

Kinetics and Mechanisms of The Oxidation of [FeEDTA]²⁻ By Aqueous Iodine

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ABSTRACT: Iodine oxidizes [FeEDTA]²⁻ in aqueous H₂SO₄ at 28.0 ± 1.0°C according to the reaction
$$2[\text{FeEDTA}]^{2-} + \text{I}_2 \rightarrow 2[\text{FeEDTA}]^{-} + 2\text{I}^{-}$$

The rate law is $-d[\text{I}_2]/dt = (b + c[\text{H}^+])[\text{I}_2][\text{FeEDTA}]^{2-}$. The rate of the reaction is first order in oxidant and reductant concentrations. On the basis of interaction with added cat ions, Michaelis-Menten plots and the absence of intermediates, the outer-sphere electron transfer mechanism is proposed for the reaction.

KEY WORDS: kinetic, iodine, mechanisms, EDTA

I. INTRODUCTION

Outer-sphere electron transfer reactions have been investigated for a number of main-group molecules. For diatomic molecules, estimate of the self-exchange rate constants have been made for the O₂/O₂⁻, NO⁺/NO, I₂/I₂⁻, Br₂/Br₂⁻, and Cl₂/Cl₂⁻ systems. Of these, only the O₂/O₂⁻ system has received extensive scrutiny, in the case of the NO⁺/NO system, only one reaction has been found that appears to fall in the outer-sphere class. There are scattered reports for the halogen systems, but serious reservations relate to the derived self-exchange rate constant. The first estimate of the I₂/I₂⁻ self-exchange rate constant (8.5 x 10⁴dm³mol⁻¹s⁻¹) was published in 1974. Woodruff, and Margerum(1974). The reaction of I₂ with [Co(sep)]²⁺ is clearly outer-sphere and is not limited to diffusion control Rudgewick-Brown (1974).

In the present paper, we report on the reaction of I₂ with [FeEDTA]²⁻ in acidic tetraoxosulphate (vi) acid media. This reaction most likely has an outer-sphere electron-transfer mechanism.

II. EXPERIMENTAL

Materials

Iodine (A.R grade), sodium sulphate, tetraoxosulphate (vi) acid. Corning Colorimeter-253

Stoichiometry

The Stoichiometry was determined by the mole ratio method using Corning Colorimeter-253 titration at 490nm. The iodine concentration was kept constant at 7.8 x 10⁻⁴mol dm⁻³ and the concentration of iron(II)EDTA varied between (1.0 to 10.8) x 10⁻⁴mol dm⁻³ at [H⁺] = 2.0 x 10⁻⁵mol dm⁻³ and I = 0.5 mol dm⁻³ (Na₂SO₄).

III. KINETICS

Kinetic measurements were carried out at the wavelength of 490nm by measuring the decrease in absorbance of the reaction mixture as the reaction progressed.

The reaction was carried out under Pseudo-first order conditions with the concentration of iron(II)EDTA 20-fold in excess over that of iodine. Ionic strength of the reaction mixture was kept constant at 0.50 mole dm⁻³(Na₂SO₄) and [H⁺] at 2.0 x 10⁻⁵mol dm⁻³. Plot of (A_t - A_∞) versus time were linear for over 90% extent of reaction. Pseudo-first order rate constants, k₁ were determined as the slopes of the above plots as given by the equation:

$$(A_t - A_{\infty}) = (A_t - A_{\infty})e^{-k_1 t} \dots \dots \dots (1)$$

Second order rate constants, k₂ were obtained as the ratios of k₁ to [FeEDTA]²⁻

IV. RESULTS AND DISCUSSION

A plot of absorbance versus [FeEDTA]²⁻ gives a mole ratio of 1:2 as shown in equation (2)



At constant ionic strength under pseudo-first order conditions with $[\text{FeEDTA}]^{2-}$ at least 20-fold excess over $[\text{I}_2]$, pseudo-first order plot is linear for greater than 90% extent of reaction. This implies that the order of the reaction is one with respect to iodine concentration. Pseudo-first order rate constants determined as slopes of these plots, are shown in Table 1. The rate of the reaction increases with increase in $[\text{FeEDTA}]^{2-}$ with a slope of 1.0, suggesting that the reaction is first-order in $[\text{FeEDTA}]^{2-}$ as shown in Fig.1. Similar first order dependence of rate of reaction was observed for ruthenium (II) with iodine (Jiafei and Stanbury, 1997). The rate law for the reaction is given as equation (3)

$$-\frac{d[\text{I}_2]}{dt} = k_2[\text{FeEDTA}]^{2-}[\text{I}_2] \dots \dots \dots (3)$$

Within the range $4.0 \times 10^{-6} \text{ mol dm}^{-3} \leq [\text{H}^+] \leq 4.4 \times 10^{-5} \text{ mol dm}^{-3}$ and constant ionic strength $0.50 \text{ mole dm}^{-3} \text{ Na}_2\text{SO}_4$. The rate of the reaction decreases with increase in $[\text{H}^+]$ (Table1). A plot of second-order rate constant, k_2 versus $[\text{H}^+]^{-1}$ in the above acid range is linear and fitted equation (4)

$$K_2 = b + c[\text{H}^+]^{-1} \dots \dots \dots (4)$$

Where b and c were determined by the method of least mean square to be $0.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2.75 \times 10^{-6} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ respectively at $28.0 \pm 1.0 \text{ }^\circ\text{C}$ and $I = 0.50 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. Substituting the expression for k_2 into equation (3) gives equation (5)

$$\frac{d[\text{I}_2]}{dt} = (b + [\text{H}^+]^{-1}[\text{I}_2][\text{FeEDTA}]^{2-} \dots \dots \dots (5)$$

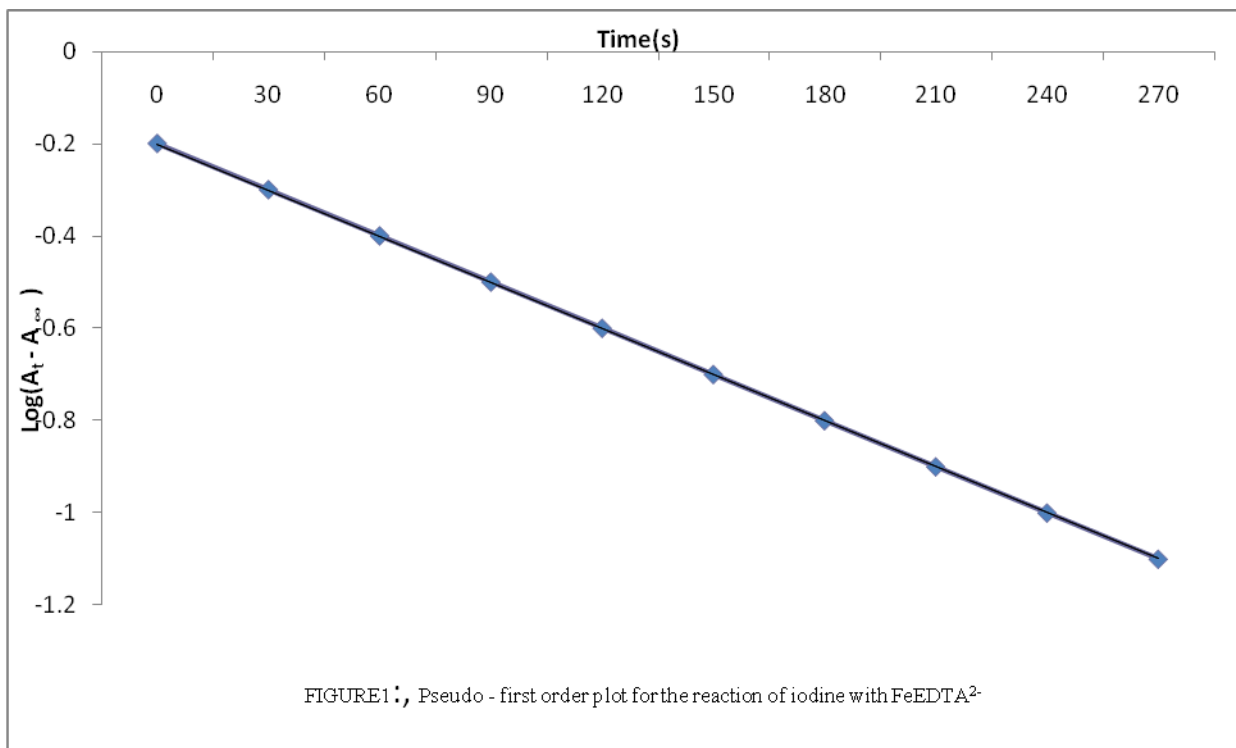
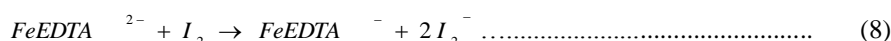
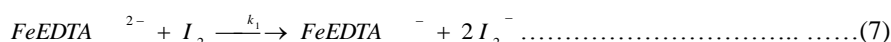


Table I Pseudo-first order and second order rate constant for the reaction of iodine with [FeEDTA]²⁻
 [I₂] = 7.8 x 10⁻⁴ mol dm⁻³, I = 0.50 mol dm⁻³ (Na₂SO₄) T = 28.0 ± 1.0 °C λ_{max} = 490nm

10 ² [FeEDTA] ²⁻ Mol dm ⁻³	10 ⁵ [H ⁺]mol dm ⁻³	I [Na ₂ SO ₄]mol dm ⁻³	10 ³ k ₁ , s ⁻¹	10 ² k ₂ dm ³ s ⁻¹ mol ⁻¹
0.74	2.0	0.5	2.45	33.1
1.14	2.0	0.5	3.78	33.2
1.54	2.0	0.5	5.11	33.2
1.94	2.0	0.5	6.40	33.0
2.34	2.0	0.5	7.60	32.5
2.34	0.4	0.5	10.55	45.1
2.34	1.2	0.5	9.83	42.0
2.34	2.0	0.5	7.67	32.8
2.34	2.8	0.5	6.84	29.2
2.34	3.6	0.5	6.35	37.2
2.34	4.4	0.5	5.97	25.5
2.34	2.0	0.1	12.00	51.3
2.34	2.0	0.2	10.23	43.7
2.34	2.0	0.3	9.12	39.0
2.34	2.0	0.4	8.37	35.8
2.34	2.0	0.5	7.67	32.8
2.34	2.0	0.6	7.02	30.0

Plausible mechanism consistence with the reaction of I₂ with FeEDTA²⁻ is



$$Rate = k_1[FeEDTA]^{2-}[I_2] + k_2[FeEDTAOH^{3-}][I_2] \dots\dots\dots(11)$$

From equation (6)

$$[FeEDTAOH^{3-}] = \frac{K[FeEDTA]^{2-}}{[H^+]} \dots\dots\dots(12)$$

Substituting equation (12) into equation (11) gives equation (13)

$$Rate = k_1 [FeEDTA]^{2-} [I_2] + Kk_2 [H^+]^{-1} [FeEDTA]^{2-} [I_2] \dots\dots\dots(13)$$

$$Rate = (k_1 + Kk_2 [H^+]^{-1}) [FeEDTA]^{2-} [I_2] \dots\dots\dots(14)$$

Equation (14) confirms with equation (5) the observed rate law where k₁ = b and Kk₂ = c
 On scanning the reaction mixture there was neither enhancement in absorbance nor shift in λ_{max}.
 Also from Michaelis-Menten plot, there was no intercept. Addition of cations (Hg²⁺, Ag⁺, Cu²⁺) was found to catalyze the reaction.
 Based on these reasons, the reaction might be occurring by the outer-sphere mechanism.

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