Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1037–1040

Kinetics of Oxidative Decarboxylation of β-Benzoylpropionic Acid by Manganese (III) Acetate

G. SIKKANDAR
Research and Post-Graduate Department of Chemistry
Jamal Mohamed College, Tiruchirappalli-620 023, India

The kinetics of oxidative decarboxylation of β-benzoylpropionic acid by manganese(III) acetate in aqueous acetic acid medium have been studied. The reaction is first order each in [substrate], [oxidant] and [H^+] ion. The effects of solvent polarity and temperature on the rate of oxidation have been measured. Activation parameters are evaluated and a suitable mechanism consistent with the experimental results has been proposed.

INTRODUCTION

Manganese(III) acetate is one of the group of metal ion oxidants which apparently react *via* one electron steps in the oxidation of several organic compounds[1–3]. Kinetics of oxidation of keto acids by acid permanganate have been reported[4], though similar studies with manganese(III) acetate have not been carried out. The present paper deals with the kinetic study of oxidative decarboxylation of β-benzoylpropionic acid by manganese(III) acetate.

EXPERIMENTAL

All the chemicals used during the investigation were of AR grade. β-Benzoylpropionic acid was prepared by Friedel-Craft's reaction between benzene and succinic anhydride in presence of anhydrous $AlCl_3$ and purified[5]. Manganese(III) acetate was prepared by the literature procedure[6]. The stock solutions of manganese(III) acetate were prepared in doubly distilled glacial acetic acid. The reactions were carried out under pseudo first order conditions in thermostat (± 0.1°C).

The rate of reaction was followed by estimating the unreacted manganese(III) acetate by iodometric procedure. The rate constants were computed with an accuracy of 2–3% in duplicate runs. The products of the reaction were identified and the stoichiometry of the oxidation was determined under the condition [substrate] ≪ [Mn(III) acetate].

$$C_6H_5—CO—CH_2—CH_2—COOH + 2Mn(OAc)_3 \longrightarrow C_6H_5—CO—CH{=}CH_2 + 2Mn(OAc)_2 + 2AcOH + CO_2$$

RESULTS AND DISCUSSION

The kinetics of oxidation of β-benzoylpropionic acid by manganese(III) acetate have been studied in 50% aqueous acetic acid medium. The order of the reaction with respect of Mn(III) acetate is unity since the observed rate constant remains constant for different concentrations of the oxidant (Table-1). The reaction is found to be first order in the keto acid concentration as the values of k_1/[keto acid] remain constant (Table-1). The rate constant of the reaction increases with increase in concentration of sulphuric acid, suggesting that the reactions under study are acid catalysed (Table-1). The plot of log k_1 against log $[H^+]$ is linear with a slope of unity which indicates that the reaction is first order with respect to $[H^+]$ ion.

TABLE-1
RATE CONSTANTS FOR THE OXIDATION OF β-BENZOYLPROPIONIC ACID BY MANGANESE(III) ACETATE

Solvent: Acetic acid-water (50% v/v); Temp = 303 K

10^3 [Mn(III)] (mol dm^3)	[Keto acid] (mol dm^3)	$[H^+]$ (mol dm^3)	10^5 k_1 (s^{-1})
2.0	0.02	1.0	2.53
3.0	0.02	1.0	2.57
4.0	0.02	1.0	2.59
5.0	0.02	1.0	2.63
6.0	0.02	1.0	2.67
0.04	1.0	1.0	1.28
0.04	2.0	1.0	2.58
0.04	3.0	1.0	3.90
0.04	4.0	1.0	5.08
0.04	5.0	1.0	6.45
4.0	0.05	0.4	2.47
4.0	0.05	0.7	3.94
4.0	0.05	1.0	5.61
4.0	0.05	1.3	7.48
4.0	0.05	1.6	9.95

The increase in the amount of acetic acid in the reaction mixture enhances the reaction rate significantly (Table-2). The lowering of dielectric constant of the reaction medium may facilitate enolisation of keto group of the substrate and this may be responsible for the enhancement of reaction rate.[7] The addition of salts to the reaction mixture show negligible effect on the rate of reaction indicating that the rate determining step involves an ion and a neutral molecule[8]. When vinyl monomers are added to the reaction mixture, polymer formation has been observed. This ascertains that the reaction occur through free radical mechanism.

The rate measurements have been made at different temperatures and the corresponding rate constants (k_1) are found out (Table-2). Linear Arrhenius plots are obtained when log k_2 is plotted against 1/T. The calculated values of E_a, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ are 28.9 kJ mol^{-1}, 26.4 kJ mol^{-1}, 74.2 kJ mol^{-1} and –155 J mol^{-1} K^{-1} respectively.

TABLE-2
EFFECT OF PERCENTAGE COMPOSTION OF ACETIC ACID

[keto acid] = 2.0×10^{-3} mol dm^{-3} [Mn (III) acetate] = 4.0×10^{-3} mol dm^{-3}
$[H_2SO_4]$ = 1.0 mol dm^{-3} Temp = 313 K

Percentage of acetic acid	50	60	65	70	75
$k_1 \times 10^5$ s^{-1}	5.71	12.3	15.4	19.2	28.8

EFFECT OF TEMPERATURE OF RATE CONSTANT

[keto acid] = 2.0×10^{-3} mol dm^{-3} [Mn(III) acetate] = 2.0×10^{-3} mol dm^{-3}
$[H_2SO_4]$ = 1.0 mol dm^{-3} HOAc-H_2O = 50% v/v

Temperature	303	308	313	318	323
$k_1 \times 10^{-5}$ s^{-1}	2.56	3.40	4.24	5.85	7.52

Mechanism and rate expression

Based on the experimental facts, a scheme of mechanism involving the formation of a complex which decomposes to a free radical species which is subsequently oxidised to various products has been suggested[9,10].

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \quad (1)$$

where S stands for substrate,

$$SH^+ + Mn(OAc)_3 \xrightarrow[\text{slow}]{k_2} \text{Complex} + AcOH + H^+ \quad (2)$$

$$\text{Complex} \xrightarrow{\text{fast}} \text{radical} + Mn(OAc)_2 \quad (3)$$

$$\text{Radical} \xrightarrow[\text{fast}]{Mn(OAc)_3} \text{Products} \quad (4)$$

On applying steady state approximation,

$$\frac{-d[Mn(III)]}{dt} = \frac{k_1 k_2 [s][H^+][Mn(III)]}{k_{-1} + k_2 [Mn(III)]}$$

Since, $k_{-1} \gg k_2$,

$$\frac{-d[Mn(III)]}{dt} = Kk_2 [s][H^+][Mn(III)]$$

where $K = k_1/k_{-1}$

The derived rate law is in consistent with the experimental facts.

ACKNOWLEDGEMENTS

The author is thankful to University Grants Commission, New Delhi for a research project grant and authorities of Jamal Mohamed College for providing facilities.

REFERENCES

1. K.B. Wiberg, Oxidation in Organic Chemistry, Academic Press, New York, p 186 (1965).
2. A.Y. Drummond and W.A. Water, *J. Chem. Soc.*, 497 (1955).
3. J.B. Bush (Jr.) and H. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 5903 (1968).
4. G. Sikkandar, K.A. Basheer Ahmed and S. Kannan, *Indian J. Chem.*, **31A**, 845 (1992).
5. A.I. Vogel, Text Book of Practical Organic Chemistry, Longmans Green, London, p. 737 (1962).
6. P.J. Andrulis (Jr.), M.J.S. Dewar, R. Dietz and R.L. Hunt, *J. Am. Chem. Soc.*, **88**, 5483 (1966).
7. N.P. Marigangiah and K.K. Banerji, *Indian J. Chem.*, **14A**, 660 (1976).
8. K.J. Laidler, Chemical Kinetics, Harper & Row Publishers, New York, p. 198 (1987).
9. J. Barck and A. Berka, *Collen Czech. Chem. Commun.*, **39**, 3278 (1974).
10. C.F. Wells and L.V. Kuritsyn, *J. Chem. Soc. (A)*, 676 (1970).

(*Received:* 28 March 2000; *Accepted:* 1 June 2000) AJC-2049