

Kinetics and mechanism of oxidation of ethylacetate by potassium permanganate in acidic medium

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Abstract

Kinetics of oxidation of ethylacetate (EtAc) by potassium permanganate (KMnO_4) in sulphuric acid medium has been investigated. Analysis of kinetic data revealed that the reaction exhibits a rate law, $\text{rate} = k[\text{KMnO}_4][\text{EtAc}][\text{H}^+]^2$, where overall rate constant, $K = 1.0 \times 10^{-3} \text{ mol}^{-3} \text{ l}^3 \text{ s}^{-3}$ at 303 K. The stoichiometry of the reaction has been established as $\text{KMnO}_4 : \text{EtAc} = 2:1$ and final product identified as acetic acid. A mechanistic pathway, consistent with the kinetic studies, involving formation of the powerful oxidant H_2MnO_4^+ followed by slow hydride transfer from the ester to the oxidant has been proposed.

Key words : ethylacetate, potassium permanganate, kinetics, mechanism, oxidation, acidic.

1. Introduction

Metal ions/complexes play a dominant role in synthetic organic chemistry as they have the potential to oxidize a wide variety of organic compounds (Rao et al, 1979; Audeh and Smith, 1970). Although considerable work has been done on the oxidation of organic compounds by KMnO_4 , very little attention has been paid to the kinetics of oxidation of esters. In our continuing effort (Wimalasena et al, 1992; Kulasena and Deraniyagala, 1994; Deraniyagala and Ekanayake, 1995) to examine products and rates of oxidation of organic compounds by metal ions/ complexes, the reaction between ethylacetate (hereafter referred as $\text{CH}_3\text{COOC}_2\text{H}_5$ or EtAc or ester) and KMnO_4 in acidic medium is reported. A preliminary account of this investigation has already been presented. (Deraniyagala and Premasiri, 1998).

2. Materials and methods

Materials

All chemicals used were of analytical grade and used as received. Ethylacetate (pure grade) was always freshly distilled before use. Acetonitrile/water mixture (1:1, V/V) was used to prepare the ethylacetate solution. Potassium permanganate solution was standardized using sodium oxalate.

Experimental theory

The overall reaction can be expressed as



and the rate law can be expressed as

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]^a [\text{KMnO}_4]^b [\text{H}^+]^c$$

Since the decrease in KMnO_4 concentration is monitored, the rate law may be expressed as

$$\frac{-d[\text{KMnO}_4]}{dt} = k [\text{CH}_3\text{COOC}_2\text{H}_5]^a [\text{KMnO}_4]^b [\text{H}^+]^c \quad (1)$$

where k = rate constant, a = order with respect to $[\text{CH}_3\text{COOC}_2\text{H}_5]$, b = order with respect to $[\text{KMnO}_4]$, c = order with respect to $[\text{H}^+]$

By applying pseudo-order conditions i.e. ethylacetate and acid are used in excess, the above equation reduces to

$$\frac{-d[\text{KMnO}_4]}{dt} = k_1 [\text{KMnO}_4]^b \quad (2)$$

$$\text{where } k_1 = k [\text{CH}_3\text{COOC}_2\text{H}_5]^a [\text{H}^+]^c \quad (3)$$

If $b = 0$, then the integrated rate equation is,

$$[\text{KMnO}_4]_t = -k_1 t + c', \text{ where } c' \text{ is a constant.}$$

At $t = 0$, $[\text{KMnO}_4] = [\text{KMnO}_4]_0$ i.e. initial concentration of $[\text{KMnO}_4]$ in the reaction mixture. Therefore $c' = [\text{KMnO}_4]_0$ and rate law becomes,

$$[\text{KMnO}_4]_t = -k_1 t + [\text{KMnO}_4]_0 \quad (4)$$

Similarly, when $b = 1$, rate law becomes

$$\ln [\text{KMnO}_4]_t = -k_1 t + \ln [\text{KMnO}_4]_0 \quad (5)$$

and $b = 2$

$$\frac{1}{[\text{KMnO}_4]_t} = -k_1 t + \frac{1}{[\text{KMnO}_4]_0} \quad (6)$$

Since low concentrations of KMnO_4 obey Beer's law, (figure I, $A = \epsilon cl$)

absorbance values can be used in place of concentrations.

Here A = absorbance of $[\text{KMnO}_4]$ at 525 nm, ϵ = molar absorption coefficient, c = concentration of KMnO_4 , l = path length of the cell in cm.

Therefore $c = A/(\epsilon l)$, then the equation (4) reduces to

$$\begin{aligned} A_t/(\epsilon l) &= -k_1 t + A_0/(\epsilon l) \\ A_t &= -k_1 t + A_0 \end{aligned} \quad (7)$$

where A_t = absorbance of $[\text{KMnO}_4]$ at time t , A_0 = initial absorbance of $[\text{KMnO}_4]$

Similarly, equation 5 reduces to

$$\ln A_t = -k_1 t + \ln A_0 \quad (8)$$

and equation (6) to

$$\frac{1}{A_t} = -k_1 t + \frac{1}{A_0} \quad (9)$$

Consider equation 3

$$k_1 = k[\text{CH}_3\text{COOC}_2\text{H}_5]^a [\text{H}^+]^c$$

By keeping $[\text{H}^+]$ is constant, equation (3) becomes

$$k_1 = k_2 [\text{CH}_3\text{COOC}_2\text{H}_5]^a \quad (10)$$

$$\text{where } k_2 = k[\text{H}^+]^c \quad (11)$$

Taking the logarithm of equation 10

$$\ln k_1 = a \ln [\text{CH}_3\text{COOC}_2\text{H}_5] + \ln k_2 \quad (12)$$

Again using pseudo-order conditions, but varying the concentration of ethylacetate at constant $[\text{H}^+]$, we can utilize the equation 12 to determine the value of 'a' which is the order with respect to ethylacetate concentration i.e. from the gradient of the graph of $\ln k_1$ versus $\ln [\text{CH}_3\text{COOC}_2\text{H}_5]$.

Consider equation 3 once again,

$$k_1 = k[\text{CH}_3\text{COOC}_2\text{H}_5]^a[\text{H}^+]^c$$

Again using pseudo-order conditions, kinetic studies could be performed by varying the pH of the reaction mixture at constant $[\text{EtAc}]$. Then the above equation can be expressed as

$$k_1 = k_3 [\text{H}^+]^c \quad (13)$$

$$\text{where } k_3 = k[\text{CH}_3\text{COOC}_2\text{H}_5]^a$$

Taking logarithm of equation 9

$$\ln k_1 = c \ln [\text{H}^+] + \ln k_3 \quad (14)$$

If the plot of $\ln k_1$ versus $\ln [\text{H}^+]$ is a straight line then the order with respect to hydrogen ion concentration can be determined.

Hence the overall rate constant can be calculated using equation 11

Stoichiometry

A known amount of ethylacetate was mixed with known excess of potassium permanganate in sulphuric acid medium at 30°C for ten hours. The unreacted potassium permanganate was titrated with standard sodium oxalate solution. It was found that 1 mole of ester reacts with two moles of potassium permanganate. The experiment was performed in triplicate to test the reproducibility.

Product analysis

The product of oxidation, acetic acid, was identified in the following manner. Ethylacetate was mixed with excess potassium permanganate in sulphuric acid medium and kept at 30 °C for eight hours. The mixture was then extracted with methylene chloride. The organic layer was then separated and the formation of acetic acid was confirmed by gas liquid chromatography. (column- TC-1, dimethylpolysiloxane)

Strengths of reagents used in the kinetic study

The concentration of potassium permanganate solution was 4×10^{-3} M. The concentration of the ethylacetate prepared was 1.0 M. These solutions were used to determine order with respect to KMnO_4 and EtAc. The strength of the H_2SO_4 used in the aforementioned studies was 4.72 M. In the experiment to determine order with respect to H^+ , the strength of H_2SO_4 was 4.62 M.

Applicability of Beer's law

The applicability of Beer's law for low concentration of KMnO_4 was examined at 520 nm. Figure 1 shows the plot of absorbance versus known concentrations of KMnO_4 . This is a straight line ($r=0.9998$) which confirms that Beer's law is obeyed within the concentration range us

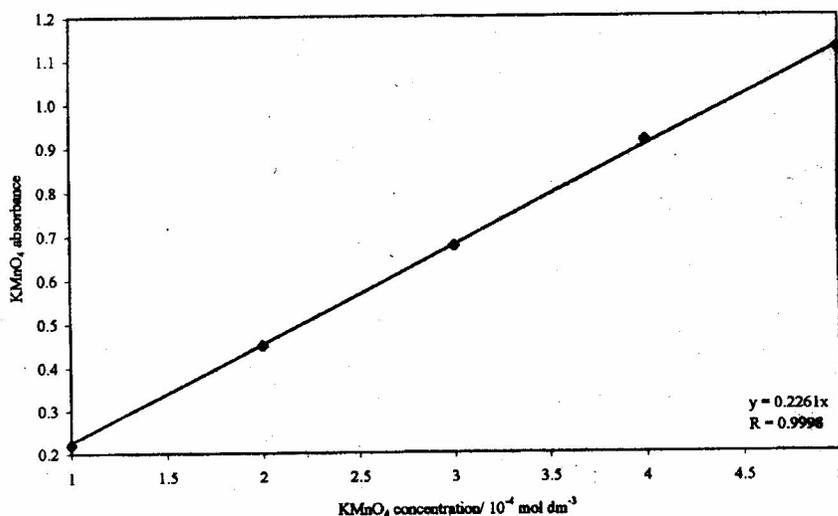


Figure 1 The plot of KMnO_4 absorbance vs concentration at 520 nm

Kinetic Studies

Kinetic studies were carried out under pseudo-order conditions by reacting KMnO_4 with excess ethylacetate (EtAc) under acidic condition in aqueous acetonitrile (1:1, V/V). The progress of the reaction was monitored colorimetrically by measuring the decrease in absorbance of KMnO_4 over a period of five minutes (at 15 second intervals) at 520 nm at different EtAc concentrations at constant pH and *vice versa*.

In all experiments, the total volume of the reaction mixture was kept at 20.00 cm³. The volumes of reagents used in the determination of orders with respect to KMnO₄, EtAc and H⁺ are given in table I and II.

Table I Volumes (cm³) of reagents used to determine order with respect to KMnO₄ and EtAc.

1 M EtAc	4.27 M H ₂ SO ₄	H ₂ O	4 x 10 ⁻³ M KMnO ₄
5.0	8.0	5.0	2.0
6.0	8.0	4.0	2.0
7.0	8.0	3.0	2.0
8.0	8.0	2.0	2.0
9.0	8.0	1.0	2.0

Table II Volumes (cm³) of reagents used to determine order with respect to H⁺

1 M EtAc	4.62 M H ₂ SO ₄	H ₂ O	4 x 10 ⁻³ M KMnO ₄
6.0	7.0	5.0	2.0
6.0	8.0	4.0	2.0
6.0	8.5	3.5	2.0
6.0	9.5	2.5	2.0

3. Results

Under the condition [EtAc] >> [KMnO₄] in 4.72 M H₂SO₄, the kinetic runs were recorded keeping the concentration of KMnO₄ and H⁺ at 4 x 10⁻⁴ M and 1.89 M respectively and varying the concentration of EtAc from 0.25 to 0.45 M (table I). Plots of ln (absorbance) versus time was found to be straight lines [figure 2, r(mean)=0.9984, co-efficient of variation=0.08%] showing that the reaction is first order with respect to KMnO₄ (equation 8). The pseudo first order rate constant k₁, was calculated from the slopes of the straight lines. Form equation 12, a plot of ln k₁ versus ln [EtAc] was found to be a straight line with a gradient (b) of 0.998 (figure 4). This shows first order dependence of rate on ethylacetate.

Kinetic runs were also carried at different $[\text{H}^+]$ at constant $[\text{EtAc}]$ (0.30 M) and $[\text{KMnO}_4]$ (4×10^{-4} M.) (table II). Plots of \ln (absorbance) versus time were also linear as shown in figure 3. $[r$ (mean)= 0.99985, co-efficient of variation=0.006%]. A set of k_1 values were then calculated from slopes. From equation 14, a plot of $\ln k_1$ versus $\ln [\text{H}^+]$ was also found to be a straight line ($r=0.9957$) with a gradient (c) equal to 1.978 (figure 5). This indicates second order dependence of rate on H^+ .

The overall rate k was calculated using equation 11,

$$k = \frac{k_2}{[\text{H}^+]^c}$$

Here $c=2$ and k_2 can be determined from the plot $\ln k_1$ versus $\ln [\text{EtAc}]$ (figure 4).

Thus the rate law observed for the oxidation of ethylacetate by KMnO_4 in sulphuric acid medium can be written as

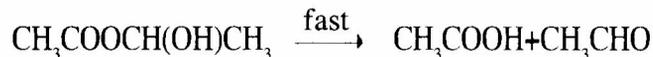
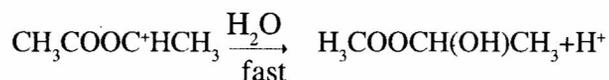
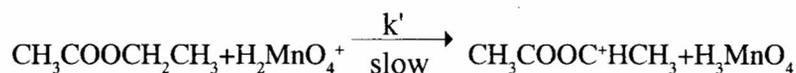
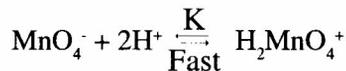
$$\frac{-d[\text{KMnO}_4]}{dt} = k[\text{KMnO}_4][\text{EtAc}][\text{H}^+]^2$$

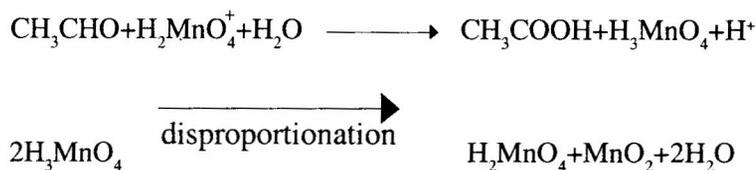
where k has been worked out to be $1.0 \times 10^{-3} \text{ mol}^{-3} \text{ l}^3 \text{ s}^{-3}$ at 303 K.

4. Discussion

Since the rate law takes the form $\frac{-d[\text{KMnO}_4]}{dt} = k[\text{KMnO}_4][\text{EtAc}][\text{H}^+]^2$

a stoichiometric mechanism involving a rapid equilibrium to form the powerful oxidant H_2MnO_4^+ (Cotton & Wilkinson, 1988) followed by slow attack (rate determining step) of this species on the alcohol moiety of the ester with the transfer of hydride ion from α -carbon of the ethoxy group to the oxidant to form acetic acid and aldehyde has been proposed (scheme 1)





Scheme 1

A similar process can be envisaged for the further oxidation of aldehyde to acid. This type of hydride transfer has been proposed in the oxidation of alcohols, aldehydes and ethers by KMnO_4 in acid solution (Barter & Littler, 1967; Steward, 1965). The formation of a brown precipitate, on standing, confirms the formation of MnO_2 as one of the reduced products of KMnO_4 .

Taking the second step in the proposed mechanism as the rate determining step the rate of disappearance of KMnO_4 is given by the equation 15

$$\frac{-d[\text{KMnO}_4]}{dt} = k' [\text{EtAc}][\text{H}_2\text{MnO}_4^+] \quad (15)$$

$$\text{However } K = \frac{[\text{H}_2\text{MnO}_4^+]}{[\text{H}^+]^2[\text{MnO}_4]}$$

$$\text{Therefore } \frac{-d[\text{MnO}_4]}{dt} = k' K [\text{MnO}_4] [\text{EtAc}] [\text{H}^+]^2 \quad (16)$$

Hence the equation 16 provides satisfactory explanation all experimental results.

5. Conclusion

Kinetics of the oxidation of ethylacetate by potassium permanganate to acetic acid in acidic medium is governed by the rate law,

$$\frac{-d[\text{KMnO}_4]}{dt} = k[\text{KMnO}_4][\text{EtAc}][\text{H}^+]^2$$

where $k = 1.0 \times 10^{-3} \text{ mol}^{-3} \text{ l}^3 \text{ s}^{-3}$ at 303 K. The mechanism of oxidation is believed to involve the transfer of an hydride ion to the oxidant, H_2MnO_4^+ from the ester.

6. Acknowledgement

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7. References

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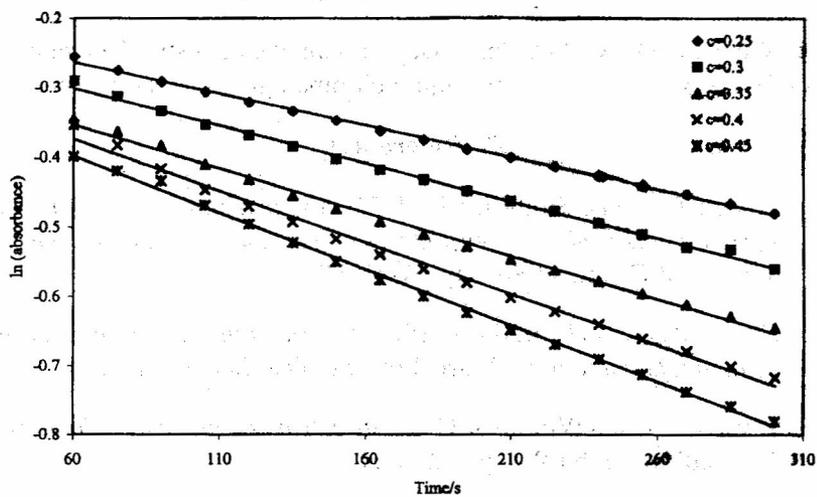


Figure 2 The plot of $\ln(\text{KMnO}_4 \text{ absorbance})$ vs time at different ester concentrations ($c, \text{mol dm}^{-3}$) $[\text{H}^+] = 1.888 \text{ mol dm}^{-3}$

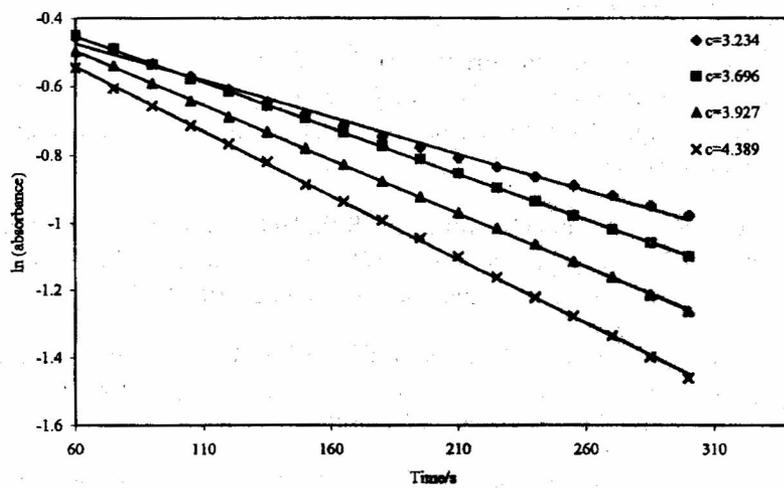
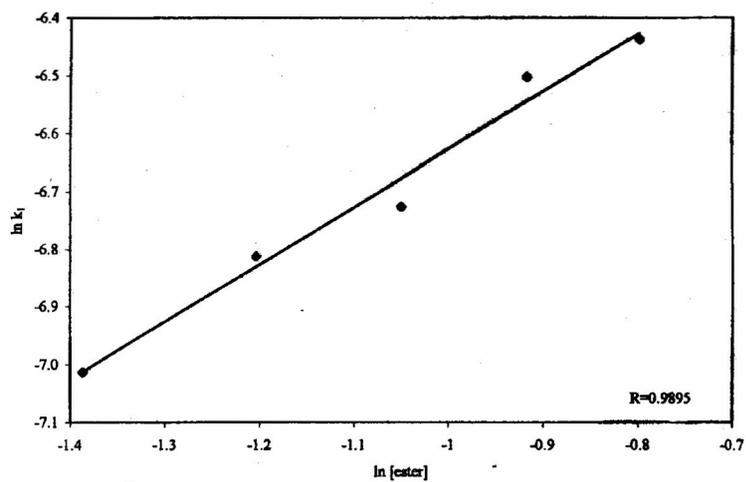
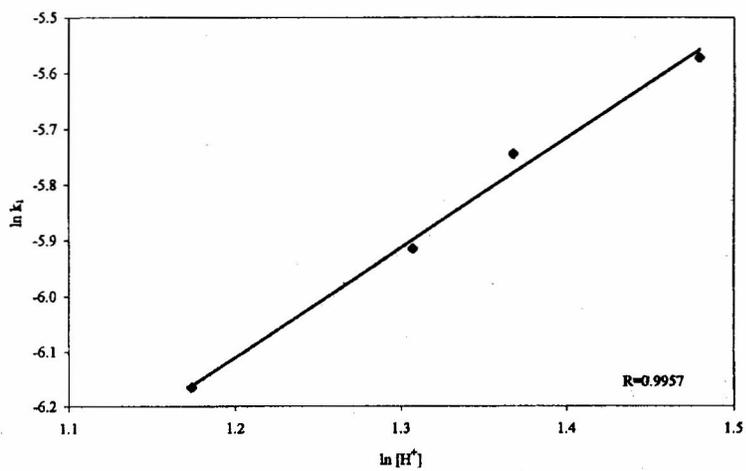


Figure 3 The plot of $\ln(\text{KMnO}_4 \text{ absorbance})$ vs time at different H^+ concentrations ($c, \text{mol dm}^{-3}$) $[\text{ester}] = 0.30 \text{ mol dm}^{-3}$

Figure 4 The plot $\ln k_1$ vs $\ln [\text{ester}]$ Figure 5 The plot of $\ln k_1$ vs $\ln [\text{H}^+]$