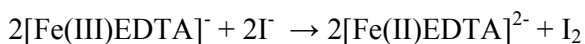


Kinetic Approach to the Reduction of Ethylenediaminetetraacetateferrate(III) Complex by Iodide Ion in Aqueous Acidic Medium

ABSTRACT

The kinetic approach to the reduction of ethylenediaminetetraacetateferrate(III) complex (hereafter $[\text{Fe(III)EDTA}]^-$) 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 $28 \pm 1^\circ\text{C}$, $I = 0.43 \text{ mol dm}^{-3}$ (KNO_3) and $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$. The $[\text{Fe(III)EDTA}]^-$ complex was reduced according to the reaction;



The rate law is $-\text{d}[\text{Fe(III)EDTA}]^-/\text{dt} = k[\text{I}^-][\text{Fe(III)EDTA}]^-$. 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, Ethylenediaminetetraacetateferrate(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 with other species revealed the liberation of iodine gas [3,4,5]. The

32 aminocarboxylatoferrate(III) complex has been reduced by a few number of substrates
33 [6,7,8].

34 In this paper, we report the kinetics and mechanistic pathway of reduction of [Fe(III)EDTA]⁻
35 by iodide ion in aqueous nitric acid medium.

36 2. Experimental

37 The [Fe(III)EDTA]⁻ complex was prepared according to the method of Xiao-juan [6] and was
38 characterized spectrophotometrically. The UV/Visible spectrum of [Fe(III)EDTA]⁻ was
39 scanned between ranges of 300 – 800 nm and gave λ_{\max} of 308 and 470 nm.

40 Standard solution of nitric acid (Sigma-Aldrich) was prepared by diluting concentrated acid
41 (70 %, specific gravity 1.413) using distilled water. KNO₃ (BDH) was used to maintain ionic
42 strength. The complex stock solution had a concentration of about 0.05 mol dm⁻³. A stock
43 solution of calcium nitrate was prepared by weighing known amount and dissolving in known
44 volume of distilled water.

45

46 2.1 Stoichiometric studies

47 The stoichiometry was determined by spectrophotometric titration using the mole ratio
48 approach [9] under the reaction condition [Fe(III)EDTA]⁻ = 4.0 × 10⁻³ mol dm⁻³, I = 0.1 mol
49 dm⁻³, [H⁺] = 5.0 × 10⁻² mol dm⁻³, [I⁻] = (0.56 – 1.04) × 10⁻² mol dm⁻³.

50 2.2 Kinetic measurements

51 The kinetic measurements were carried out at the wavelength of 470 nm by monitoring the
52 decrease in absorbance of the reaction mixture as the reaction progressed. The reaction was
53 carried out under Pseudo-first order conditions with the concentration of iodide ion 10-fold in
54 excess over [Fe(III)EDTA]⁻. Ionic strength of the reaction mixture was kept constant at 0.43
55 mole dm⁻³ (KNO₃) and [H⁺] at 5.0 × 10⁻² mol dm⁻³. A plot of (A_t - A_∞) versus time were
56 linear for over 80 % extent of reaction. Pseudo-first order rate constants, k₁ were determined
57 as the slopes of the above plots as given by the equation:

$$58 \log(A_t - A_\infty) = \frac{kt}{2.303} + \log(A_t - A_\infty) \quad (1)$$

59 The second order rate constants, k₂ were obtained as the ratios of k₁ to [I⁻].

60 The influence of [H⁺] on the rate of the reaction was investigated using nitric acid in the
61 range 6.0 × 10⁻² mol dm⁻³ ≤ [H⁺] ≤ 1.0 × 10⁻¹ mol dm⁻³, while the [Fe(III)EDTA]⁻ and [I⁻]
62 were kept constant. The reaction was carried out at 28 ± 1°C and I = 0.43 mol dm⁻³ (KNO₃).

63 The effect of ionic strength on the rate of the reaction was investigated in the range $I = 0.05 -$
 64 $0.07 \text{ mol dm}^{-3} \text{ KNO}_3$, while the concentration of other reagents was kept constant.

65 The effect of added oxalate ions on the rate of the reaction was investigated for $\text{Ca}^{2+} = (5.0 -$
 66 $6.4) \times 10^{-3} \text{ mol dm}^{-3}$ while the concentrations of all other reactants were kept constant.

67

68 **2.3 Product analysis**

69 The UV/Visible spectrum of the reaction product was scanned between wavelength ranges of
 70 $400 - 600 \text{ nm}$ gave a λ_{max} of 520 nm , which is characteristic of the Fe(II) product [10,11], and
 71 the appearance of a brown solution which turns to soil precipitate on addition of potassium
 72 permanganate reveals the presence of Fe(II) product [12].

73 **3. Results and discussion**

74 The spectrophotometric titrations showed oxidant - reductant ratio of 1:1 represented by the
 75 stoichiometric equation;



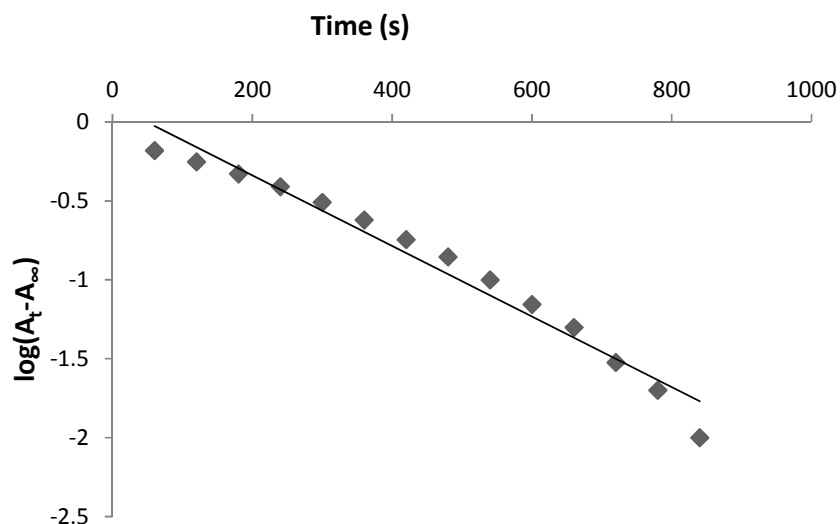
77 Stoichiometry 1:1 obtained in this reaction has been documented with reaction involving
 78 iodide ions [3,4,5].

79 The pseudo-first order plot is linear for greater than 80 % extent of reaction. This implies that
 80 the order of the reaction is one with respect to $[\text{Fe(III)EDTA}]^-$ concentration (Figure 1). The
 81 rate of the reaction increases with increase in $[\text{I}^-]$ with a slope of 0.920, suggesting that the
 82 reaction is first-order in $[\text{I}^-]$ as shown in Table 1. A similar first order dependence of rate of
 83 reaction was observed for iodide ion [3,4,5] and for $[\text{Fe(III)EDTA}]^-$ [13,14,15,16,17].

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

$$85 \quad -\frac{d[\text{Fe(III)EDTA}^-]}{dt} = k[\text{I}^-][\text{Fe(III)EDTA}^-] \quad (3)$$

86 Within the range $6.0 \times 10^{-2} \text{ mol dm}^{-3} \leq [\text{H}^+] \leq 1.0 \times 10^{-1} \text{ mol dm}^{-3}$ and constant ionic strength
 87 $0.43 \text{ mole dm}^{-3} \text{ KNO}_3$. The rate of the reaction decreases with increase in $[\text{H}^+]$ (Table 1). The
 88 plot of k_2 versus $[\text{H}^+]^{-1}$ was linear with an intercept and the acid dependence of this nature
 89 indicates that there are two pathways for the electron transfer: one being independent of
 90 hydrogen ion concentration and the other has inverse dependence on the hydrogen ion
 91 concentration. The two rate-controlling paths are preceded by rapid deprotonation
 92 equilibrium, and both protonated and deprotonated forms are reactive [18].



93

94

95

96 **Figure 1:** Typical Pseudo-first Order Plot for the Reaction of [Fe(III)EDTA]⁻ and I⁻ at
 97 [Fe(III)EDTA]⁻ = 4.0 × 10⁻³ mol dm⁻³, [I⁻] = 9.0 × 10⁻² mol dm⁻³, I = 0.43 mol dm⁻³ (KNO₃),
 98 [H⁺] = 5.0 × 10⁻² mol dm⁻³, T = 28 ± 1°C, and λ_{max} = 470 nm.

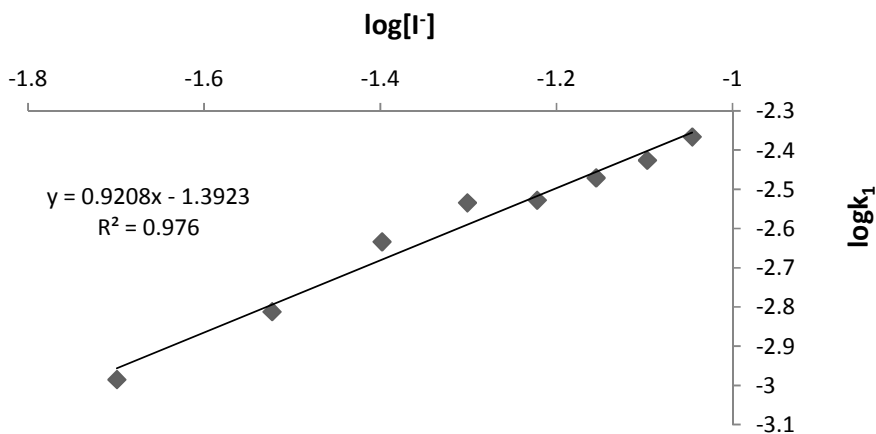
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100 **Table 1:** Pseudo-first Order and Second Order Rate Constants for the Reaction of
 101 [Fe(III)EDTA]⁻ and I⁻ at [Fe(III)EDTA]⁻ = 4.0 × 10⁻³ mol dm⁻³, I = 0.43 mol dm⁻³ (KNO₃),
 102 [H⁺] = 5.0 × 10⁻² mol dm⁻³, T = 28 ± 1°C and λ_{max} = 470 nm.

103	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
104	2.0	0.5	0.43	1.04	5.18
105	3.0	0.5	0.43	1.54	5.14
106	4.0	0.5	0.43	2.33	5.81
107	5.0	0.5	0.43	2.93	5.84
108	6.0	0.5	0.43	2.97	4.95
109	7.0	0.5	0.43	3.39	4.84
110	8.0	0.5	0.43	3.75	4.69
111	9.0	0.5	0.43	4.31	4.79
112	9.0	0.6	0.43	2.88	3.19
113	9.0	0.7	0.43	2.72	3.02
114	9.0	0.8	0.43	2.56	2.84
115	9.0	0.9	0.43	2.33	2.58
116	9.0	1.0	0.43	2.17	2.41
117	9.0	0.5	0.50	4.56	5.07
118	9.0	0.5	0.54	4.89	5.43

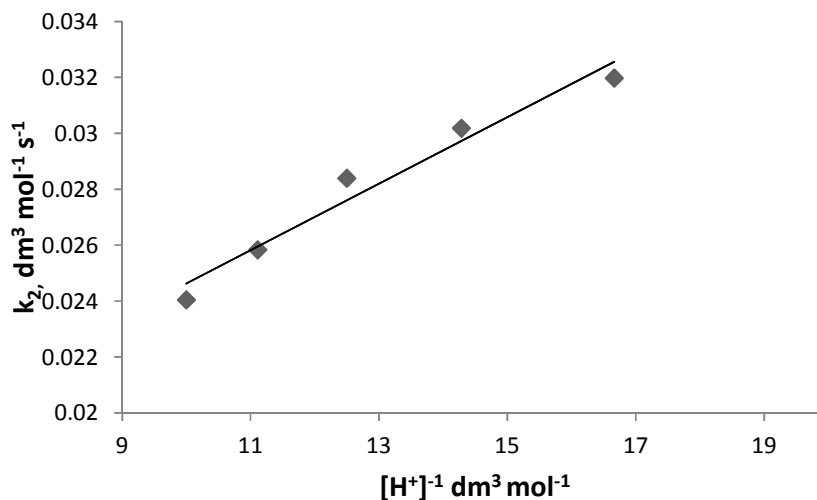
119	9.0	0.5	0.58	5.26	5.84
120	9.0	0.5	0.62	5.37	5.97
121	9.0	0.5	0.66	5.90	6.56
122	9.0	0.5	0.70	6.21	6.90

123



124

125 **Figure 2:** Plot of $\log k_1$ versus $\log [I^-]$ for the Reaction of $[\text{Fe(III)EDTA}]^-$ and I^- at
 126 $[\text{Fe(III)EDTA}]^- = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[I^-] = (2.0 - 9.0) \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.43 \text{ mol}$
 127 dm^{-3} (KNO_3), $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $T = 28 \pm 1^\circ\text{C}$, and $\lambda_{\text{max}} = 470 \text{ nm}$



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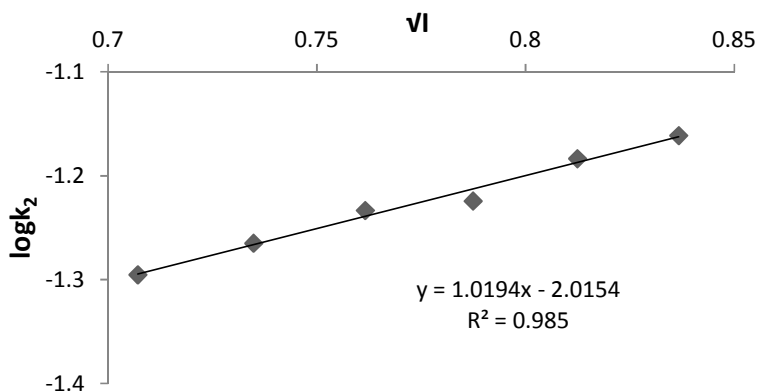
129 **Figure 3:** Plot of k_2 versus $[\text{H}^+]^{-1}$ for the Reaction of $[\text{Fe(III)EDTA}]^-$ and I^- at $[\text{Fe(III)EDTA}]^-$
 130 $= 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[I^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.43 \text{ mol dm}^{-3}$ (KNO_3), $[\text{H}^+] = (0.6$
 131 $- 1.0) \times 10^{-1} \text{ mol dm}^{-3}$, $T = 28 \pm 1^\circ\text{C}$, and $\lambda_{\text{max}} = 470 \text{ nm}$

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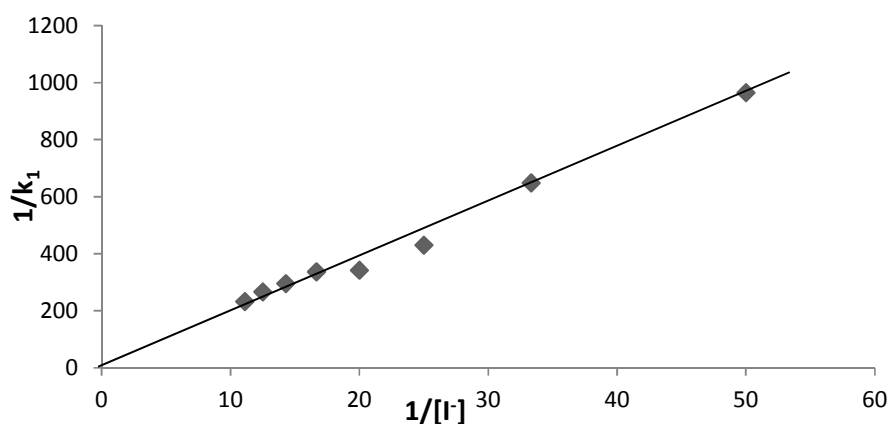
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135 The change in ionic strength from 0.5 to 0.7 mol dm⁻³ led to a progressive increase in the
 136 observed rate constant, k₁ (Table 1). Since the reductant and oxidant are anions, the
 137 observation is consistent with positive Bronsted–Debye salt effect, implying that the activated
 138 complex is composed of reactants of like charges [19].



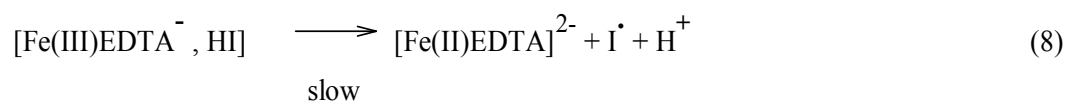
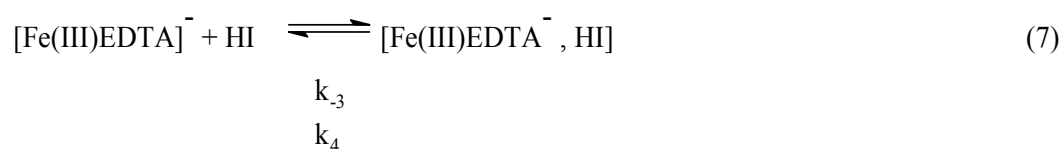
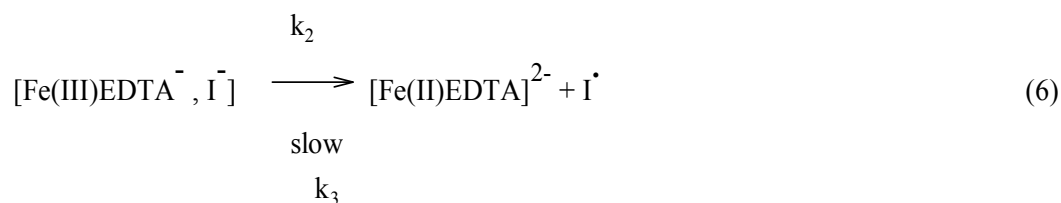
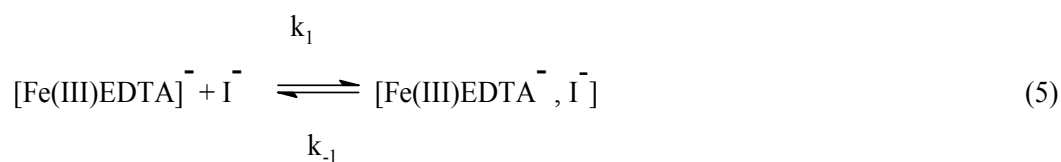
139
 140 **Figure 4:** Plot $\log k_2$ versus \sqrt{I} for the Reaction of $[\text{Fe(III)EDTA}]^-$ and I^- at $[\text{Fe(III)EDTA}]^- =$
 141 $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{I}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = (0.5 - 0.7) \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times$
 142 $10^{-2} \text{ mol dm}^{-3}$, $T = 28 \pm 1^\circ\text{C}$, and $\lambda_{\text{max}} = 470 \text{ nm}$

143 The plot of k_1^{-1} versus $[\text{I}]^{-1}$ gave a negligible intercept, suggesting unstable binuclear
 144 intermediate formation. Also, the added Ca^{2+} ions had effect on the rate of reaction by
 145 initiating an increase in the reaction rate. Since the reactant species are negatively charged,
 146 Ca^{2+} ion is expected to accelerate the rate by acting as a bridge between the reactants through
 147 an outer-sphere complex formation [20].



148
 149
 150 **Figure 5:** Michaelis-Menten Plot of $1/k_1$ versus $1/[\text{I}^-]$ for the Reduction of $[\text{Fe(III)EDTA}]^-$ by
 151 I^-

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



154

$$\text{Rate} = k_2[Fe(III)EDTA^-, I^-] + k_4[Fe(III)EDTA^-, HI] \quad (10)$$

156 From equation (6);

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

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

159 From equation (9);

$$k_3[Fe(III)EDTA^-, HI] = k_3[Fe(III)EDTA^-][HI] \quad (13)$$

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

162 From equation (4);

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

164 Substitute equation (15) into (14);

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

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

$$167 \quad \text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{Fe(III)EDTA}^-][\text{I}^-] + \frac{k_4 k_3 K_{eq} [\text{H}^+]}{k_{-3}} [\text{Fe(III)EDTA}^-][\text{I}^-] \quad (17)$$

$$168 \quad \text{Rate} = \frac{k_2 k_1}{k_{-1}} + \frac{k_4 k_3 K_{eq} [\text{H}^+]}{k_{-3}} ([\text{Fe(III)EDTA}^-][\text{I}^-]) \quad (18)$$

$$169 \quad \text{Rate} = k [\text{Fe(III)EDTA}^-][\text{I}^-] \quad (19)$$

$$170 \quad \text{Where } k = \frac{k_2 k_1}{k_{-1}} + \frac{k_4 k_3 K_{eq} [\text{H}^+]}{k_{-3}}$$

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

172 4. Conclusion

173 The kinetics of reduction of ethylenediaminetetraacetateferrate(III) complex by iodide ion
 174 was studied in aqueous acidic medium. A mole ratio of 1:1 (Complex: Oxidant) was
 175 obtained. The analysis of other kinetic data obtained under the pseudo-first order condition
 176 gave an overall order of second order; first order with respect to the concentration of the
 177 oxidant and reductant. Rationalizing the pieces of evidence obtained in the study favors the
 178 outer-sphere mechanism and a plausible mechanistic pathway which explains the kinetic data
 179 obtained is proposed.

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