Asian Journal of Chemistry Vol. 4, No. 2 (1992), 280–284

A Kinetic Study of Induced Catalysed Oxidation of Alcohols by Chlorite Ions in Acidic Medium

VIVEK TIWARI and S. K. SOLANKI*
Department of Chemistry
Vikram University, Ujjain–456 010, India

The kinetics of catalysed oxidation of *iso*-propanol and *n*-propanol by chlorite ion in acidic medium has been carried out. The catalyst ($Fe^{2+} + Cu^{2+}$) shows predominant accelerating effect on reaction velocity. The reaction follows first and zero order with respect to oxidant and substrate concentration respectively. The reaction rate is directly proportional to the catalyst concentration. Different kinetic and activation parameters have been computed. A probable reaction mechanism has been proposed.

INTRODUCTION

From earlier papers it has been found that in the cases of peroxydisulphate oxidation reaction Ag^+ and Cu^{2+} have good catalysing power[1–3]. In conformity with Mccurdy and Guilbault's[4] observation, it was found that the catalytic effect of mixture of $Ag^+ + Cu^{2+}$ was much greater than the effects due to the two catalysts taken separately in the oxidation reactions of peroxydisulphate ion. Recently Kudesia[5] has studied the kinetics of oxidation of primary alcohols with chlorite ion in acidic medium and has indicated first order dependency with respect to oxidant concentration. In this paper, investigations of oxidation of aliphatic alcohols with chlorite ion catalysed by the mixture of ($Fe^{2+} + Cu^{2+}$) ions have been presented.

EXPERIMENTAL

All solutions were prepared in doubly distilled water. Distilled *iso*-propanol and *n*-propanol were used, and the purity of these alcohols was checked by standard methods.[6] Sulphuric acid (AR grade) was used after purification[7]. Required amounts of the substrate catalyst, oxidant and acid solutions were taken in the glass stoppered bottles, which were painted black from outside to check any photochemical reaction and thermostated at desired temperature. The rate measurements were made by estimating unreacted chlorite ion by iodometric method in given time intervals.

RESULTS AND DISCUSSIONS

The order with respect to [ClO_2^-] was found to be one in the presence of ($Fe^{2+} + Cu^{2+}$) catalyst. The plot of log (a – x) versus time shows parallel lines with unit slope values, which confirms the first order dependency with respect to chlorite ion concentration. The results are summarised in Table 1.

TABLE 1

ORDER WITH RESPECT TO [ClO_2^-]

[Alcohol] = 15×10^{-2} mol dm^{-3} Temp. = 313°K
[$Fe^2 + Cu^{2+}$] = 1.0×10^{-4} mol dm^{-3} pH = 3.0

[ClO_2^-] × 10^3 mol dm^{-3}	k × 10^4 sec^{-1}	
	n-Propanol	*iso*-Propanol
2.0	1.25	2.46
3.0	1.24	2.44
4.0	1.23	2.42
5.0	1.21	2.41
6.0	1.20	2.40

The first order rate constant values did not alter with the change in concentration of each aliphatic alcohol, indicating that the order in [Substrate] is zero. The observations are given in Table 2.

TABLE 2

ORDER WITH RESPECT TO [SUBSTRATE]

[$NaClO_2$] = 5.0×10^{-3} mol dm^{-3} Temp = 331°K
[$Fe^{2+} + Cu^{2+}$] = 1.0×10^{-4} mol dm^{-3} pH = 3.0

[Alcohol] × 10^2 mol dm^{-3}	k × 10^4 sec^{-1}	
	n-Propanol	*iso*-Propanol
05	1.20	2.41
10	1.22	2.40
15	1.21	2.41
20	1.22	2.42
25	1.19	2.41

The first order rate constant value increases with the increases in the Fe^{2+} or ($Fe^{2+} + Cu^{2+}$) concentration but the rate values in the presence of ($Fe^{2+} + Cu^{2+}$) mixture was much greater than the rate values in the presence of Fe^{2+}, when taken separately under similar conditions. The results are presented in Table 3.

The reaction was studied at different pH (range 1.1–3.5) of appropriate buffer solution and it was observed that the rate value increases

TABLE 3

EFFECT OF [Fe^{2+} + Cu^{2+}] AND [Fe^{2+}] ON THE REACTION RATE

[Alcohol] = 15×10^{-2} mol dm^{-3} Temp. = 313°K

[ClO_2^-] = 5.0×10^{-3} mol dm^{-3} pH = 3.0

[Fe^{2+} + Cu^{2+}] $\times 10^4$ mol dm^{-3}	k $\times 10^4$ sec^{-1}		[Fe^{2+}] $\times 10^4$ mol dm^{-3}	k $\times 10^4$ sec^{-1}	
	u-Propanol	*iso*-Praponal		*n*-Propanol	*iso*-Propanol
—	0.12	0.23	—	—	—
0.5	0.92	2.11	0.5	0.52	1.16
1.0	1.21	2.41	1.0	0.63	1.22
1.5	1.41	2.72	1.5	0.81	1.31
2.0	1.57	3.05	2.0	0.89	1.46
2.5	1.92	3.30	2.5	1.01	1.54

upto pH 2.0 (*n*-propanol) and 2.5 (*iso*-propanol) then decreases at higher pH values.

It was observed that the rate values did not alter with the addition of different amount of salts (5.0×10^{-3} mol dm^{-3} to 20×10^{-3} mol dm^{-3}), i.e. KCl and $NaClO_4$, to the reaction mixture. The thermodynamic parameters have been computed in both the cases. The calculated values of activation parameters are presented in the Table 4.

TABLE 4

ACTIVATION PARAMETERS

[Alcohol] = 15×10^{-2} mol dm^{-3} [$NaClO_2$] = 5.0×10^{-3} mol dm^{-3}

[Fe^{2+} + Cu^{2+}] = 1.0×10^{-4} mol dm^{-3} pH = 3.0, Temp = 308°K

Parameters	*n*-Propanol	*iso*-Propanol
E_a (KJ mol^{-1})	50.92	36.70
log A	8.57	6.35
ΔH^* (KJ mol^{-1})	48.36	34.14
ΔS^* (JK^{-1} mol^{-1})	−84.73	−127.20
ΔG^* (KJ mol^{-1})	73.32	74.46

The rate dependency with respect to substrate indicates that substrate may be involved in the fast step of the probable reaction mechanism.

The rate dependency on catalyst (Fe^{2+}) clearly shows that it should be involved in the slow *i.e.* rate determining step. The sequence of possible reaction of the proposed mechanism are shown by the given scheme.

$$H^+ + ClO_2^- \overset{K_1}{\rightleftharpoons} HClO_2^+ \qquad (1)$$

$$HClO_2 + H^+ \overset{K_2}{\rightleftharpoons} H_2ClO_2^+ \qquad (2)$$

$$H_2ClO_2^+ + Fe^{2+} \xrightarrow{k_1} H_2O + FcClO^+ \quad \text{(slow)} \qquad (3)$$

$$FeClO^+ + Cu^{2+} \overset{K_3}{\rightleftharpoons} [X] + Cl^- \qquad (4)$$

$$[X] + S + 2H^+ \xrightarrow{k_2} \substack{RCHO \\ R{-}COR'} + H_2O + Fe^{2+} + Cu^{2+} \qquad (5)$$

By applying steady state condition for the intermediate species [X], the expression is as

$$-\frac{d[ClO_2^-]}{dt} = \left\{\frac{K_1[H^+] + K_2[H^+]^2 + k_1(Fe^{2+}]}{K_1[H^+]\,K_2[H^+]}\right\}[ClO_2^-]\,[S]^0$$

Since the uncatalysed oxidation rate of substrate is too slow, the catalysed reaction is fast one and substrate has zero order dependency. The catalyst Fe^{2+} catalyses the reaction by forming intermediate complex with Cu^{2+} which induces the catalysis process. In this catalysis process the intermediate forms of iron II and IV may play an important role, which is one of the basic causes of catalytic power of Fe^{2-} as compared to Cu^{2+} species; such observations were pointed out earlier.[8,9] Cu^{2+} or Fe^{2+} is well known to be a good electron donor[10]. Due to this behaviour the rate values in the case of Fe^{2+} or Cu^{2+} are lower than the rate values in the presence of ($Fe^{2+} + Cu^{2+}$) mixture. The increase in the rate in the presence of ($Fe^{2+}+Cu^{2+}$) could, therefore, be attributed due to easier electron transfer in their presence.

The zero order dependency with respect to substrate concentration shows that substrate is involved in fast step as shown in the proposed reaction mechanism.

The products analysis of the reaction indicates that the major product of substrate was aldehyde in the case of *n*-propanol, whereas, ketone in the case of *iso*-propanol, which were confirmed by the spot test[11].

REFERENCES

1. M. G. Ram Reddy, B. Sethuram and T. Navaneeth Rao, *Z. Phys. Chem.*, **256**, 880 (1975).
2. ——, *Indian J. Chem.*, **16A**, 31 (1978).
3. ——, *Indian J. Chem.*, **17A**, 378 (1979).
4. W. H. McCurdy (Jr.) and Guilbault, *Analyt. Chem.*, **32**, 647 (1960); **33**, 580 (1961).

5. V. P. Kudesia, *Revue-Roum. Chim.*, **24**, 313 (1979).
6. D. D. Perrin, W. L. Armarago and D. D. Perrin, Purification of Organic Compounds, Pergamon Press, London (1966).
7. A. I. Vogel, Quantitative Inorganic Analysis, Longmans Green and Co. Ltd., London.
8. J. M. Anderson and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 2450 (1970).
9. J. K. Kochi, J. D. Bacha and T. W. Bethea. *J. Am. Chem. Soc.*, **89**, 6538 (1967).
10. R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 6688 (1968).
11. H. Singh, A. Kumar, Advanced Practical Chemistry, Vol. II, p. 62 (1987).

[*Received*: 14 May 1990; *Accepted*: 1 March 1991] AJC–266