Asian Journal of Chemistry Vol. 10, No. 2 (1998), 324–327

Mechanistic Study of Oxidation of Propanal by Potassium Ferricyanide Catalysed by Osmium Tetroxide in Alkaline Media

H.N. SINGH*, O.P. SRIVASTAVA† and KAMAL KISHOR SINGH‡
Chemical Laboratory
A.M. College, Gaya, India

The title reaction in alkaline medium shows first order dependence each on [Oxidandt], [Substrate] and [OH^-] in the absence of catalyst But in the presence of catalyst, the reaction shows zero order with respect to oxidant and first order with respect to catalyst.

INTRODUCTION

Kinetic study of oxidative reactions involving aliphatic alchohols, aldehydes and ketones by potassium ferricyanide in alkaline media has been reported by many workers.[1–4] In the present work, we report the oxidation of propanal by potassium ferrocyanide in alkaline media in the presence of osmium tetroxide.

EXPERIMENTAL

AR grade propanal and other chemicals have been used in the present investigations. The solution of the catalyst osmium tetroxide was prepared in sodium hydroxide. The carbonate-bicarbonate buffer solution was prepared. The ceric sulphate solution was prepared in sulphuric acid and was standardised. The ferroin has been used as an indicator. The freshly prepared standard solution of potassium ferricyanide has been employed during the experiment.

Kinetic procedure was adopted as suggested by Pandey and Singh[1] and the results are being presented in the Tables (1 to 9).

RESULTS AND DISCUSSION

From the results given in the Tables 1 and 2, it is evident that the order of reaction with respect to oxidant is unity, whereas order of reaction with respect to oxidant in the presence of catalyst is zero which explains the involvent of oxidant in the presence of catalyst in the fast process of disappearance or oxidant in the kinetic procedure.

The analytical study of Tables 3 and 4 makes it clear that in the absence and in the presence of the catalyst order of reaction with respect to substrate is unity which throws light on the same kinetic procedure with respect to substrate.

---

†P.G. Department of Chemistry, Magadh University, Bodh-Gaya-824 234 India.
‡Department of chemistry, Gaya College, Gaya-823 001 Bihar, India

TABLE-1

Temperature 303 K
[Substrate] = 0.5×10^{-2} mol dm^{-3}
[CO_3^{2-}] = 1.25 mol dm^{-3}

[$K_3Fe(CN)_6$] × 10^{-2} (mol dm^{-3})	$k_s \times 10^5$ (mol dm^{-3} min^{-1})
0.330	8.70
0.200	5.392
0.120	3.356
0.110	3.210
0.100	2.889

TABLE-2

Temperature 303 K
[Substrate] = 0.5×10^{-2} mole dm^{-3}
[CO_3^{2-}] = 1.25 mol dm^{-3}
[OsO_4] = 3.20×10^{-5} Mol dm^{-3}

[$K_3(Fe(CN)_6)$] × 10^{-2} (mol dm^{-3})	$k_s \times 10^5$ (mol dm^{-3} min^{-1})
0.40	1.3200
0.35	1.2830
0.30	1.3113
0.25	1.2926
0.15	1.2860
0.08	1.2626

TABLE-3

Temperature 303 K
[$K_3Fe(CN)_6$] = 0.20×10^{-2} Mol dm^{-3}
[CO_3^{2-}] = 10.00×10^{-2} mol dm^{-3}
[HCO_3^-] = 2.00×10^{-2} mol dm^{-3}

[Substrate] × 10^2 (mol dm^{-3})	$k_s \times 10^5$ (mol dm^{-3} min^{-1})
2.00	2.15
1.40	1.50
1.00	1.08
0.70	0.76
0.50	0.56

TABLE-4

Temperature 303 K
[$K_3Fe(CN)_6$] = 0.20×10^{-2} mol dm^{-3}
[OsO_4] = 3.20×10^{-5} mol dm^{-3}
[CO_3^{2-}] = 10.00×10^{-2} mol dm^{-3}
[HCO_3^-] = 2.00×10^{-2} mol dm^{-3}

[Substrate] × 10^2 (mol dm^{-3})	$k_s \times 10^5$ (mol dm^{-1} min^{-1})
2.00	2.746
1.40	1.922
1.00	1.373
0.70	0.961
0.50	0.686

TABLE-5

Temperature 303 K
[Substrate] = 1.20×10^{-2} mole dm^{-3}
[Oxidant] = 0.20×10^{-2} mol dm^{-3}

[OH^-] × 10^5 (mol dm^{-3})	$k_s \times 10^6$ (Mol dm^{-3} min^{-1})
1.250	5.787
1.000	3.650
0.793	2.242
0.631	2.894

TABLE-6

Temperature 303 K
[Substrate] = 1.20×10^{-2} mol dm^{-3}
[Oxidant] = 0.20×10^{-2} mol dm^{-3}
[OsO_4] = 3.20×10^{-5} mol dm^{-3}

[OH^-] × 10^5 (mol dm^{-3})	$k_s \times 10^6$ (mol dm^{-3} min^{-1})	
7.93	7.77	7.70
11.23	1.12	11.20
14.14	1.32	13.20
25.12	0.87	8.70

From the observations of Tables 5 and 6 it is found that rate is affected with rise in concentration of [OH^-] ions when there is use or no use of catalyst.

Results shown in Table-7 indicate that catalyst influences the kinetic oxidation of propanal by oxidant in the presence of carbonate and bicarbonate buffer and order of reaction with respect to catalyst is unity.

TABLE-7

Temperature 303 K
[Substrate] = 2.00×10^{-2} mol dm^{-3}
[Oxidant] = 0.20×10^{-2} mol dm^{-3}
[CO_3^{2-}] = 10.00×10^{-2} mol dm^{-3}
[HCO_3^-] = 2.00×10^{-2} mol dm^{-3}

[OsO_4] × 10^5 (mol dm^{-3})	$k_s \times 10^5$ (mol dm^{-3} min^{-1})
8.00	5.60
6.00	4.68
4.00	2.80
3.00	2.34
1.50	1.18

TABLE-8

[Substrate] = 0.70×10^{-2} mol dm^{-3}
[Oxidant] = 0.20×10^{-2} mol dm^{-3}
[CO_3^{2-}] = 10.00×10^{-2} mol dm^{-3}
[HCO_3^-] = 2.00×10^{-2} mol dm^{-3}

Temp. (K)	$k_s \times 10^5$ (mol dm^{-3} min^{-1})	E_a (k.hs.)
298	5.076	13.895
303	6.912	—
308	10.250	—

TABLE-9

[Substrate] = 0.70×10^{-2} mol dm^{-3}
[Oxidant] = 0.20×10^{-2} mol dm^{-3}
[CO_3^{2-}] = 10.00×10^{-2} mol dm^{-3}
[HCO_3^-] = 2.00×10^{-2} mol dm^{-3}

Temp. (K)	$k_{10} \times 10^3$	$k_s \times 10^{+6}$ (mol dm^{-3} min^{-1})	E_a (k.hs.)
297	3.36	4.339	14.948
301	3.32	8.568	—
305	3.278	12.621	—
309	3.236	17.220	—

Results presented in Tables 8 and 9 indicate the influence of temperature and in both cases activation energy is almost nearly equal and the temperature coefficient value is nearly two which indicates that with the rise of ten degrees in temperature, the reaction rate becomes double in both cases which confirms the suggestion of Arrhenius related to the theory of reaction rate. The values of activation energy obtained in both cases reveal that in the oxidative reaction, reacting species must be neutral molecules. Hence from the above discussions, we came to the conclusion to suggest the kinetics of oxidation of propanal by potassium ferrocyanide in the absence and in presence of catalyst according to the following schemes:

Scheme-1

$$S + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + H_2O \tag{i}$$

$$\text{enolate} + Fe(CN)_6^{3-} \xrightarrow{k_3} \text{Product} + Fe(CN)_6^{4-} \tag{ii}$$

Based on the steps (i) and (ii) the rate law (iii) has been deduced as,

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = K[S][OH^-][Fe(CN)_6^{3-}]$$

$$\text{where } K = \frac{k_1k_2/k_{-1}}{H_2O} \text{ assuming } [H_2O] \gg \frac{k_2}{k_{+1}}[Fe(CN)_6^{-3}] \qquad \text{(iii)}$$

This rate law confirms on experimental findings recorded in Tables 1,3 and 5.

Scheme-2

$$S + OH^- \underset{k_{-1}(\text{slow})}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + H_2O \qquad \text{(i)}$$

$$\text{Enolate} + Os^{8+} \rightarrow \text{Complex} + (X) \qquad \text{(ii)}$$

$$X \xrightarrow[\text{fast}]{k_3} \text{Product } Os^{6+} \qquad \text{(iii)}$$

$$Os^{6+} + 2[Fe(CN)_6^{3-}] \xrightarrow[\text{fast}]{k_4} Os^{8+} + 2[Fe(CN)_6^{4-}] \qquad \text{(iv)}$$

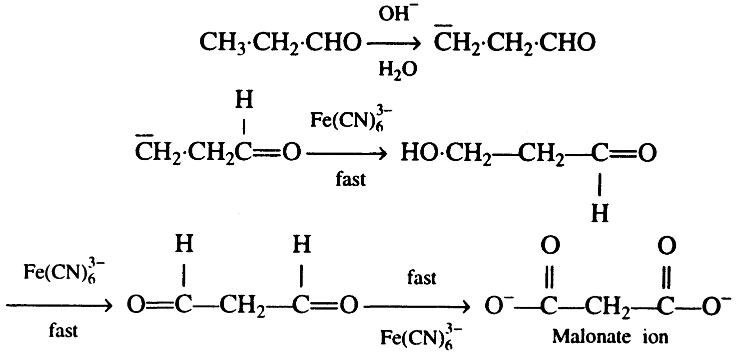
On the basis of above steps of this oxidative reaction the rate law (v) has been deduced as—

$$\frac{d[Fe(CN)_6^{3-}]}{dt} = K[S][OH^-][Os^{8+}]$$

$$\text{where } K = \frac{k_1k_2}{[H_2O]} = \frac{(k_1/k_{-1})\cdot k_2}{[H_2O]} \text{ neglecting the term } k_2/k - 1(O_s^{8+}).$$

This rate law confirms the result obtained in Tables 4, 7 and 8. The scheme suggested is in good agreement with the finding of Pandey and Singh.[1]

Product analysis indicates formation of malonic acid which may be explained as:



$$CH_3\cdot CH_2\cdot CHO \xrightarrow[H_2O]{OH^-} \bar{C}H_2\cdot CH_2\cdot CHO$$

$$\bar{C}H_2\cdot CH_2\overset{H}{\overset{|}{C}}{=}O \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} HO\cdot CH_2—CH_2—\underset{H}{\underset{|}{C}}{=}O$$

$$\xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} O{=}\overset{H}{\overset{|}{C}}—CH_2—\overset{H}{\overset{|}{C}}{=}O \xrightarrow[Fe(CN)_6^{3-}]{\text{fast}} O^-—\overset{O}{\overset{\|}{C}}—CH_2—\overset{O}{\overset{\|}{C}}—O^-$$

Malonate ion

ACKNOWLEDGEMENT

The authors are grateful to Prof. E.B. Singh (Magadh University, Bodh-Gaya) for his valuable suggestions.

REFERENCES

1. P.C. Pandey and V.N. Singh, *Indian J. Chem.*, **9**, 430 (1971).
2. G.K. Khewat and G.D. Menghani, *J. Indian Chem. Soc.*, **64**, 766 (1987).
3. B. Madhava Rao and U.R. Choudhary, *Asian J. Chem.*, **1**, 318 (1989).
4. N.C. Khandual, *J. Indian Chem. Soc.*, **67**, 561 (1990).

(*Received*: 15 October 1997; *Accepted*: 10 November 1997) AJC-1387