Kinetics and Mechanism of The Oxidation of [Fe (H$_2$O)]$^{2+}$ By Aqueous Iodine

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Abstract: *The kinetics and mechanism of the oxidation of [Fe(H$_2$O)]$^{2+}$ by aqueous iodine was studied in aqueous acidic medium, ionic strength I = 0.5 mol dm^{-3} (Na$_2$SO$_4$) at (28.0 ± 1.0 ^{o}C). The stoichiometry is 1:2 mole ratios (oxidant/reductant). The rate of reaction is first order in oxidant and reductant concentrations. The rate of the reaction increases with increase in hydrogen ion concentration. On scanning the reaction mixturethere was no change in the absorption maximum of iodine indicating absence of a reaction intermediates. On the basis of added cations and the Michaelis-Menten plot, a plausible mechanism is proposed for this reaction. The result is aimed at studying the factors which might be responsible for the depletion of iodine in the thyroid gland which usually led to goiter.*
Key words: *kinetics, iodine, 1ron (II), Rate, mechanism*

I.   Introduction

The mechanism by which an excess of iron (II) ion reacts with aqueous chlorine dioxide to produce iron (III) ion and chlorine ion has been determined Evan et al; (2004). The reaction proceeds via the formation of chlorite ion, which in turn reacts with additional ion (II) to produce the observed products. The rate is independent of pH over the range from 3.5 to 7.5, but the reaction is assisted by the presence of acetate ion. At ionic strength of 2.0 mol dm^{-3}at a temperature of 25°C, k$_{1=}$ (3.9 ± 0.1) x 10^3 dm^3 mol^{-1}s^{-1} and k$_2$ = (6.0 ±1.0) x 10^4 dm^3 mol^{-1}s^{-1}.

The rate equation for the oxidation of Ti(H$_2$O)$_6$ by iodine was found to be

$$-d\frac{[I_2]}{dt} = k_2 k_a ([H^+) + k_a)^{-1}[Ti(III)][I_2] + k_2 k_a ([H^+] + k_a)^{-1}[Ti(III)][I_3^-]$$

For the conditions [H$^+$] = 0.0036 – 0.20 mol dm^{-3}, I = 0.1 mol dm^{-3} (LiCl), and I = 25°C,
k$_1$ = 5.3 x 10^2 dm^3 mol^{-1} s^{-1}, k$_2$ = 6.9 dm^3 mol^{-1}s^{-1} and k$_a$ = 3.2 x 10^{-3}mol dm^{-3}. The reaction was supposed to proceed by univalent electron transfer steps involving I$_2^-$ as the transient intermediate species. The mechanism consistent with the kinetic data is an outer-sphere electron transfer mechanism, Adegite and Iyun (1979).
In the present paper, we report on the reaction of I$_2$ with [Fe(H$_2$O)]$^{2+}$ in acidic tetraoxosulphate (VI) solution.

II.   Experimental

Materials
Iodine (AR grade), sodium sulphate, tetraoxosulphate (VI) acid, mercury chloride, silver nitrate, copper (II) chloride, iron(II) sulphate,
Stoichiometry
The stoichiometry was determined by the mole ratio method using Corning Colorimeter 253 titration at 490 nm. The [I$_2$] was kept constant at 7.8 x 10^{-4}mol dm^{-3} and the concentration ofiron (II) varied between (1.0 to 10.0) x 10^{-4} mol dm^{-3} at [H$^+$] = 0.2 mol dm^{-3} and I = 0.5 mol dm^{-3} (Na$_2$SO$_4$).

KINETICS
Kinetic measurements were conducted at 490 nm (the wavelength of maximum absorption for iodine in aqueous solution) 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 iron(II) concentrations in at least 20-fold excess over that of iodine. Ionic strength of the reaction was kept constant at 0.5 mol dm^{-3} (Na$_2$SO$_4$) and [H$^+$] at 0.2 mol dm^{-3}.
Plot of (A$_t$ - A$_\infty$) against, t, (where A$_t$ and A$_\infty$ are the absorbance's at time t and at the end of the reaction respectively) were linear for over 90% extent of reaction. Pseudo-first order rate constants, k$_1$ were determined from the slopes of the above plots as given by the equation

$$(A_t - A_\infty) = (A_t - A_0)e^{k_1,t} \quad \text{..........................(1)}$$

A_0 is the absorbance at the beginning of the reaction. Second order rate constants, k_2, were obtained as ratios of

k_1 to $[Fe^{2+}]$

III. Results And Discussion

Mole ratio determination showed that for every two moles of iron (II) oxidized, one mole of iodine is reduced. A plot of absorbance versus $[Fe^{2+}]$ gives a mole ratio of 1:2 as shown in equation (2).

$$2Fe^{2+} + I_2 \rightarrow 2Fe^{3+} + 2I^- \quad \text{.............................(2)}$$
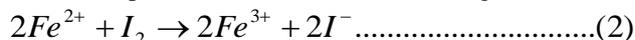
Under pseudo-first order conditions with $[Fe^{2+}]$ at least 20-fold excess over $[I_2]$ and at constant ionic strength, pseudo-first order plot is linear for greater than 90% extent of reaction. This implies that the order of reaction with respect to iodine concentration is one. Plot of $Logk_1$ versus $Log[Fe^{2+}]$ was linear with a slope of one, suggesting that the reaction is first-order with respect to $[Fe^{2+}]$ as shown in Fig.I. The rate law for the reaction is given as equation (3).

$$-\frac{d[I_2]}{dt} = k_2[Fe^{2+}][I_2] \quad \text{...(3)}$$

The rate of the reaction increases with increase in $[H^+]$ (Table I) within the range $0.04 \leq [H^+] \leq 0.28$ mol dm⁻³ at $[I_2] = 7.8 \times 10^{-4}$ mol dm⁻³ and constant ionic strength of 0.5 mol dm⁻³.
Also, plot of second-order rate constants, k_2 versus $[H^+]$ in the above acid range is linear and fitted equation (4).

$$k_2 = b + c[H^+] \quad \text{..(4)}$$

Where b and c were determined from the least square method to be 0.32 dm³ mol⁻¹s⁻¹ and 3.0 dm⁶ mol⁻²s⁻¹ respectively at 28.0 ±1.0°C and I = 0.50 mol dm⁻³. Substituting the expression for k_2 into equation (3) gives equation (5).

$$-\frac{d[I_2]}{dt} = (b + c[H^+])[Fe^{2+}][I_2] \quad \text{.......................................(5)}$$

TABLE I
Pseudo-first order and second order rate constants for the reaction of iodine with Fe²⁺ at:
$[I_2] = 7.8 \times 10^{-4}$ mol dm⁻³, I = 0.5 mol dm⁻³ (NaSO₄), T = 28.0 ±1.0°C, and λ_{max} = 490 nm.

$10^3[Fe^{2+}]$ Mol dm⁻³	$[H^+]$ mol dm⁻³	I[NaSO₄] mol dm⁻³	10^3k_1 s⁻¹	$10^2 k_2$ dm³ mol⁻¹ s⁻¹
5.6	0.20	0.50	5.36	95.7
7.6	0.20	0.50	7.09	93.3
9.6	0.20	0.50	9.20	95.8
11.6	0.20	0.50	11.20	96.5
13.6	0.20	0.50	12.60	92.6
15.6	0.20	0.50	14.50	93.0
15.6	0.04	0.50	6.84	43.8
15.6	0.08	0.50	8.73	55.9
15.6	0.12	0.50	10.71	68.6
15.6	0.16	0.50	12.56	80.5
15.6	0.20	0.50	14.50	93.0
15.6	0.24	0.50	15.86	101.6
15.6	0.28	0.50	18.08	115.8
15.6	0.20	0.36	11.26	72.2
15.6	0.20	0.45	12.88	82.6
15.6	0.20	0.50	13.80	88.5
15.6	0.20	0.60	15.36	98.5
15.6	0.20	0.80	19.05	122.1
15.6	0.20	0.95	22.25	142.6

Logk₁
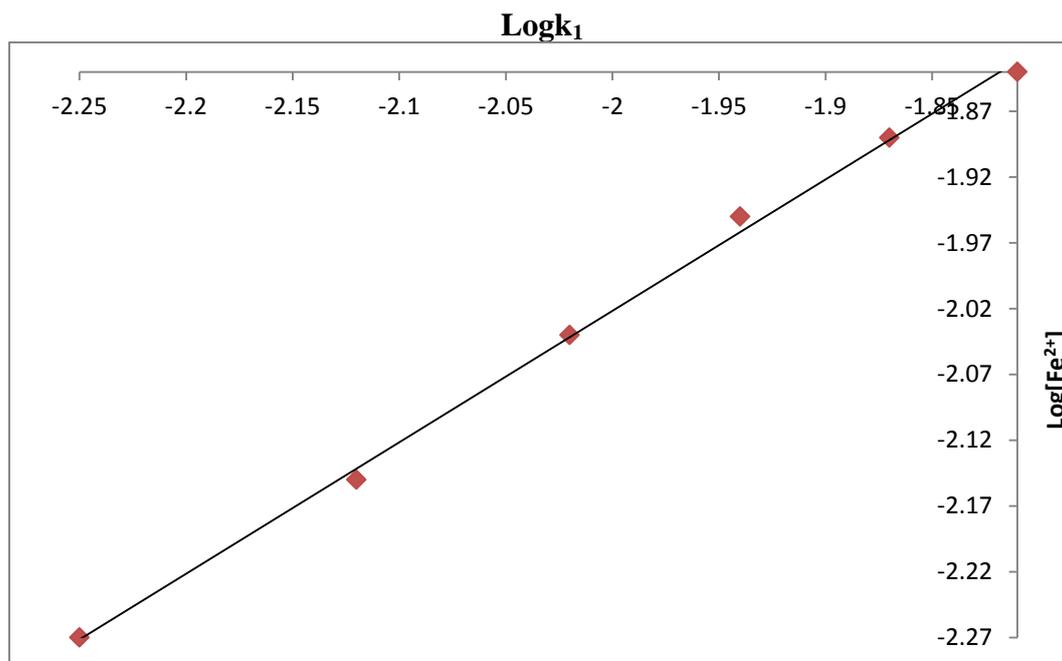
Fig. I: Plot of log k₁ versus log [Fe²⁺]

The mechanism below is proposed for the reaction of I_2 with Fe^{2+}.

$$H^+ + I_2 \xleftrightarrow{\ K\ } H.I_2^{\ +} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6)$$

$$Fe^{2+} + H.I^+ \xrightarrow{\ k_1\ } Fe^{3+} + HI_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

$$H^+ + HI_2 + Fe^{2+} \xrightarrow{\ k_2\ } Fe^{3+} + 2HI \dots\dots\dots\dots\dots\dots\dots(8)$$

$$Fe^{2+} + I_2 \xrightarrow{\ k_3\ } Fe^{3+} + I_2^{\ -} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

$$Fe^{2+} + I_2^{\ -} \xrightarrow{\ k_4\ } Fe^{3+} + 2I^- \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(10)$$

$$Rate = k_1[Fe^{2+}][HI_2^{\ +}] + k_3[Fe^{2+}][I_2] \dots\dots\dots\dots\dots\dots\dots(11)$$

From equation (6)

$$H.I_2^{\ +} = K[I_2][H^+] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(12)$$
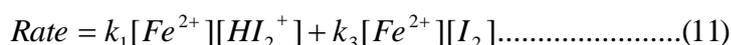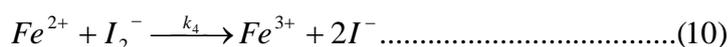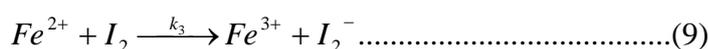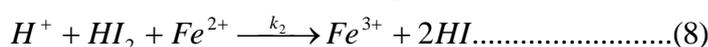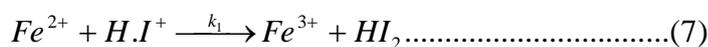
Substituting equation (12) into equation (11) gives equation (13).

Equation (14) confirms with the observed rate law, equation (5), where $k_3 = b$ and $Kk_1 = c$.

Least square plot of Michaelis-Menten gave no intercept and there was no shift in λ_{max} of the spectrum of the reaction mixture suggesting that there was no intermediate complex formation. The cations (Cu^{2+}, Hg^{2+} and Ag^+) were found to increase the reaction rate (Table II). These reasons suggest that the reaction is occurring by the outer-sphere mechanism.

Table II: Rate data for the effect of added cations on the second order rate constants for the reaction of iodine and iron(II). [I₂] = 7.8 x 10⁻⁴mol dm⁻³, [H⁺] = 0.2 mol dm⁻³, I = 0.5 mol dm⁻³ (Na₂SO₄), [Fe²⁺] = 1.56 x 10⁻²mol dm⁻³, λmax = 490 nm and T = 28 ±1.0ᵒC

Cation M^{n+}	$10^3[M^{n+}]$ mol dm⁻³	$10^3 k_1$, s⁻¹	$10^2 k_2$ dm³ mol⁻¹s⁻¹
Hg^{2+}	2.0	16.3	104.50
	4.0	18.40	117.9
	6.0	20.50	131.40
	8.0	22.30	142.90
Ag^+	2.0	13.90	89.10
	4.0	13.54	86.79
	6.0	13.13	84.16

	8.0	12.79	81.98
Cu^{2+}	2.0	14.60	93.60
	4.0	15.60	100.00
	6.0	16.50	105.80
	8.0	17.70	113.50

IV. Conclusion

The redox reaction of iodine was studied with Fe^{2+} in aqueous medium. The stoichiometry of 1:2 was observed. The order of the reaction with respect to the oxidant and reductant was one. The rates of the reaction showed a positive intercept which confirms with the following rate equation

$$-\frac{d[I_2]}{dt} = (b+c)[H^+])[Fe^{2+}][I_2].......................................(5)$$

The following rate constant for the system under study was observed:
$k_2(Fe^{2+})$ = (0.945 ± 0.017) dm³ mol⁻¹s⁻¹ the rate of the reaction showed positive salt effect on the reacting system. The addition of cation was found to catalyze the reaction. The result of Michaelis-Menten analysis and spectroscopic investigations showed no evidence of intermediate complex formation. From the experimental result obtained, the reaction of iodine with iron(II) ion occurred through the outer-sphere mechanism. Hence, such mechanism is proposed as being plausible for the reaction.

Recommendations

It is recommended that;
*   Compounds similar to the thyroid hormones be investigated or synthesized
*   Kinetic studies are carried out on such compounds with iodine so as to ascertain the mechanistic pathways of their reactions
*   Such mechanisms are employed so as to determine the required quantity of iodine suitable for use as food additives

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