mmol dm$^{-3}$ $Fe^{3+}$ the optical density did not reach a constant value, but continued to rise very slowly after the expected time of completion of the reaction had elapsed. We suggest that under such conditions there is a very slow reaction between iron(2+) and an adduct formed between iodine(I) and allyl alcohol. The mean value of the stoicheiometry of the reaction between iron(2+) and iodate estimated from such experiments was $4.03 \pm 0.10$. For most kinetic experiments with iron(2+) present in excess, agreement between $4[IO_3^-]_0$ and $[Fe^{3+}]_\infty - [Fe^{3+}]_0$ was within 2%. The results of a few experiments with a larger (>5%) disparity between these quantities were discarded.

Kinetic experiments with very low iron(2+) concentrations were followed at 310 nm by using the strong absorption of the complex $[Fe(IO_3)]^{2+}$. Reaction mixtures were made up under argon as described previously. A mixture (3.0 cm$^3$) of all constituents except iron(2+) was introduced by syringe into a 1-cm optical cell fitted with a silicone rubber stopper and previously flushed with argon. The cell was placed in the temperature-controlled cell holder of a spectrophotometer. After temperature equilibration, 0.25 cm$^3$ of iron(2+) perchlorate was added by syringe, the contents of the cell were mixed by shaking, and a continuous record of optical density was taken. In making up the mixture prior to the addition of the iron(2+) solution a precipitate of potassium perchlorate was formed, since $[KIO_3] \geqslant 0.024$ mol dm$^{-3}$ and $[NaClO_4] + [HClO_4]$ = *ca.* 3.0 mol dm$^{-3}$. However, this precipitate settled and did not obstruct the removal of the 3.0-cm$^3$ sample. Tests showed that no potassium iodate was co-precipitated with the potassium perchlorate. The proportion of iron(3+) converted into $[Fe(IO_3)]^{2+}$ was 4—16%, but was constant during a given experiment because of the large excess of iodate present. The reaction was found to be of first order in both iron(2+) and iodate under these conditions; consequently it was sufficient to plot $\ln(D_\infty - D_t)$ against $t$ to obtain the corresponding pseudo-first-order rate constant, $D_\infty$ being the final stable optical density and $D_t$ the optical density at time $t$.

The various kinetic experiments were at initial concentrations of 0.1—75 mmol dm$^{-3}$ $Fe^{2+}$ and 0.24—48 mmol dm$^{-3}$ $IO_3^-$; whichever reactant was present in excess the consumption of iodate did not exceed 2.0 mmol dm$^{-3}$. In most experiments the allyl alcohol concentration was 7.7 mmol dm$^{-3}$, giving a ratio of allyl alcohol to iodate consumed of at least 3.8 : 1. Experiments in which this ratio was increased to 200 : 1 showed no effect on the rate of reaction. The ionic strength was adjusted to 3.1—3.2 mol dm$^{-3}$ by using sodium perchlorate. For the majority of experiments, the sum $[Fe^{2+}] + [Mg^{2+}]$ was made equal to the highest value of $[Fe^{2+}]_0$ in any experiment at the same value of $[H^+]$. All kinetic experiments were at 35.0 °C.

Several experiments were done to determine the stoicheiometry of the reaction between iron(2+) and iodine(I) in 0.8 mol dm$^{-3}$ $HClO_4$ at 25.0 °C. With 7.8 mmol dm$^{-3}$ $Fe^{2+}$ and 1.12 mmol dm$^{-3}$ iodine(I) a value of $\Delta[Fe^{3+}] : [\text{iodine(I)}]_0$ of *ca.* 1.05 : 1 was obtained after 4 h, but there was a slow increase in this ratio up to *ca.* 1.3 : 1 after 100 h. Experiments with the same initial concentrations of iron(2+) and iodine(I) gave values of the ratio of 0 : 1 after 2 h and *ca.* 0.05 : 1 after 4 h in the presence of 6.0 and 12.0 mmol dm$^{-3}$ allyl alcohol. All these experiments were conducted in the presence of air. We conclude that allyl alcohol is an efficient scavenger of iodine(I) in the presence of iron(2+) under conditions similar to those of our kinetic experiments.

The spectrophotometers employed were Unicam SP 500 (manual), Perkin-Elmer 356 (recording), and Perkin-Elmer 402 (recording), as appropriate.

## RESULTS

Preliminary kinetic experiments employing the sampling technique gave pseudo-first-order rate plots which showed only small curvature, provided one or other of the reactants was present in large excess. In contrast, the corresponding second-order treatment, applied to experiments in which neither reagent was present in large excess, did not give satisfactory rate plots. In some of these experiments substantial concentrations of iron(3+) were added initially. Compared with otherwise identical experiments at low initial concentrations of iron(3+), the effect on the course of reaction was small, and it was concluded that iron(3+) does not enter into the rate equation. Consequently, the initial concentration of iron(3+) is not normally recorded in the tables of results; unless otherwise stated this concentration varied between 0.2 and *ca.* 5% of the initial iron(2+) concentration, depending upon the age of the stock solution of iron(2+) perchlorate.

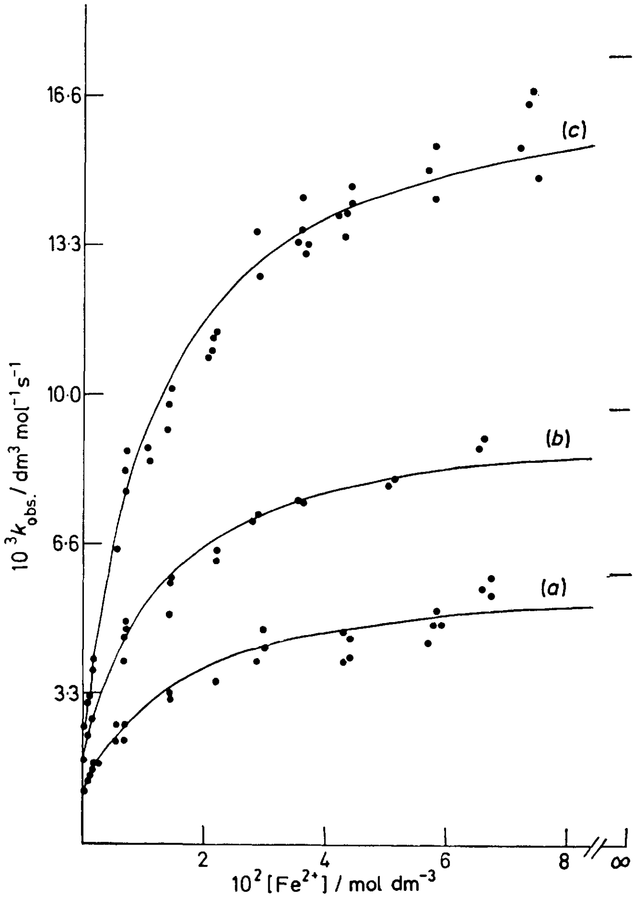

FIGURE 1 Variation of $k_{obs.}$ with [$Fe^{2+}$]: (*a*) [$H^+$] = 0.530, (*b*) [$H^+$] = 1.105, and (*c*) [$H^+$] = 2.115 mol dm$^{-3}$. The lines on the right-hand side give the values of $k_{obs.}$ for [$Fe^{2+}$]$\rightarrow\infty$

Even with a fairly large excess of one reactant, its relative change in concentration in a reaction was not negligible and so results of experiments under these conditions have been treated by using the second-order equation (3). Plots of $\ln(4[IO_3^-]) - \ln[Fe^{2+}]$ against time $t$ were linear over at

$$d[Fe^{3+}]/dt = -4d[IO_3^-]/dt = 4k_{obs.}[Fe^{2+}][IO_3^-] \quad (3)$$

least the first 50% of reaction, but many of them showed slight curvature, corresponding to an apparent decrease in $k_{obs.}$ during the later stages of the reaction. The data for these preliminary experiments and others performed subsequently under similar conditions are deposited in Supplementary Publication No. SUP 22729 (6 pp.) * which includes 103 experiments at [$H^+$] = 0.530, 1.105, and 2.115 mol dm$^{-3}$ with [$Fe^{2+}$] = 1.7—76.2 mmol dm$^{-3}$ and [$IO_3^-$] = 0.24—18.1 mmol dm$^{-3}$.

The dependence of $k_{obs.}$ upon the iron(2+) concentration is evident from these data and Figure 1. The limiting value of $k_{obs.}$ as the iron(2+) concentration tends to zero was required at each hydrogen-ion concentration, but sufficiently low values of the iron(2+) concentration could not be used in experiments involving the sampling technique. A summary of the relevant experiments is in SUP 22729 which includes 54 experiments at [$H^+$] = 0.530, 1.105, and 2.115 mol dm$^{-3}$ with [$Fe^{2+}$] = 0.09—1.65 mmol dm$^{-3}$ and [$IO_3^-$] = 11.6—48.0 mmol dm$^{-3}$. Most of these experiments employed the measurement of the u.v. absorption of the complex [$Fe(IO_3)$]$^{2+}$, a convenient method, but one which can be used satisfactorily only if a large excess of iodate is present. The pseudo-first-order constants obtained were divided by $4[IO_3^-]_0$ to give $k_{obs.}$. Each limiting value of $k_{obs}$

TABLE 1

Velocity constants for oxidation of iron(2+) by iodate with neither reactant present in large excess, $I$ = 3.1 mol dm$^{-3}$

| [$H^+$] / mol dm$^{-3}$ | [$Fe^{2+}$]$_0$ / mmol dm$^{-3}$ | [$IO_3^-$]$_0$ / mmol dm$^{-3}$ | $10^3R$ / dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^3k_1$ / dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| Values chosen $k_2/k_{-1}$ = 0.200 and $k_3/k_2$ = 380 dm$^3$ mol$^{-1}$ | | | | |
| 1.040 | 7.20 | 0.965 | 1.42 | 8.53 |
| 1.040 | 7.20 | 2.896 | 1.34 | 8.06 |
| 1.116 | 18.5 | 0.965 | 1.66 | 9.99 |
| 1.116 | 18.5 | 1.931 | 1.66 | 9.98 |
| At [$H^+$] = 1.105 mol dm$^{-3}$, $k_2/k_{-1}$ = 0.219, $k_3/k_2$ = 456 dm$^3$ mol$^{-1}$, $10^3R$ = 1.74 dm$^3$ mol$^{-1}$ s$^{-1}$, and $10^3k_1$ = 9.68 dm$^3$ mol$^{-1}$ s$^{-1}$ [a] | | | | |
| Values chosen $k_2/k_{-1}$ = 0.157 and $k_3/k_2$ = 545 dm$^3$ mol$^{-1}$ | | | | |
| 2.002 | 7.37 | 0.965 | 2.16 | 15.9 |
| 2.002 | 7.37 | 2.896 | 2.05 | 15.1 |
| 2.039 | 18.8 | 0.965 | 2.40 | 17.7 |
| 2.039 | 18.8 | 1.931 | 2.25 | 16.6 |
| 2.186 [b] | 18.1 | 1.931 | 2.95 | 21.7 |
| 2.191 [c] | 18.7 | 1.931 | 2.60 | 19.2 |
| At [$H^+$] = 2.115 mol dm$^{-3}$, $k_2/k_{-1}$ = 0.159, $k_3/k_2$ = 585 dm$^3$ mol$^{-1}$, $10^3R$ = 2.40 dm$^3$ mol$^{-1}$ s$^{-1}$, and $10^3k_1$ = 17.5 dm$^3$ mol$^{-1}$ s$^{-1}$ [a] | | | | |
| Values chosen $k_2/k_{-1}$ = 0.150 and $k_3/k_2$ = 741 dm$^3$ mol$^{-1}$ | | | | |
| 2.962 | 18.9 | 0.965 | 2.79 | 21.4 |
| 2.962 | 18.9 | 1.931 | 2.93 | 22.5 |
| 2.965 | 7.48 | 0.965 | 2.82 | 21.6 |
| 2.965 | 7.48 | 2.896 | 3.04 | 23.3 |
| 3.038 [d] | 7.48 | 2.896 | 3.03 | 23.2 |
| 3.038 [e] | 7.48 | 2.896 | 2.79 | 21.4 |
| At [$H^+$] = 2.99 mol dm$^{-3}$, $k_2/k_{-1}$ = 0.139, $k_3/k_2$ = 720 dm$^3$ mol$^{-1}$, $10^3R$ = 2.84 dm$^3$ mol$^{-1}$ s$^{-1}$, and $10^3k_1$ = 23.3 dm$^3$ mol$^{-1}$ s$^{-1}$ [f] | | | | |

[a] Mean values derived from deposited data. [b] [$Fe^{3+}$]$_0$ = 8.17 mmol dm$^{-3}$. [c] [$Fe^{3+}$]$_0$ = 0.34 mmol dm$^{-3}$. [d] [$Fe^{3+}$]$_0$ = 0.11 mmol dm$^{-3}$. [e] [$Fe^{3+}$]$_0$ = 7.80 mmol dm$^{-3}$. [f] Values extrapolated from Table 2.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

was obtained by a short linear least-squares extrapolation to $[Fe^{2+}]_0 = 0$ of a plot of $k_{obs.}$ against $[Fe^{2+}]_0$ at constant hydrogen-ion concentration. Certain of these experiments with relatively high initial concentrations of iron(3+) showed that under these conditions the kinetics of the reaction are not affected by this species.

Finally, the results of preliminary experiments involving the sampling technique in which neither reactant was present in large excess are summarised in Table 1. No simple reaction plot can be applied to the results of these experiments; their evaluation is described in the Discussion.

## DISCUSSION

The experiments summarised in SUP 22729 show that the kinetic behaviour of the iron(2+) plus iodate system in the presence of allyl alcohol can be expressed reasonably well by equation (3) with $k_{obs.}$ varying from a limit at very low concentrations of iron(2+) to a higher limit at higher concentrations (see Figure 1). The corresponding second-order rate constant for the oxidation of aquavanadium(3+) by iodate varies similarly between limits, but this variation depends on the ratio of the concentrations of these reactants,[4] in contrast to our finding of a dependence on the cation alone. In case this effect was due to a non-specific catalysis by doubly charged cations, many of the experiments were done in pairs. In one member of a pair the total concentration of doubly charged cations $[Fe^{2+}] + [Mg^{2+}]$ was made equal to the maximum value of $[Fe^{2+}]$ for the group of experiments at a particular value of $[H^+]$; the other member was identical except that magnesium(2+) was absent. It became clear that the variation of $k_{obs.}$ is a specific effect of iron(2+).

TABLE 2

Summary of velocity constants for oxidation of iron(2+) by iodate ($I$ = *ca.* 3.2 mol dm$^{-3}$) at 35.0 °C

| Source | $[H^+]$ / mol dm$^{-3}$ | $10^3R$ / dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^3k_1$ / dm$^3$ mol$^{-1}$ s$^{-1}$ | $(k_2/k_{-1})$ | $(k_3/k_2)$ / dm$^3$ mol$^{-1}$ | $k_1/R$ |
|---|---|---|---|---|---|---|
| *a* | 0.530 | 1.12 ± 0.03 | 6.12 ± 0.47 | 0.223 ± 0.018 | 350 ± 42 | 5.48 |
| *b* | 1.08 | 1.52 ± 0.17 | 9.14 ± 1.00 | 0.200 [c] | 380 [c] | 6.00 |
| *a* | 1.105 | 1.74 ± 0.05 | 9.68 ± 0.59 | 0.219 ± 0.016 | 456 ± 63 | 5.57 |
| *b* | 2.08 | 2.40 ± 0.33 | 17.7 ± 2.4 | 0.157 [c] | 545 [c] | 7.37 |
| *a* | 2.115 | 2.40 ± 0.10 | 17.5 ± 1.0 | 0.159 ± 0.010 | 585 ± 51 | 7.28 |
| *b* | 2.99 | 2.90 ± 0.12 | 22.2 ± 0.9 | 0.150 [c] | 741 [c] | 7.67 |

[a] Deposited data. [b] Table 1. [c] Value assumed for group of experiments.

Various mechanisms lead to kinetic equations of the form required to reproduce Figure 1. The two which seem most satisfactory are A and B, in both of which

$$\begin{array}{llll}
\text{A} & Fe^{2+} + IO_3^- \rightleftharpoons (Fe,\ IO_3)^+ & & k_1, k_{-1} \\
 & (Fe,\ IO_3)^+ \longrightarrow Fe^{3+} + \cdot IO_2 & & k_2 \\
 & Fe^{2+} + (Fe,\ IO_3)^+ \longrightarrow 2Fe^{3+} + IO_2^- & & k_3 \\
\text{B} & Fe^{2+} + IO_3^- \longrightarrow Fe^{3+} + \cdot IO_2 & & k_4 \\
 & Fe^{2+} + IO_3^- \rightleftharpoons (Fe,\ IO_3)^+ & & k_5, k_{-5} \\
 & Fe^{2+} + (Fe,\ IO_3)^+ \longrightarrow 2Fe^{3+} + IO_2^- & & k_6
\end{array}$$

subsequent steps in the reduction to iodine(I) are rapid. These mechanisms lead to the following dependences of $k_{obs.}$ upon $[Fe^{2+}]$ [equations (4) and (5)].

$$\text{A}\quad k_{obs.} = k_1(k_2 + k_3[Fe^{2+}])/(k_{-1} + k_2 + k_3[Fe^{2+}]) \qquad (4)$$

$$\text{B}\quad k_{obs.} = k_4 + k_5k_6[Fe^{2+}]/(k_{-5} + k_6[Fe^{2+}]) \qquad (5)$$

However, equations (4) and (5) are equivalent with $R = k_4 = k_1k_2/(k_{-1} + k_2)$; $k_5 = k_1k_{-1}/(k_{-1} + k_2)$; and $k_{-5}/k_6 = (k_{-1} + k_2)/k_3$. Consequently, it is not possible to distinguish between them by finding the dependence of $k_{obs.}$ upon $[Fe^{2+}]$. As discussed later, we marginally prefer A. It can be seen from these expressions that the linear extrapolation to $[Fe^{2+}] = 0$ of values of $k_{obs.}$ obtained at sufficiently low $[Fe^{2+}]$ should give $R$. Having obtained values of $R$ from experiments at $[Fe^{2+}] \leqslant 1.65$ mmol dm$^{-3}$ in SUP 22729 it was then possible to evaluate other constants or ratios from the experiments at corresponding values of $[H^+]$. Equation (4) can be written in the form

$$1/(k_{obs.} - R) = (k_1 + k_2)/k_{-1}k_{-1} + [(k_{-1} + k_2)^2/k_1k_{-1}k_3] \times 1/[Fe^{2+}] \qquad (6)$$

(6). Appropriate weighted least-squares plots of $1/(k_{obs.} - R)$ against $1/[Fe^{2+}]$ yielded values of the gradient and intercept on the $y$-axis. From these and $R$, values of $k_1$, $k_2/k_{-1}$, and $k_3/k_2$ were obtained for $[H^+] = 0.530$, 1.105, and 2.115 mol dm$^{-3}$ as summarised in Table 2.

As well as A and B we also considered mechanism C

$$\begin{array}{llll}
\text{C} & Fe^{2+} + IO_3^- \rightleftharpoons [Fe(IO_3)]^+ & & K_1' \\
 & [Fe(IO_3)]^+ \longrightarrow Fe^{3+} + \cdot IO_2 & & k_2' \\
 & Fe^{2+} + [Fe(IO_3)]^+ \longrightarrow 2Fe^{3+} + IO_2^- & & k_3'
\end{array}$$

where $[Fe(IO_3)]^+$ represents a complex, inner-sphere or outer-sphere, between $Fe^{2+}$ and $IO_3^-$. If this mechanism is correct, it can be shown for experiments with iron(2+) present in large excess that the $y$-axis intercept/gradient for the plot described in the preceding paragraph is $K_1'$. (This constant has the same value as the quotient $k_3/(k_{-1} + k_2)$ obtained if mechanism A is correct.) Values of this parameter are 63.9, 81.9, and 80.4 dm$^3$ mol$^{-1}$ at $[H^+] = 0.530$, 1.105, and 2.115 mol dm$^{-3}$ respectively. As described above we found $K$ = *ca.* 4 dm$^3$ mol$^{-1}$ for the equilibrium $Fe^{3+} + IO_3^- \rightleftharpoons [Fe(IO_3)]^{2+}$ by a spectrophotometric method. We expect $K_1'$ for the corresponding reaction with iron(2+) to be smaller, not larger, than this value. Moreover, at the highest concentrations of iodate employed, the proportion of iron(2+) converted into the complex would be *ca.* 2/3 if $K_1'$ *ca.* 70 dm$^3$ mol$^{-1}$. Under these conditions the rate of reaction would no longer be proportional to $[IO_3^-]$. However, the second-order constants shown in SUP

22729 were calculated by assuming a first-order dependence upon $[IO_3^-]$ and their constancy as this concentration is changed shows that this assumption is correct. Consequently, we regard mechanism C as incorrect, although it is possible that a complex between iron(2+) and iodate is a precursor of the intermediate species shown in curved brackets in mechanisms A and B.

Initially, we were unable to interpret the changes in the concentrations of reactants with time for the experiments summarised in Table 1. If, as we now suppose, the kinetic equation for the reaction is (7), obtained from (3)

$$-d[Fe^{2+}]/dt = 4k_1[IO_3^-][Fe^{2+}](k_2 + k_3[Fe^{2+}])/(k_{-1} + k_2 + k_3[Fe^{2+}]) \quad (7)$$

and (4), then on integration we obtain (8) where $a = [Fe^{2+}]_0$, $b = 4[IO_3^-]_0$, $P = [k_3k_{-1}/k_2(k_{-1} + k_2)]/[k_3/k_2 - 1/(b - a)]$, and $R = k_1k_2/(k_{-1} + k_2)$, as defined previously.

$$\ln[Fe^{2+}] - (1 - P)\ln(4[IO_3^-]) - P\ln([Fe^{2+}] + k_2/k_3) = -(b - a)Rt + \text{constant} \quad (8)$$

If $P$ is known, the left-hand side of (8) can be plotted against $t$, and so $R$ can be found. Two of the groups of experiments in Table 1 are at values of $[H^+]$ (*ca.* 1.1 and 2.1 mol dm$^{-3}$) near to those of experiments in SUP 22729 from which $k_1$, $k_2/k_{-1}$, and $k_3/k_2$ have already been obtained, and so appropriate values of $P$ could be calculated for preliminary plots of (8). No experiments in SUP 22729 are at *ca.* 3.0 mol dm$^{-3}$ $H^+$ and so $k_1$, $k_2/k_{-1}$, and $k_3/k_2$ were obtained by extrapolation from their corresponding values at lower $[H^+]$; these extrapolated values are included in Table 1, following the relevant group of experiments. The value of $R$ derived from a plot of (8), together with the value of $k_2/k_{-1}$ employed, enabled $k_1$ to be calculated. Although linear plots were obtained in this way, better concordance was found between such values of $k_1$ and those obtained from the experiments deposited if the ratios $k_2/k_{-1}$ and $k_3/k_2$ used in evaluating $P$ were adjusted by up to *ca.* 20% from the values used for preliminary plots. The values of these ratios finally chosen are shown at the head of each group of experiments in Table 1. Plots for the experiments at $[H^+]$ *ca.* 1.1 mol dm$^{-3}$ are shown in Figure 2.

When the value of $[Fe^{2+}]_0/[IO_3^-]_0$ exceeds 40, the proportional change in $[Fe^{2+}]$ during a kinetic experiment is less than 10%. However, in many of the experiments summarised in SUP 22729 this value is less than 40, and the proportional change in $[Fe^{2+}]$ is not negligible. The gentle curvature of several of the second-order plots for $k_{obs.}$ is ascribed to this change. Strictly, equation (8) should be used, in a treatment similar to that described above. We have not followed this approach because the extraction of $k_1$, $k_2/k_{-1}$, and $k_3/k_2$ is much simpler by the chosen method of analysing the dependence of $k_{obs.}$ upon $[Fe^{2+}]$. An examination of the significance of experimental values of $k_{obs.}$ was clearly necessary and was made in the following way. By using equation (8) with appropriate values of $k_1$, $k_2/k_{-1}$, and $k_3/k_2$, corresponding values of $[Fe^{2+}]$, $[IO_3^-]$, and $t$ were calculated at various stages during the reaction for several typical initial reactant concentrations with $[Fe^{2+}]_0/[IO_3^-]_0$ in the range 0.4—30. Each set of values was plotted in the usual second-order form for obtaining $k_{obs.}$, *i.e.* $\ln(4[IO_3^-]) - \ln[Fe^{2+}]$ was plotted against $t$. It was generally found that the gradient of the first virtually linear part of the plot, corresponding to 0—50% completion of the reaction, yielded a value of $k_{obs.}$ in good agreement with that calculated by substituting $k_1$, $k_2/k_{-1}$, and $k_3/k_2$ into equation (4), provided the value of $[Fe^{2+}]$ used in this equation was that at 25% completion of the reaction. Hence, in applying equation (6) to the results deposited, in which initial concentrations of reactants are tabulated, the values of $[Fe^{2+}]$ corrected to 25% completion have been used; the derived velocity constants or ratios have been obtained in this way. The stoicheiometry of the reaction in the presence of allyl alcohol is 4.0 and so the corrections are simply obtained: $[Fe^{2+}]_{25\%} = [Fe^{2+}]_0 - [IO_3^-]_0$ if $Fe^{2+}$ is in excess, and $[Fe^{2+}]_{25\%} = 3/4[Fe^{2+}]_0$ if iodate is in excess.

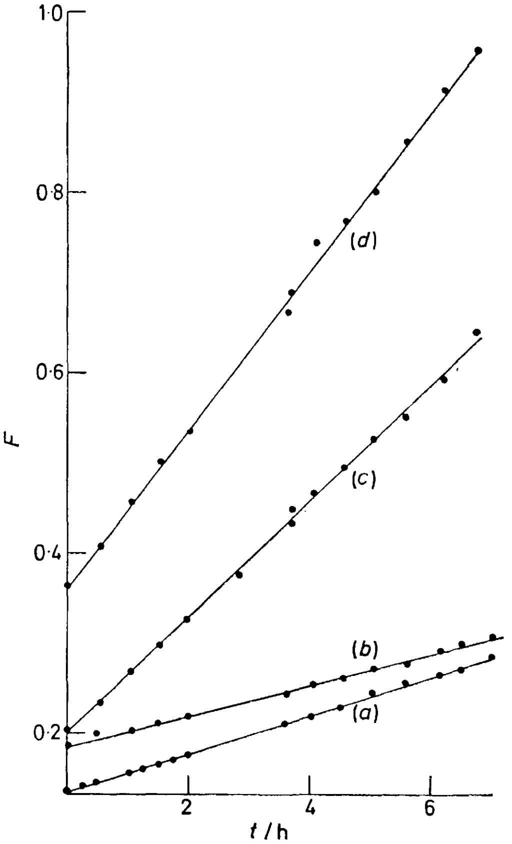

FIGURE 2 Plots of the function $F = \ln[Fe^{2+}] - (1 - P)\ln(4[IO_3^-]) - P\ln([Fe^{2+}] + k_2/k_3)$ against time $t$ for the experiments at $[H^+]$ *ca.* 1.1 mol dm$^{-3}$ in Table 1: (*a*) $[Fe^{2+}] = 7.2$, $[IO_3^-] = 2.90$, 50% reaction completed; (*b*) $[Fe^{2+}] = 7.2$, $[IO_3^-] = 0.97$, 45% reaction completed; (*c*) $[Fe^{2+}] = 18.5$, $[IO_3^-] = 1.93$, 85% reaction completed; (*d*) $[Fe^{2+}] = 18.5$, $[IO_3^-] = 0.97$ mmol dm$^{-3}$, 90% reaction completed

The results for $k_1$ and various ratios of velocity constants are summarised in Table 2. At *ca.* 1.1 and *ca.* 2.1 mol dm$^{-3}$ $H^+$ there is fairly good agreement between such values obtained under conditions of large excess of one reactant, from experiments in SUP 22729, and the corresponding values obtained when the excess is small, from experiments in Table 1. We consider this to be further evidence for the kinetic equation (7). Although the experiments cover the range 0.53—2.99 mol dm$^{-3}$ H$^+$, the results do not permit a quantitative interpretation of the hydrogen-ion dependence of the reaction, partly because the association constant for protonation of iodate is not known at an ionic strength of *ca.* 3 mol dm$^{-3}$. Also, there is evidence of association between iodate and singly charged cations,[5] so that the decrease in [Na$^+$] as [H$^+$] is increased presents a further complication. However, various qualitative deductions can be made. Table 2 shows that $k_1$ and $R$ vary in a very similar way with [H$^+$]. If mechanism B is correct, this is equivalent to concluding that $k_4$ and $k_5$ fortuitously show a very similar dependence on [H$^+$]. The reactions corresponding to these two constants are independent and so do not of necessity involve the same dependence on [H$^+$]. If A holds, there is a common first step for the two routes of reaction, and $k_1/R$ is determined by $k_2/k_{-1}$, the ratio of rate constants for two different modes of decomposition of the common intermediate. Both these reactions could well involve no dependence upon [H$^+$], leaving the formation of the intermediate as the process dependent on [H$^+$]. On these grounds, we marginally prefer mechanism A.

Accepting mechanism A as correct, with the incorporation of a proton into the primary intermediate, we also note the variation in $k_3/k_2$ with [H$^+$]. We have suggested above that the breakup of this intermediate by the reactions corresponding to $k_2$ and $k_{-1}$ does not involve a proton transfer, in which case a dominant path for the reaction corresponding to $k_3$ must involve the uptake of a proton. Tentatively we can rewrite mechanism A, in which no account was taken of the hydrogen-ion dependence, in the more explicit form D with $k_3 = k_{3a} + k_{3b}[\mathrm{H}^+]$.

$$\begin{array}{lll}
\mathrm{D} & \mathrm{Fe}^{2+} + \mathrm{HIO_3} \rightleftharpoons (\mathrm{Fe, HIO_3})^{2+} & k_1', k_{-1}' \\
& (\mathrm{Fe, HIO_3})^{2+} \longrightarrow [\mathrm{Fe(OH)}]^{2+} + {\cdot}\mathrm{IO_2} & k_2 \\
& \mathrm{Fe}^{2+} + (\mathrm{Fe, HIO_3})^{2+} \longrightarrow & \\
& [\mathrm{Fe(OH)}]^{2+} + [\mathrm{Fe^{III}(IO_2)}]^{2+} & k_{3a} \\
& \mathrm{H}^+ + \mathrm{Fe}^{2+} + (\mathrm{Fe, HIO_3})^{2+} \longrightarrow & \\
& \mathrm{Fe}^{3+} + \mathrm{H_2O} + [\mathrm{Fe^{III}(IO_2)}]^{2+} & k_{3b}
\end{array}$$

The dependence of $k_1$ upon [H$^+$] may be attributed primarily to the equilibrium $\mathrm{H}^+ + \mathrm{IO_3}^- \rightleftharpoons \mathrm{HIO_3}$.

Our experiments do not justify the proposal of a more detailed mechanism than that given above. Indeed, there are obviously other possible formulations differing in detail. We do not know for example whether iodite is formed as a complex with Fe$^{3+}$, as shown, or in an uncomplexed form. The structure of the intermediate shown as (Fe, HIO$_3$)$^{2+}$ is similarly uncertain. The mechanisms of the reduction of ·IO$_2$ and IO$_2^-$, ultimately to iodine(I), are also unknown. In some reactions involving the reduction of oxohalogen anions by metal ions it is believed that halogen species of oxidation state intermediate between reactants and products may react together or with the halogen-containing reactant in steps which affect the rate of reaction.[4,6] There is no kinetic evidence for such steps under the conditions of study of the iodate plus iron(2+) system.

*Reaction in the Presence of Molecular Iodine.*—In the absence of allyl alcohol, molecular iodine accumulates as a reaction product, and under our conditions the rate of reaction between iodate and iron(2+) is an order of magnitude faster than in the presence of allyl alcohol. Although catalysis by iodine was recognised by Mitzner *et al.*,[1] they have interpreted their findings as if catalysis by iodine is important only when this species is added at the beginning of the reaction. An experiment conducted by us under very similar conditions to that shown in Figure 1 of Mitzner's paper [1] gave similar results. In the presence of 8 mmol dm$^{-3}$ allyl alcohol the reaction rates obtained were less than one quarter of the rates at comparable stages in the absence of allyl alcohol. We consider that neither Mitzner's experimental results nor his mechanistic interpretation are relevant to the reaction uncatalysed by molecular iodine.

We have also briefly investigated the reaction in the presence of iodine by similar methods and under similar conditions to those employed for reactions with allyl alcohol present. Some experiments were conducted under argon in vessels stoppered with silicone rubber closures. To prevent absorption of molecular iodine by these closures other experiments were conducted in glass-stoppered vessels, but in this case the solution was in contact with a small volume of air. Very similar results were obtained by the two methods. Two different sets of reaction concentrations were used for these experiments which, except for the absence of allyl alcohol and addition of iodine, were under similar conditions to experiments in our study of the uncatalysed reaction. In one set, $[\mathrm{Fe}^{2+}]_0 = 1.8$—14.4, $[\mathrm{IO_3}^-]_0 = 0.16$—0.48, $[\mathrm{I_2}]_0 = 0.192$—0.96 mmol dm$^{-3}$, and in the other, $[\mathrm{Fe}^{2+}]_0 = 0.107$—0.908, $[\mathrm{IO_3}^-]_0 = 23.4$—96, $[\mathrm{I_2}]_0 = 0.058$—1.73 mmol dm$^{-3}$. Both sets were at [H$^+$] = 0.54 mol dm$^{-3}$, ionic strength = 3.1 mol dm$^{-3}$ (NaClO$_4$), and 35.0 °C. We are unable to suggest a kinetic equation which accords with all our results, but various generalisations can be made. In both sets of conditions the rate of reaction increases with increase in [Fe$^{2+}$] and [IO$_3^-$]; the order in each is nearer to 0.5 than to unity. The order in I$_2$ does not exceed 0.5, and the rate appears to be independent of [Fe$^{3+}$].

These results enable one possible mechanism to be excluded as a major contributor to the overall reaction: $2\mathrm{Fe}^{2+} + \mathrm{I_2} \longrightarrow 2\mathrm{Fe}^{3+} + 2\mathrm{I}^-$ as the slow step, followed by the rapid scavenging of iodide by iodate. The initial reaction between iodide and iodate may yield iodine-containing intermediates capable of oxidising iron(2+), the overall set of scavenging reactions being $\mathrm{I}^- + \mathrm{IO_3}^- + 4\mathrm{Fe}^{2+} \longrightarrow \mathrm{I_2} + 4\mathrm{Fe}^{3+}$. The reaction between iron(2+) and molecular iodine is first order in each reactant,[7] so that this mechanism for the iodine catalysis should lead to a rate independent of [IO$_3^-$] and first order in both iron(2+) and iodine, in contrast to our observations. Moreover, we have measured the initial rate of reduction of iodine by iron(2+) under conditions of reactant concentration, hydrogen-ion concentration, ionic strength, and temperature similar to those of the iodine catalysis experiments. Because of the probable induced oxidation of iron(2+) as a result of the scavenging of iodide by iodate, the rate of formation of iron(3+) may be up to ten times the rate of disappearance of molecular iodine through its direct reaction with iron(2+). Making allowance for this multiplying effect, the expected rate of oxidation of iron(2+) by iodate in the presence of iodine is less than one tenth of the observed rate. Although this set of reactions must occur, it cannot alone be responsible for the catalysis. The fractional orders in reactants may indicate the occurrence of a chain reaction, and it is possible that species, *e.g.* iodine-containing free radicals, formed in the scavenging reactions may act as chain carriers.

*Stoicheiometry in the Presence of Saturated Alcohols.*—We referred in the introduction to our unsuccessful attempt [3] to show the formation of active free radicals in the system iodate plus iron(2+) by investigating the effect of high concentrations of saturated aliphatic alcohols upon the consumption ratio $\Delta[Fe^{2+}] : \Delta[IO_3^-]$. Reaction of a free radical with the alcohol should lead to a decrease in this ratio. It was not expected that $\cdot IO_2$ or $\cdot I$ would abstract a hydrogen atom from an alcohol, but abstraction by $\cdot IO$ seemed a possibility because $\cdot BrO$ and $\cdot ClO$ show similar and considerable reactivity in this respect. We have now realised that under the conditions of these early experiments with iodate, the reaction goes predominantly by the path catalysed by iodine. This may provide alternative steps to that giving rise to the radical $\cdot IO$. Consequently we have repeated the earlier stoicheiometry experiments on the system iodate plus iron(2+) with sufficient allyl alcohol present to suppress the catalysis by iodine. Several experiments were done with initial concentrations in the region of 0.95 mmol $dm^{-3}$ $IO_3^-$, 3.8 mmol $dm^{-3}$ allyl alcohol, 19.2 mmol $dm^{-3}$ $Fe^{2+}$, and 2.0 mol $dm^{-3}$ propan-2-ol. From these, $\Delta[Fe^{2+}]/\Delta[IO_3^-] = 3.95 \pm 0.05$, giving no evidence for active free radicals. In the reactions of bromate and chlorate with iron(2+) under similar conditions a drop in consumption ratio of at least 0.7 is observed.

Thermochemical considerations suggest that the free radical $\cdot IO$ should be just as capable as $\cdot BrO$ or $\cdot ClO$ of abstracting an $\alpha$-hydrogen atom from an alcohol. The bond-dissociation energy for H–OI seems likely to be similar to that for H–OBr and H–OCl, *i.e. ca.* 410 kJ $mol^{-1}$ (calculated from data in ref. 8), and somewhat larger than that for the $\alpha$-hydrogen of an alcohol; the bond-dissociation energy for the $\alpha$-hydrogen in methanol is 385 kJ $mol^{-1}$.[9] However, the effect of an alcohol on the consumption ratio occurs through a competition for the active radical between the alcohol and iron(2+), diminishing the amount of the latter which is oxidised. The lack of induced oxidation of saturated alcohols in the iodate plus iron(2+) system may be an indication of a much more rapid electron transfer between $Fe^{2+}$ and $\cdot XO$ when X = I so that the competition between $Fe^{2+}$ and the alcohol is much less favourable for hydrogen abstraction from the latter, compared with the two cases X = Br or Cl. Alternatively, we note that except at low $[Fe^{2+}]$ the preferred step in the reduction of iodate is to iodine(III), $IO_2^-$, avoiding the formation of the free radical $\cdot IO_2$. Either by a similar reaction or by disproportionation the subsequent disappearance of iodine(III) may likewise avoid free-radical formation and proceed directly to iodine(I).

Although the mechanism of reduction of iodate by iron(2+) is uncertain in various respects, it is clear that this reaction differs markedly from the corresponding reductions of bromate and chlorate by iron(2+). The two latter reactions show similarity one to the other in their various characteristics. Each follows relatively simple kinetics, being first order in halate and in iron(2+).[10,11] As we have found, the reduction of iodate shows more complicated behaviour. Again, the bromate and chlorate systems give rise to active oxohalogen free radicals in addition to the halogen atoms. In the iodate system it is possible that the free radical $\cdot IO$ is not formed; if it is an intermediate, then its reactivity characteristics differ considerably from $\cdot BrO$ and $\cdot ClO$.

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