# Kinetic Approach to the Reduction of Ethylene diaminetetra acetatoferrate (III) Complex by Iodide Ion in Aqueous Acidic Medium

ABSTRACT

The kinetic approach to the reduction of ethylenediaminetetraacetatoferrate(III) complex (hereafter [Fe(III)EDTA]$^-$) by iodide ion has been studied spectrophotometrically in an aqueous acidic medium. The study was carried out under pseudo-first order conditions of an excess of iodide ion concentration at $28 \pm 1°C$, Ionic strength (I) = 0.43 mol dm^{-3} (KNO$_3$) and [H$^+$] = 5.0×10^{-2} mol dm^{-3}. The [Fe(III)EDTA]$^-$ complex was reduced according to the reaction;

$2[Fe(III)EDTA]^- + 2I^- \rightarrow 2[Fe(II)EDTA]^{2-} + I_2$
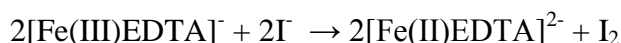
The rate law is - d[Fe(III)EDTA$^-$]/dt = k[I$^-$][Fe(III)EDTA$^-$]. The rate of the reaction is first order in oxidant and reductant concentrations. On the basis of catalysis by added anion, Michaelis-Menten plots and the absence of intermediates, the outer-sphere electron transfer mechanism is proposed for the reaction.

Keywords: Kinetics, Mechanism, Iodide, Reduction, Ethylenediaminetetraacetatoferrate(III) Complex

1. Introduction

The determination of the most common iodine-containing molecules and ions found in environmental waters such as iodine (I$_2$), iodide (I$^-$) and iodate (IO$_3^-$) is critical in fields such as biological and environmental sciences [1]. The iodide salts being mild reducing agents are easily oxidized and some enzymes readily convert it into electrophilic iodinating agents as required for biosynthesis of iodide-containing natural products. The iodide is functional as antioxidant reducing specie that can destroy reactive oxygen species such as hydrogen peroxide [2]. The usefulness of this iodide ion in electron transfer reactions is a key in gaining knowledge about its mechanistic pathways. The kinetics of oxidation of iodide ion

32 with other species revealed the liberation of iodine gas [3,4,5]. The

33 aminocarboxylatoferrate(III) complex has been reduced by a few number of substrates

34 [6,7,8].

35 In this paper, we report the kinetics and mechanistic pathway of reduction of [Fe(III)EDTA]⁻

36 by iodide ion in aqueous nitric acid medium.

2. Experimental

38 The [Fe(III)EDTA]⁻ complex was prepared according to the method of Xiao-juan [6] and was

39 characterized spectrophotometrically. The UV/Visible spectrum of [Fe(III)EDTA]⁻ was

40 scanned between ranges of 300 – 800 nm and gave λ_{max} of 308 and 470 nm.

41 Standard solution of nitric acid (Sigma-Aldrich) was prepared by diluting concentrated acid

42 (70 %, specific gravity 1.413) using distilled water. KNO_3 (BDH) was used to maintain ionic

43 strength. The complex stock solution had a concentration of about 0.05 mol dm⁻³. A stock

44 solution of calcium oxalate was prepared by weighing known amount and dissolving in

45 known volume of distilled water.

46

2.1 Stoichiometric studies

48 The stoichiometry was determined by spectrophotometric titration using the mole ratio

49 approach [9] under the reaction condition [Fe(III)EDTA⁻] = 4.0×10^{-3} mol dm⁻³, I = 0.43 mol

50 dm⁻³, [H⁺] = 5.0×10^{-2} mol dm⁻³, [I⁻] = $(0.56 – 1.04) \times 10^{-2}$ mol dm⁻³.

2.2 Kinetic measurements

52 The kinetic measurements were carried out at the wavelength of 470 nm by monitoring the

53 decrease in absorbance of the reaction mixture as the reaction progressed. The reaction was

54 carried out under Pseudo-first order conditions with the concentration of iodide ion 10-fold in

55 excess over [Fe(III)EDTA⁻]. Ionic strength of the reaction mixture was kept constant at 0.43

56 mole dm⁻³ (KNO_3) and [H⁺] at 5.0×10^{-2} mol dm⁻³. A plot between $\ln(A_t - A_\infty)$ and time, t

57 were linear for over 80 % extent of reaction. Pseudo-first order rate constants, k_1 were

58 determined as the slopes of the above plots as given by the equation:

59 $$\log(A_0 - A_\infty) - \log(A_t - A_\infty) = \frac{K_1 t}{2.303} \tag{1}$$

60 The second order rate constants, k_2 were obtained as the ratios of k_1 to [I⁻].

61 The influence of [H$^+$] on the rate of the reaction was investigated using nitric acid in the

62 range 6.0 x 10^{-2} mol dm^{-3} ≤ [H$^+$] ≤ 1.0 x 10^{-1} mol dm^{-3}, while the [Fe(III)EDTA$^-$] and [I$^-$]

63 were kept constant. The reaction was carried out at 28 ± 1°C and I = 0.43 mol dm^{-3} (KNO$_3$).

64 The effect of ionic strength on the rate of the reaction was investigated in the range I = 0.05 –

65 0.07 mol dm^{-3} KNO$_3$, while the concentration of other reagents was kept constant.

66 The effect of added oxalate ions on the rate of the reaction was investigated for Ca^{2+} = (5.0 –

67 6.4) x 10^{-3} mol dm^{-3} while the concentrations of all other reactants were kept constant.

68

69 **2.3 Product analysis**

70 The UV/Visible spectrum of the reaction product was scanned between wavelength ranges of

71 400 - 600 nm gave a λ_{max} of 520 nm, which is characteristic of the Fe(II) product [10,11], and

72 the appearance of a brown solution which turns to soil precipitate on addition of potassium

73 permanganate reveals the presence of Fe(II) product [12].

74 **3. Results and discussion**

75 The spetrophotometric titrations showed oxidant - reductant ratio of 1:1 represented by the

76 stoichiometric equation;

77 2[Fe(III)EDTA]$^-$ + 2I$^-$ → 2[Fe(II)EDTA]$^{2-}$ + I$_2$ (2)

78 Stoichiometry 1:1 obtained in this reaction has been documented with reaction involving

79 iodide ions [3,4,5].

80 The pseudo-first order plot is linear for greater than 80 % extent of reaction. This implies that

81 the order of the reaction is one with respect to [Fe(III)EDTA]$^-$ concentration (Figure 1). The

82 rate of the reaction increases with increase in [I$^-$] with a slope of 0.920, suggesting that the

83 reaction is first-order in [I$^-$] as shown in Table 1. A similar first order dependence of rate of

84 reaction was observed for iodide ion [3,4,5] and for [Fe(III)EDTA]$^-$ [13,14,15,16,17].

85 The rate law for the reaction is given as equation (3)

86 $$-\frac{d[Fe(III)EDTA^-]}{dt} = k[I^-][Fe(III)EDTA^-]$$ (3)

87 Within the range 6.0 x 10^{-2} mol dm^{-3} ≤ [H$^+$] ≤ 1.0 x 10^{-1} mol dm^{-3} and constant ionic strength

88 0.43 mole dm^{-3} KNO$_3$. The rate of the reaction decreases with increase in [H$^+$] (Table 1). The

89 plot of k$_2$ versus [H$^+$]$^{-1}$ was linear with an intercept and the acid dependence of this nature

90 indicates that there are two pathways for the electron transfer: one being independent of

hydrogen ion concentration and the other has inverse dependence on the hydrogen ion concentration. The two rate-controlling paths are preceded by rapid deprotonation equilibrium, and both protonated and deprotonated forms are reactive [18].
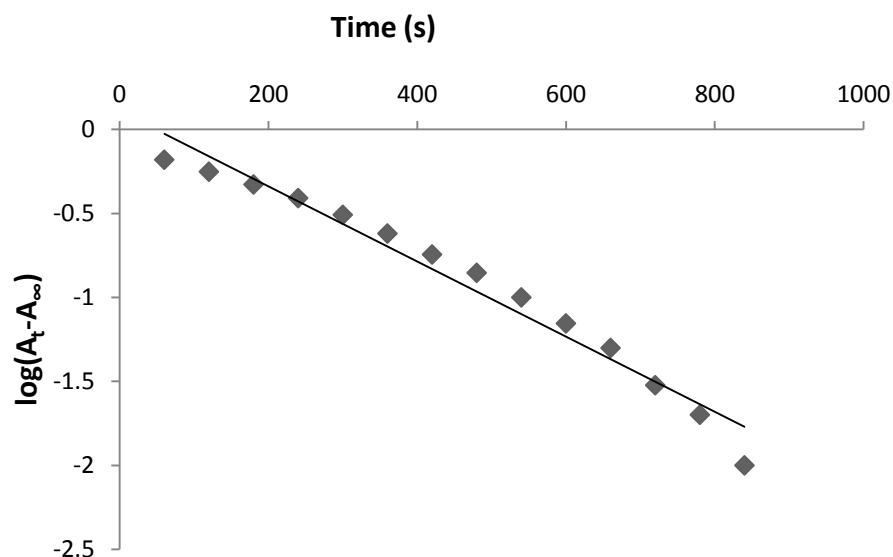
Figure 1: Typical Pseudo-first Order Plot for the Reaction of [Fe(III)EDTA]$^-$ and I$^-$ at [Fe(III)EDTA$^-$] = 4.0 × 10^{-3} mol dm^{-3}, [I$^-$] = 9.0 × 10^{-2} mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO$_3$), [H$^+$] = 5.0 × 10^{-2} mol dm^{-3}, T = 28 ± 1°C, and λ_{max} = 470 nm.
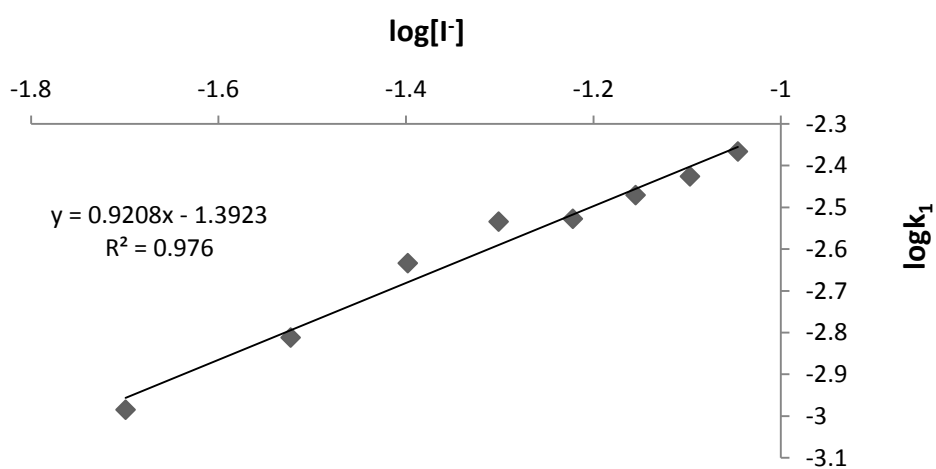
Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of [Fe(III)EDTA]$^-$ and I$^-$ at [Fe(III)EDTA$^-$] = 4.0 x 10^{-3} mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO$_3$), [H$^+$] = 5.0 x 10^{-2} mol dm^{-3}, T = 28 ± 1°C and λ_{max} = 470 nm.

10^2[I$^-$], mol dm^{-3}	10^1[H$^+$]	I, mol dm^{-3}	10^{3}k$_1$, s^{-1}	10^{2}k$_2$, dm^3 mol^{-1} s^{-1}
2.0	0.5	0.43	1.04	5.18
3.0	0.5	0.43	1.54	5.14
4.0	0.5	0.43	2.33	5.81
5.0	0.5	0.43	2.93	5.84
6.0	0.5	0.43	2.97	4.95
7.0	0.5	0.43	3.39	4.84
8.0	0.5	0.43	3.75	4.69
9.0	0.5	0.43	4.31	4.79
9.0	0.6	0.43	2.88	3.19
9.0	0.7	0.43	2.72	3.02
9.0	0.8	0.43	2.56	2.84

4

116	9.0	0.9	0.43	2.33	2.58
117	9.0	1.0	0.43	2.17	2.41
118	9.0	0.5	0.50	4.56	5.07
119	9.0	0.5	0.54	4.89	5.43
120	9.0	0.5	0.58	5.26	5.84
121	9.0	0.5	0.62	5.37	5.97
122	9.0	0.5	0.66	5.90	6.56
123	9.0	0.5	0.70	6.21	6.90

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Figure 2: Plot of log k_1 versus log $[I^-]$ for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[I^-] = (2.0 - 9.0) \times 10^{-2}$ mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO$_3$), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, T = 28 ± 1°C, and λ_{max} = 470 nm

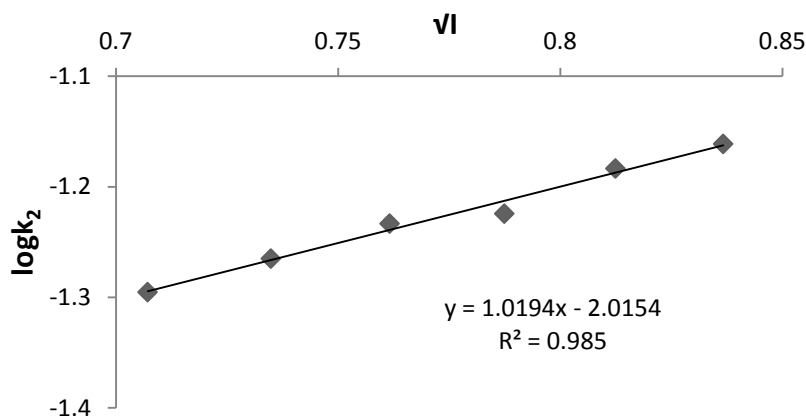
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Figure 3: Plot of k_2 versus $[H^+]^{-1}$ for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-]$ = 5.0×10^{-3} mol dm^{-3}, $[I^-] = 9.0 \times 10^{-2}$ mol dm^{-3}, $I = 0.43$ mol dm^{-3} (KNO$_3$), $[H^+] = (0.6 - 1.0) \times 10^{-1}$ mol dm^{-3}, $T = 28 \pm 1°C$, and $\lambda_{max} = 470$ nm

The change in ionic strength from 0.5 to 0.7 mol dm^{-3} led to a progressive increase in the observed rate constant, k_1 (Table 1). Since the reductant and oxidant are anions, the observation is consistent with positive Bronsted–Debye salt effect, implying that the activated complex is composed of reactants of like charges [19].

y = 1.0194x - 2.0154
R² = 0.985

Figure 4: Plot log k_2 versus $\sqrt{I}$ for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-]$ = 5.0×10^{-3} mol dm^{-3}, $[I^-] = 9.0 \times 10^{-2}$ mol dm^{-3}, $I = (0.5 - 0.7)$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, $T = 28 \pm 1°C$, and $\lambda_{max} = 470$ nm

The plot of k_1^{-1} versus $[I^-]^{-1}$ gave a negligible intercept, suggesting unstable binuclear intermediate formation. Also, the added Ca^{2+} ions had effect on the rate of reaction by initiating an increase in the reaction rate. Since the reactant species are negatively charged, Ca^{2+} ion is expected to accelerate the rate by acting as a bridge between the reactants through an outer-sphere complex formation [20].
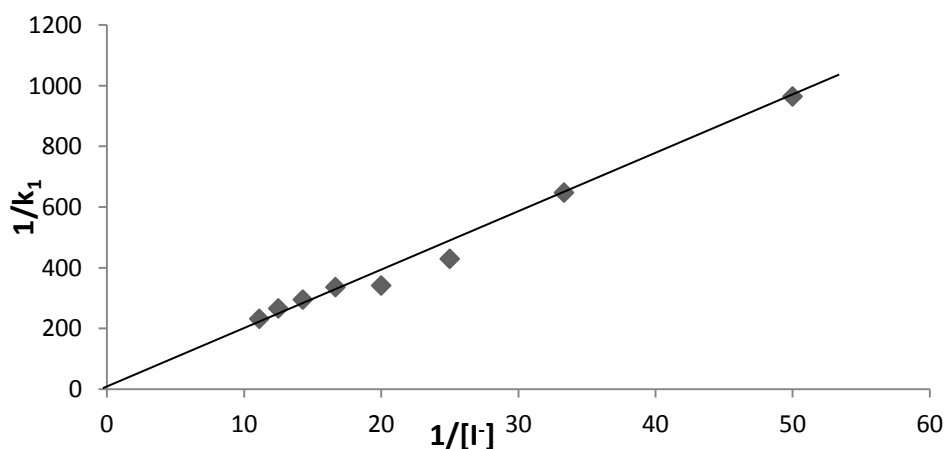
Figure 5: Michaelis-Menten Plot of $1/k_1$ versus $1/[I^-]$ for the Reduction of $[Fe(III)EDTA]^-$ by I^-

The outer-sphere mechanism is proposed for this reaction on ground that there was no detectable binuclear intermediate and the reaction is catalyzed by added ion.

$$I^- + H^+ \underset{}{\overset{K_{eq}}{\rightleftharpoons}} HI \tag{4}$$

$$[Fe(III)EDTA]^- + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(III)EDTA^-, I^-] \tag{5}$$

$$[Fe(III)EDTA^-, I^-] \xrightarrow[\text{slow}]{k_2} [Fe(II)EDTA]^{2-} + I^\bullet \tag{6}$$

$$[Fe(III)EDTA]^- + HI \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(III)EDTA^-, HI] \tag{7}$$

$$[Fe(III)EDTA^-, HI] \xrightarrow[\text{slow}]{k_4} [Fe(II)EDTA]^{2-} + I^\bullet + H^+ \tag{8}$$

$$I^\bullet + I^\bullet \xrightarrow[\text{fast}]{k_5} I_2 \tag{9}$$
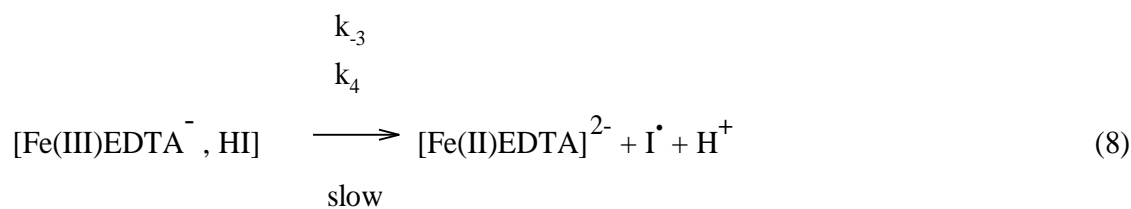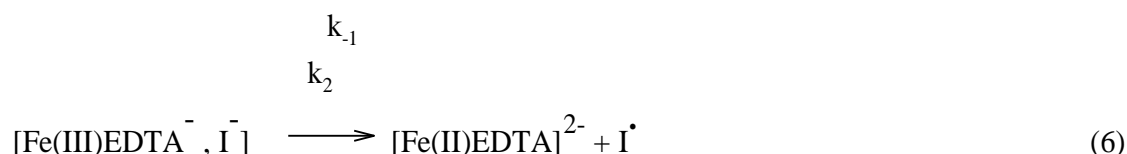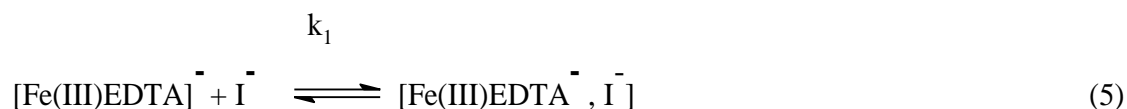
Rate $= k_2[Fe(III)EDTA^-, I^-] + k_4[Fe(III)EDTA^-, HI]$ $\qquad$ (10)

From equation (6);

$k_{-1}[Fe(III)EDTA^-, I^-] = k_1[Fe(III)EDTA^-][I^-]$ $\qquad$ (11)

$[Fe(III)EDTA^-, I^-] = \dfrac{k_1}{k_{-1}} [Fe(III)EDTA^-][I^-]$ $\qquad$ (12)

From equation (9);

$k_{-3}[Fe(III)EDTA^-, HI] = k_3[Fe(III)EDTA^-][HI]$ $\qquad$ (13)

$[Fe(III)EDTA^-, HI] = \dfrac{k_3}{k_{-3}} [Fe(III)EDTA^-][HI]$ $\qquad$ (14)

From equation (4);

$[HI] = K_{eq}[H^+][I^-]$ $\qquad$ (15)

163 Substitute equation (15) into (14);

164 $\quad$ $[\text{Fe(III)EDTA}^-, \text{HI}] = \dfrac{k_3 K_{eq[H^+]}}{k_{-3}} [\text{Fe(III)EDTA}^-][\text{I}^-]$ $\qquad$ (16)

165 Substitute equation (12) and (16) into (10);

166 $\quad$ Rate $= \dfrac{k_2 k_1}{k_{-1}} [\text{Fe(III)EDTA}^-][\text{I}^-]$ $+$ $=$ $\dfrac{k_4 k_3 K_{eq[H^+]}}{k_{-3}} [\text{Fe(III)EDTA}^-][\text{I}^-]$ $\qquad$ (17)

167 $\quad$ Rate $= \dfrac{k_2 k_1}{k_{-1}} + \dfrac{k_4 k_3 K_{eq[H^+]}}{k_{-3}} \left([\text{Fe(III)EDTA}^-][\text{I}^-]\right)$ $\qquad$ (18)

168 $\quad$ Rate $= k[\text{Fe(III)EDTA}^-][\text{I}^-]$ $\qquad$ (19)

169 $\quad$ Where k $= \dfrac{k_2 k_1}{k_{-1}} + \dfrac{k_4 k_3 K_{eq[H^+]}}{k_{-3}}$

170 The equation (19) conforms to the experimental rate law at equation (3).

171 **4. Conclusion**

172 The kinetics of reduction of ethylenediaminetetraacetatoferrate (III) complex by iodide ion

173 was studied in aqueous acidic medium and obtained a mole ratio of 1:1 (Complex: Oxidant).

174 The analysis of other kinetic data obtained under the pseudo-first order condition gave an

175 overall scenario of second order derivative. Further research is to be needed to obtain the

176 outer-sphere mechanistic pathway and plausible mechanistic pathway kinetic data.

177

178 **References**

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