

Full Length Research Paper

Kinetics and mechanism of the oxidation of potassium trisoxalatoferate(iii) by permanganate ion in aqueous hydrochloric acid medium

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The kinetics and mechanisms of the oxidation $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ by permanganate ion in acid solution has been studied. The data are consistent with the rate law: $\frac{d[Fe(C_2O_4)_3]}{dt} = (a + b[H^+])[Fe_2(C_2O_4)_3][MnO_4]$ with $a = 0.12 \text{ s}^{-1}$ and $b = 1.35 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$, at $T = 27.0 \pm 1.0^\circ\text{C}$, $[H^+] = 0.2 \text{ mol dm}^{-3}$, $I = 0.2 \text{ mol dm}^{-3}$ (NaCl), and $\lambda_{max} = 420 \text{ nm}$. There is evidence for the formation of an intermediate complex of significant stability and free radicals are important in the reaction. The reaction is rationalised in terms of an inner-sphere mechanism.

Key words: Kinetics, mechanism, rate constants.

INTRODUCTION

There has been a lot of interest in the study of the oxidation-reduction reactions involving Trisoxalato complexes with a variety of substrates (Horacio and Nina, 2006; Fico and Treindl, 1972; Mamman and Iyun, 2008). This interest is due to the fact that these complexes have played a leading role in many aspects of co-ordination chemistry especially in their spectroscopic behavior, kinetic behavior in solution and in some cases their resolution into enantiomers (Baran and Lawrence, 2002). These complexes have found useful applications in photography, medicine, analytical chemistry and in actinometry.

$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is most abundantly used in

platinum/palladium photographic printing, where its aqueous solution is first converted to the acidic hydrogen ferric oxalate, after which the resulting acid is then used as a sensitizer in developing a photographic prints (Shun, 1994). The compound has been successfully used in volumetric analysis to estimate iodine in iodized salt (Ramanjaneyulu and Shukla, 1956). In medicine the complex is used as a desensitizer in patients that exhibit a hypersensitive dental condition (Teinkink and Whitehouse, 1995). $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is also used in chemical actinometers because of its sensitivity over a wide range of wavelengths (Sahul et al., 1997). Recently, we have investigated the redox reaction of

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$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ with SO_4^{2-} (Ogori and Lohdip, 2015). In continuation of our effort in this direction, we now report the results of the redox reaction of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ with MnO_4^- in aqueous hydrochloric acid.

EXPERIMENTAL

Materials and reagents

The complex, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ was synthesized and characterized according to a known procedure involving the direct reaction of potassium oxalate monohydrate and iron(III)chloride hexahydrate as reported in the literature (Rendle et al., 1969). Sodium chloride (BDH, analar) stock solution was prepared without further purification or standardization and used to maintain the ionic strength at 0.2 mol dm^{-3} while HCl was used to investigate the effect of hydrogen ions on the rate of the reaction. All other chemicals were used as supplied.

Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentrations of MnO_4^- and varying concentrations of $[Fe(C_2O_4)_3^{3-}]$ (0.01 - $0.040 \text{ mol dm}^{-3}$) were reacted at $[H^+] = 0.05 \text{ mol dm}^{-3}$, $[MnO_4^-] = 0.001 \text{ mol dm}^{-3}$ and $I = 0.2 \text{ mol dm}^{-3}$ (NaCl) and allowed to stand for 24 h for the reaction to go to completion. The absorbance of the solutions was measured at 420 nm and the stoichiometry was evaluated from the plot of absorbance versus mole ratio.

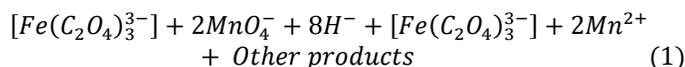
Kinetic measurements

All kinetic runs were performed under pseudo-first order conditions with the concentration of $[Fe(C_2O_4)_3^{3-}]$ in at least 10 fold excess over that of MnO_4^- . The rate of reaction was monitored by measuring the rate of decrease in absorbance of the mixture at 420 nm using a Seaward photoelectric colorimeter [AE-11D] at $27.0 \pm 1.0^\circ\text{C}$, $[H^+] = 0.2 \text{ mol dm}^{-3}$ and $I = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$ (NaCl) unless otherwise stated. Pseudo-first order rate constants were obtained from plots of $\log(A - A_\infty)$ versus time.

RESULTS AND DISCUSSION

Stoichiometry

The results of the spectrophotometric titration indicated a 1:2 stoichiometry and the overall reaction is given by Equation 1.



Product analysis

At completion of reaction, the presence of Mn(II) ions was confirmed by adding a solution of KIO_4 to the colourless reaction mixture and warming gently. The characteristic

purple colour reappeared, owing to oxidation of Mn(II) back to Mn(VII).

Determination of order

Kinetic measurements were made under Pseudo-first order conditions with $[Fe(C_2O_4)_3^{3-}] = 0.01$ - $0.045 \text{ mol dm}^{-3}$, $[Mn] = 0.001 \text{ mol dm}^{-3}$ and $I = 0.2 \text{ mol dm}^{-3}$ (NaCl). Under this conditions, plots of $\log(A - A_\infty)$ versus time were found to be linear to more 80% of the extent of the reaction, indicating that the reaction is first order in $[MnO_4^-]$ (A and A_∞ are absorbance at time t and infinity respectively). Values of the observed rate constants are given in Table 1. A plot of $\log k$ versus $\log [Fe(C_2O_4)_3^{3-}]$ was linear. The slope of 1.2 ($r = 0.939$) signifies first order in $[Fe(C_2O_4)_3^{3-}]$ (Figure 1). The rate law for the reaction is therefore represented as:

$$\frac{d[Fe(C_2O_4)_3^{3-}]}{dt} = K_2 [(C_2O_4)_3^{3-}][MnO_4^-] \quad (2)$$

The second order rate constants calculated from $K_2 = \frac{k_1}{[MnO_4^-]}$ were fairly constant, confirming first order in $[MnO_4^-]$. The observed rate constants, k and second – order rate constants are presented in Table 1. The reaction rate was observed to increase in the presence of acid (0.02 - 0.048) mol dm^{-3} . The reaction showed a first order dependence on $[H^+]$, (Table 1). A least square plot of k versus $[H^+]$ was found to be linear ($r = 0.977$) with a positive intercept, and the relationship is given by Equation 3.

$$K_2 = a + b [H^+] \quad (3)$$

$$a = 0.12 \text{ s}^{-1} \text{ and } b = 1.35 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}.$$

Substituting the expression for k_2 into Equation 2 gives Equation 4.

$$\frac{-d[Fe(C_2O_4)_3^{3-}]}{dt} = (a + b[H^+])[Fe(C_2O_4)_3^{3-}][MnO_4^-] \quad (4)$$

The first order dependence of $[H^+]$ suggests the existence of two parallel pathways for the reaction, involving a protonated and unprotonated species. It has been noted that redox reactions of many oxoanions are strongly acid dependent (Iyun et al., 1992).

Ionic strength

The effect of ionic strength on the rate of the reaction was studied over the range 0.2 - 1.0 , mol dm^{-3} using NaCl, while keeping all other conditions constant. The results

Table 1. Second order rate constants for the oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by MnO_4^- . $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} = (0.01\text{-}0.040)$ mol dm^{-3} , $[\text{Mn}] = 0.001 \text{ mol dm}^{-3}$ $I = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$ (NaCl), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda = 42 \text{ nm}$.

$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ Mol dm^{-3}	$10[\text{H}^+]$ mol dm^{-3}	I , (NaCl), mol dm^{-3}	$10[\text{k}_2]$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.010	2.0	0.2	1.68
0.015	2.0	0.2	2.14
0.020	2.0	0.2	1.80
0.025	2.0	0.2	1.55
0.030	2.0	0.2	1.41
0.035	2.0	0.2	1.25
0.040	2.0	0.2	1.15
0.020	2.0	0.2	1.56
0.020	2.4	0.2	1.66
0.020	2.8	0.2	1.69
0.020	3.2	0.2	1.78
0.020	3.6	0.2	1.80
0.020	4.0	0.2	1.89
0.020	4.4	0.2	1.91
0.020	2.0	0.2	1.02
0.020	2.0	0.3	1.05
0.020	2.0	0.4	1.11
0.020	2.0	0.5	1.21
0.020	2.0	0.6	1.24
0.020	2.0	0.7	1.32
0.020	2.0	0.8	1.34
0.020	2.0	0.9	1.50
0.020	2.0	1.0	1.63

Acid dependence

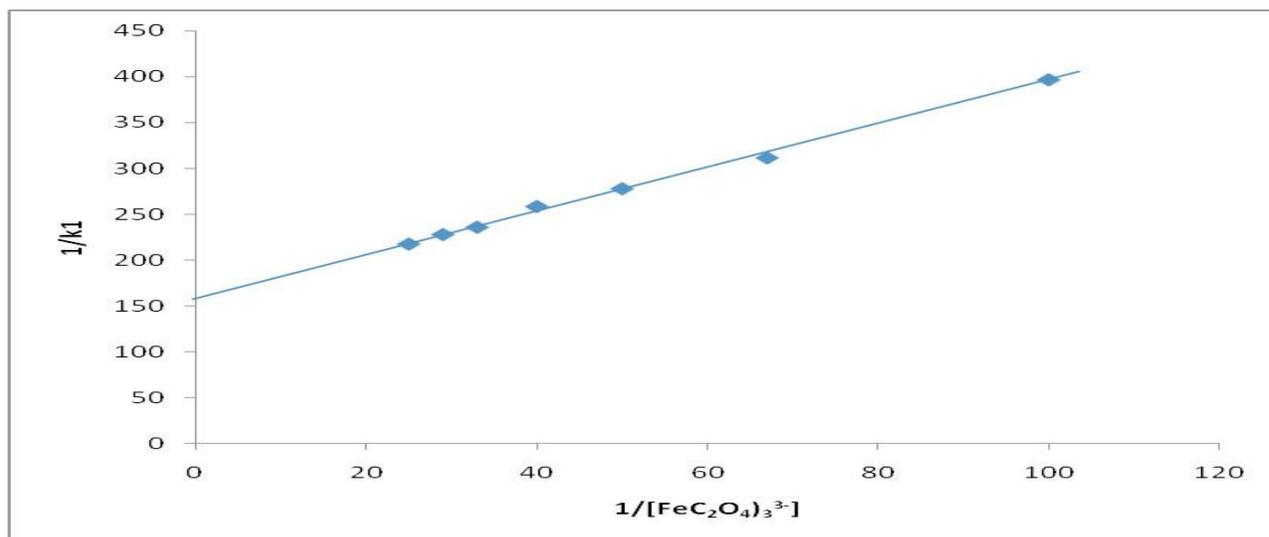


Figure 1. Plot of $1/k$ versus $1/[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ for the oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by MnO_4^-

presented in Table 1, show that the rate constants increase with increase in ionic strength, suggesting a positive Bronsted-Debye salt effect (Bronsted, 1922;

Birck, 1978). This is an indication that the rate determining steps, or one or more of such steps involve(s) charged ion(s) (Hassan, 1991).

Table 2. Effect of added anions on the second order rate constants for the oxidation of $[Fe(C_2O_4)_3]^{3-}$ by MnO_4^- at $[Fe(C_2O_4)_3]^{3-} = (0.01 - 0.045) \text{ moldm}^{-3}$, $[MnO_4^-] = 0.001 \text{ moldm}^{-3}$, $[H^+] = 0.2 \text{ moldm}^{-3}$, $I = 2.0 \times 10^{-1} \text{ moldm}^{-3}$ (NaCl), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda = 420 \text{ nm}$.

X	$10^2[x], \text{ moldm}^{-3}$	$10^3k_1, \text{ s}^{-1}$	$10k_2, \text{ dm}^3\text{mol}^{-1} \text{ s}^{-1}$
CH_3COO^-	2.0	4.22	2.11
	4.0	4.07	2.04
	6.0	4.07	2.04
	8.0	3.90	1.95
	10.0	3.65	1.83
NO_3^-	2.0	4.42	2.21
	4.0	4.00	2.00
	6.0	3.89	1.95
	8.0	3.52	1.76
	10.0	3.39	1.69

Dielectric constant

The dielectric constant was varied by varying acetone/water concentration. It was observed that the reaction rate was enhanced as a function of $1/D$ ($D =$ dielectric constant). This is also an indication that the rate determining step or one of the rate determining steps involves oppositely charged species (Hassan, 1991).

Anion dependence

The rate constant of the reaction was found to decrease with increase in concentration of CH_3COO^- and NO_3^- as tabulated in Table 2. This is suggestive of an outer sphere mechanism because outer sphere reactions are expected to be affected by presence of anions, but they should have no effect on inner sphere reactions (Adegbite et al., 1977).

Test for free radicals

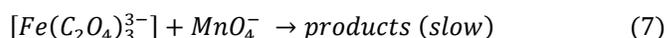
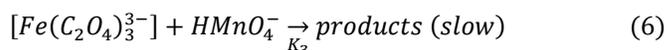
Addition of acrylamide to partially reacted mixture gave a gel in the presence of excess methanol. This suggests that free radicals are important intermediate in this reaction.

Michaelis-Menten plot

Least squares analysis of $1/k_1$ versus $1/[Fe(C_2O_4)_3]^{3-}$ gave a straight line with a significant positive intercept (Figure 2), indicating the formation of intermediates prior to electron transfer. The presence of kinetic evidence for precursor complex in this reaction indicates that the reaction most probably proceeded by an inner-sphere mechanism.

Reaction mechanism

On the basis of the kinetics and stoichiometric results, a plausible mechanism is proposed for the reaction:



From Equations 6 and 7, the rate equation can be given as

$$\text{Rate} = K_2[Fe(C_2O_4)_3]^{3-}[HMnO_4^-] + K_3[MnO_4^-][Fe(C_2O_4)_3]^{3-} \quad (8)$$

From Equation 5,

$$[HMnO_4^-] = K_1[MnO_4^{2-}][H^+] \quad (9)$$

Substituting Equation 9 into 8, gives

$$\begin{aligned} \text{Rate} &= K_2K_1[Fe(C_2O_4)_3]^{3-}[MnO_4^-][H^+] \\ &\quad + K_3[Fe(C_2O_4)_3]^{3-}[MnO_4^-] \end{aligned} \quad (10)$$

$$\text{Rate} = (K_3 + K_2 + K_1[H^+])[Fe(C_2O_4)_3]^{3-}[MnO_4^-] \quad (11)$$

Equation 11 is analogous to Equation 4, where $k = a = 0.12 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ and $k_1 k_2 = b = 1.35 \text{ dm}^6\text{mol}^{-2}\text{s}^{-1}$.

A key point of interest is whether the reaction occurs via the inner or outer-sphere mechanism or a combination

of both. This issue was addressed as follows:

(a) Addition of acrylamide to the partially oxidized reaction mixture gave a gel in the presence of excess methanol, suggesting the presence of free radicals in the reaction. This evidence is in support of the inner sphere pathway.

(b) From Table 2, it can be observed that the reaction rate decreased in the presence of acetate and nitrate ions, which supports outer-sphere mechanism.

(c) A Lineweaver-Burk modification of Michaelis-Menten plot of $\frac{1}{K_1}$ versus $\frac{1}{[Fe(C_2O_4)_3]}$ was linear with a significant positive intercept on the $\frac{1}{K_1}$ axis. This supports the inner-sphere mechanism.

(d) Also, acid-catalysis of the reaction was observed, which also is in favour of inner- sphere mechanism.

From the above reasoning (a)-(d), it can be inferred that the reaction occurred through an inner-sphere mechanism.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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