# Kinetics & Mechanism of Reduction of Iodine by Fe(II) in the Presence of Sodium Fluoride

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The reduction of iodine by Fe(II) in the presence of complexant sodium fluoride is first order with respect to both [iodine] and [Fe(II)] and is catalysed by fluoride ion. The reaction rate is inversely proportional to [H+] and iodide ion also retards the reaction rate. The rate constant decreases with increasing ionic strength and also with increasing dielectric constant of the medium. A suitable reaction mechanism, involving a reaction between the [FeF]+ and I2 has been suggested.

IN earlier publications from this laboratory, the kinetics of the reduction of iodine by Fe(II) in the presence of acetate buffers[1] and Fe(II)-EDTA complex[2] were reported. It has also been observed that in the presence of fluoride the reducing potentiality of iron(II) is enhanced[3,4] whereas normally ferric salts liberate iodine from a solution of potassium iodide. Berthond and Allmen[5] studied this reaction and observed that further investigation is desirable. The present paper deals with a systematic kinetic study of this reaction and a suitable mechanism is proposed.

## Materials and Methods

Ferrous ammonium sulphate (AnalaR, BDH), $H_2SO_4$ (AR grade), iodine (E. Merck), sodium thiosulphate (AnalaR, BDH), NaF, $HClO_4$ (Reidel), KI (AnalaR, BDH), sodium perchlorate (Riedel) and absolute alcohol were used. A standard stock solution of ferrous ammonium sulphate was prepared in doubly distilled water containing a known amount of $H_2SO_4$ so as to give its final acid concentration as $0.1 N$. Iodine solution was prepared by dissolving it in a solution containing known amount of potassium iodide. All other solutions were prepared in doubly distilled water and standardised wherever necessary.

The reaction was initiated by mixing the requisite quantity of iodine solution with the solutions of ferrous ammonium sulphate, NaF and $H_2SO_4$ in a reaction bottle coated black from outside. All the solutions were equilibrated before mixing.

The progress of the reaction was followed by estimating the amount of unreacted iodine after suitable intervals of time by titration against the standard sodium thiosulphate solution using starch as indicator.

## Results and Discussion

*Effect of varying [iodine]* — The order with respect to iodine was studied by isolation method employing constant excess of [KI]. The range of iodine concentration was $(1.0-2.5) \times 10^{-4}M$. A linear relationship was obtained by the plot of log $a/a-x$ against time indicating order with respect to iodine as unity. It was also observed that the reaction rate slightly decreased in the later stages and this may be attributed to an increase in [iodide] with the progress of reaction which has a retarding effect.

*Effect of varying [Fe(II)]* — The average first order rate constants at different [Fe(II)] and constant concentrations of other reactants are given in Table 1. The results show that the order with respect to iron(II) is also unity.

TABLE 1 — PSEUDO-FIRST ORDER RATE CONSTANTS AT DIFFERENT [Fe(II)]

$\{[I_2] = 2.5 \times 10^{-4}M; [KI] = 1.0 \times 10^{-3}M; [NaF] = 5.0 \times 10^{-2}M; [H_2SO_4] = 5.0 \times 10^{-2}M; \text{temp. } 30°C\}$

| [Fe(II)] × 10³ (M) | $k_1 \times 10^4$ sec⁻¹ | $k_1/$[Fe(II)] |
|---|---|---|
| 2·5 | 2·16 | 0·864 |
| 5·0 | 4·28 | 0·856 |
| 7·5 | 6·03 | 0·804 |
| 10·0 | 8·03 | 0·803 |
| 15·0 | 11·70 | 0·780 |
| 20·0 | 15·10 | 0·755 |

TABLE 2 — PSEUDO-FIRST ORDER RATE CONSTANTS AT DIFFERENT [NaF]

$\{[I_2] = 2.5 \times 10^{-4}M; [KI] = 1.0 \times 10^{-3}M; [Fe(II)] = 5.0 \times 10^{-3}M; [NaClO_4 + HClO_4] = 3.0 \times 10^{-2}M; \text{buffer } (pH\ 2) = 50 \text{ ml}; \text{temp. } 30°; \mu = 0.166\}$

| [NaF] × 10² (M) | [HClO₄] × 10² (M) | [NaClO₄] × 10² (M) | $k_1 \times 10^5$ sec⁻¹ |
|---|---|---|---|
| 0·5 | 0·5 | 2·5 | 8·55 |
| 1·0 | 1·0 | 2·0 | 9·37 |
| 1·5 | 1·5 | 1·5 | 10·76 |
| 2·0 | 2·0 | 1·0 | 11·54 |
| 2·5 | 2·5 | 0·5 | 12·57 |
| 3·0 | 3·0 | 0·0 | 13·42 |

*Effect of varying [NaF]* — Average $k_1$ values at different [NaF] are given in Table 2. Since the [H⁺] and ionic strength of the medium also influence the reaction rate, hence this study was carried out in the presence of a fixed amount of buffer of $pH$ 2 (KCl+HCl mixture) and the total ionic strength was also kept constant by adding requisite amounts of HClO₄ and NaClO₄.

A linear plot is also obtained between the rate of the reaction and [NaF]. The linear plot, however, has an intercept, which indicates that there must be a term in rate law independent of [fluoride], i.e. there must be a direct reaction between Fe(II) and iodine. A similar intercept was also observed in the reaction between Fe(II) and iodine in the presence of acetate[1]. The reaction between ferrous sulphate and iodine was earlier studied by Dhar and Banerjee[6], who also observed the inhibiting effect of acid on this reaction. Hershey and Bray[7] studied the Fe(III)-I⁻/Fe(II)-I₂ equilibrium, and they too observed the retarding effect of H⁺ and I⁻ in the reaction between Fe(II) and iodine.

*Effect of varying [acid]* — The average $k_1$ values at different [H₂SO₄] and [HClO₄] are given in Table 3. The plots of log $k_1$ vs [Free acid] are linear with similar negative slopes ($\approx -1.07$). Similarly a plot of $k_1$ vs 1/[Free acid] is also linear without any intercept. It thus shows that the reaction rate is inversely proportional to [H⁺] and there is no term free of [acid].

The [free acid] has been calculated by subtracting the [NaF] from the concentration of H₂SO₄ or HClO₄ to account for its neutralization. It is assumed that HF so produced being a weak acid[8] will not make any significant contribution towards [H⁺] in the presence of excess of H₂SO₄ or HClO₄.

*Effect of varying [iodide]* — The average $k_1$ values at different [I⁻] are given in Table 4. A plot of $1/k_1$ vs [I⁻] is linear with an intercept $=1.95 \times 10^3$ and slope $= 8.94 \times 10^5$. This shows the retarding effect of iodide ions on the reduction of iodine by Fe(II) in the presence of sodium fluoride.

*Effect of temperature* — From Arrhenius plots, the overall energy of activation ($E_a$), was calculated to be 18.5 kcal/mole. Other thermodynamic parameters calculated at 30° were: $\Delta S^\ddagger = -7.01$ e.u; frequency factor (A) $= 5 \times 10^{11}$ litre mole⁻¹ sec⁻¹; and $\Delta F^\ddagger = 20.6$ kcal mole⁻¹.

*Effect of varying solvent composition and ionic strength* — Table 5 shows the average $k_1$ values for a particular set, at varying ionic strengths and dielectric constants of the medium. Ionic strength was varied by adding different amounts of standard sodium perchlorate solution, whereas the variation of dielectric constant was achieved by changing the ethanol content of ethanol-water mixture used as the reaction medium.

The results show that the rate constants decrease with increasing ionic strength as well as dielectric constant of the medium. A plot of log $k_1$ at $\mu = 0$ (obtained by extrapolation) against $1/D$ is linear with positive slope $= 46.1$.

Such a behaviour[9,10] could be due to either a reaction between oppositely charged ions, or a reaction between a positive ion and a neutral mole-

**TABLE 3 — PSEUDO-FIRST ORDER RATE CONSTANTS AT DIFFERENT [H₂SO₄] AND [HClO₄]**

{[I₂] $= 2.5 \times 10^{-4}M$; [KI] $= 1.0 \times 10^{-3}M$; [Fe(II)] 5.0 $\times 10^{-3}M$ [NaF] $= 2.5 \times 10^{-2}M$; Temp. 30°; $\mu = 0.135$}

| [Acid] $\times 10^2 N$ | [NaClO₄] $\times 10^2 M$ | [Free acid] $\times 10^2 N$ | $pH$ | $k_1 \times 10^5$ sec⁻¹ |
|---|---|---|---|---|
| | | H₂SO₄ | | |
| 2.5 | — | — | 3.2 | 32.7 |
| 4.0 | — | 1.5 | 2.85 | 9.08 |
| 5.0 | — | 2.5 | 2.70 | 5.48 |
| 10.0 | — | 7.5 | 2.30 | 1.38 |
| 20.0 | — | 17.5 | 1.95 | 0.96 |
| | | HClO₄ | | |
| 3.0 | 7.0 | 0.5 | | 6.00 |
| 4.0 | 6.0 | 1.5 | | 4.26 |
| 5.0 | 5.0 | 2.5 | | 2.50 |
| 10.0 | — | 7.5 | | 0.55 |

**TABLE 4 — PSEUDO-FIRST ORDER RATE CONSTANTS AT DIFFERENT [I⁻]**

{[I₂] $= 2.5 \times 10^{-4}M$; [Fe (II)] $= 5.0 \times 10^{-3}M$; [NaF] $= 2.5 \times 10^{-2}M$; [H₂SO₄] $= 2.5 \times 10^{-2}M$}

| [KI] $\times 10^4 M$ | $k_1 \times 10^5$ sec⁻¹ | [KI] $\times 10^4 M$ | $k_1 \times 10^5$ sec⁻¹ |
|---|---|---|---|
| 4.0 | 42.60 | 15.0 | 31.50 |
| 5.0 | 42.00 | 20.0 | 27.25 |
| 10.0 | 33.20 | 25.0 | 23.80 |

**TABLE 5 — PSEUDO-FIRST ORDER RATE CONSTANTS AT DIFFERENT IONIC STRENGTHS AND SOLVENT COMPOSITION**

{[I₂] $= 2.50 \times 10^{-4}M$; [KI] $= 1.0 \times 10^{-3}M$; [Fe(II)] $= 5.0 \times 10^{-3}M$; [NaF] $= 2.5 \times 10^{-2}M$; [HClO₄] $= 2.5 \times 10^{-2}N$}

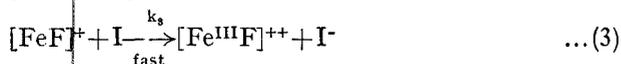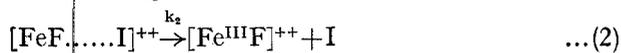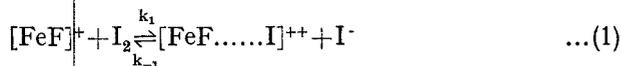| $\mu$ | Av. $k_1 \times 10^5$ sec⁻¹ | | | | |
|---|---|---|---|---|---|
| | Blank | Ethyl alcohol | | | |
| | | 5% | 10% | 15% | 20% |
| 0.061 | 23.50 | 27.53 | 28.56 | 29.60 | 30.53 |
| 0.086 | 21.28 | 24.76 | 25.90 | 27.00 | 27.61 |
| 0.111 | 19.15 | 23.20 | 23.43 | 24.78 | 25.38 |
| 0.136 | 18.03 | 21.80 | 22.30 | 22.90 | 24.00 |
| 0.0* | 76.6 | 81.3 | 82.3 | 83.5 | 84.4 |

*Extrapolated values.

cule, if a decrease in the rate constant with increasing $\mu$ could be ascribed to negative secondary salt effect.

*Mechanism* — With fluoride, ferric ion is known to form stable complexes[11] but complexation with ferrous is not very strong[12] ($K < 30$ which is comparable to FeCl²⁺ complex). Nevertheless to explain the catalytic nature of fluoride, it may be assumed, that in this reaction the ferrous ions first combine with fluoride to form [FeF⁺] complex[12] which in spite of its weak nature is present in appreciable concentration to initiate the reaction. Further as it is consumed, more of it may be produced because of the equilibrium operating therein.

It may thus explain why the reaction rate is directly proportional to $[F^-]$. Srivastava et al.[13] also assumed the formation of $[FeF^+]$ complex to explain the catalytic role of fluoride in the reduction of Se(IV) by Fe(II).

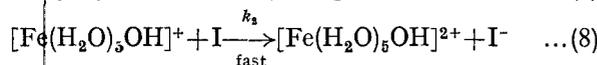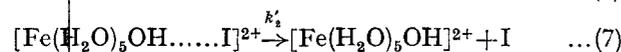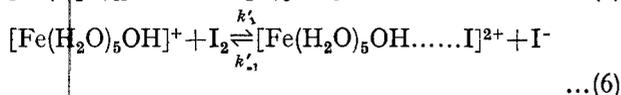Thus the reaction mechanism may be represented as shown in Eqs. (1-3).

$$[FeF]^+ + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FeF......I]^{++} + I^- \qquad ...(1)$$

$$[FeF......I]^{++} \overset{k_2}{\rightarrow} [Fe^{III}F]^{++} + I \qquad ...(2)$$

$$[FeF]^+ + I \underset{fast}{\overset{k_3}{\longrightarrow}} [Fe^{III}F]^{++} + I^- \qquad ...(3)$$

By applying steady stationary treatment the rate expression is given by Eq. (4)

$$\frac{-d[\Sigma I_2]}{dt} = \frac{k_1 k_2 K K_a [I_2][Fe^{2+}][HF]}{[H^+](k_{-1}[I^-]+k_2)} \qquad ...(4)$$

where $K_a$ is the dissociation constant of HF and $K$ is the stability constant of the complex ion $FeF^+$.

Since a plot of $k_1$ vs $[F^-]$ shows an intercept, the rate law must have a term independant of HF, i.e. there must be a direct reaction between Fe(II) and iodine, in which $H^+$ and $I^-$ ions have an inhibiting effect[7]. The mechanism for this part of the reaction may be represented by Eqs. (5-8).

$$[Fe(H_2O)_6]^{2+} \rightleftharpoons [Fe(H_2O)_5OH]^+ + H^+ \qquad ...(5)$$

$$[Fe(H_2O)_5OH]^+ + I_2 \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} [Fe(H_2O)_5OH......I]^{2+} + I^- \qquad ...(6)$$

$$[Fe(H_2O)_5OH......I]^{2+} \overset{k'_2}{\rightarrow} [Fe(H_2O)_5OH]^{2+} + I \qquad ...(7)$$

$$[Fe(H_2O)_5OH]^+ + I \underset{fast}{\overset{k_3}{\longrightarrow}} [Fe(H_2O)_5OH]^{2+} + I^- \qquad ...(8)$$

Thus the full expression may be represented by Eq. (9)

$$k = \frac{k_1 k_2 K K_a [I_2][Fe^{2+}][HF]}{[H^+](k_{-1}[I^-]+k_2)} + \frac{k'_1 k'_2 K_d [I_2][Fe^{2+}]}{[H^+](k'_{-1}[I^-]+k'_2)} \qquad ...(9)$$

where $K_d$ is the equilibrium constant for step (5) in the above scheme.

The rate expression is quite consistent with the observed experimental results discussed above. From the intercept and the slope of the plot of $1/k_1$ versus $[I^-]$, $k_1$ and $k_{-1}/k_2$ values have been estimated as $k_1 = 630$ and $k_{-1}/k_2 = 458$. Since $k_{-1} > k_2$, it is quite evident that the term $k_{-1}[I^-]$ in the rate expression is quite significant and cannot be neglected. In other words the reaction cannot be independent of $[I^-]$, which has a retarding effect, and thus it supports the proposed mechanism. The observed negative entropy may be attributed to a net increase in charge on the activated complex. Further since the product $(Fe^{III}F)^{2+}$ is a stable complex, the concentration of free $Fe^{3+}$ ions must remain suppressed, and any chance of the backward reaction between $Fe^{III}$ and $I^-$ in the $Fe^{2+}-I_2/Fe^{3+}-I^-$ equilibrium is completely prevented, so that the reduction of iodine by $Fe^{2+}$ ion in the presence of complexant fluoride proceeds to completion.

## References

1. SRIVASTAVA, R. K., SRIVASTAVA, M. N. & SAXENA, B. B. L., Z. phys. Chem., **255** (1974), 133.
2. VARMA, H. S., SRIVASTAVA, M. N. & SAXENA, B. B. L., Indian J. Chem., **13** (1975), 54.
3. MOELLER, T., Inorganic chemistry (Asia Publishing House, New Delhi), 1963, 302.
4. VARMA, H. S., SRIVASTAVA, M. N. & SAXENA, B. B. L., Vijnana Parishad anusandhan patrika (Allahabad, India), **10** (1967), 7.
5. BERTHOND, A. & ALLMEN, S. V., J. Chim. phys., **30** (1933), 186.
6. BANERJI, R. C. & DHAR, N. R., Z. anorg. allgem. Chem., **134** (1924), 172.
7. HERSHEY, A. V. & BRAY, W. C., J. Am. chem. Soc., **58** (1936), 1760.
8. VOGEL, A. I., Qualitative inorganic analysis (Longmans, London), 1953, 27.
9. FROST, A. A. & PEARSON, R. G., Kinetics and mechanism (John Wiley, New York), 1961, 148.
10. AMIS, E. S., Kinetics of chemical change in solution (Macmillan, London), 1949, 174.
11. COTTON, F. A. & WILKINSON, G., Advanced inorganic chemistry (Interscience, London), 1962, 716.
12. DODGEN, H. W. & ROLLEFSON, G. K., J. Am. chem. Soc., **71** (1949), 260.
13. SRIVASTAVA, R. K., SRIVASTAVA, V. K., SRIVASTAVA, M. N. & SAXENA, B. B. L., J. Chim. phys., **70** (1973), 918.