



## KINETIC AND MECHANISTIC STUDY OF OXIDATION OF ALLYL ALCOHOL BY DIPERIODATOCUPRATE (III) IN AQUEOUS ALKALINE MEDIUM

R. S. SHETTAR and S. T. NANDIBEWOOR\*

Post-Graduate Department of Studies in Chemistry,  
Karnatak University, DHARWAD-580 0003 (K.S.) INDIA  
E.mail: stnandibewoor@yahoo.com Fax (off): 0836-2747884

### ABSTRACT

The kinetics of oxidation of allyl alcohol by alkaline diperiodatocuprate (III) (DPC) was studied spectrophotometrically. A mechanism involving the formation of an intermediate complex between the diperiodatocuprate as the oxidant species and allyl alcohol has been proposed. The reaction constants involved in the mechanism were evaluated. The activation parameters with respect to the slow step of scheme were evaluated and discussed.

**Key words:** Allyl alcohol, Diperiodatocuprate (III), Oxidation, Kinetics.

### INTRODUCTION

The periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several compounds. The reactivity of some alcohols with diperiodatocuprate (III) (DPC) was reported in the earlier work<sup>1</sup>. DPC has been used in the estimation of amino acids<sup>2,3</sup>. Cu (III) is shown to be an intermediate in the Cu (II)-catalysed oxidation of amino acids by peroxydisulphate<sup>4</sup>. The use of diperiodatocuprate (III) as an oxidant in alkaline medium is new and restricted to a few cases due to the fact of its limited solubility and stability in aqueous medium. Moreover, when the Cu (III) periodate complex is oxidant and since multiple equilibria between the different copper (III) species are involved, it is necessary to know, which of the species is the active oxidant.

Allyl alcohol (AA) finds a number of industrial applications in the preparations of resins, plasticisers, pharmaceuticals and many organic compounds. Different products were obtained with different oxidants<sup>5,6</sup> for the oxidation of allyl alcohol. The kinetic study of amino acids, alcohols, amines, diamines and triamines, diols, and many carbohydrates using diperiodatocuprate (III) are reported earlier<sup>7,8</sup>. In view of multiple equilibria embracing different copper (III) periodate species and the complexity of the title reaction, a detailed study of the reaction is undertaken.

## EXPERIMENTAL

The solution of allyl alcohol (sd fine) was prepared and standardized<sup>9</sup> by dissolving a known amount in distilled water. The copper (III) periodate complex was prepared by standard procedure<sup>10,11</sup>. Periodate solution was prepared by weighing out the required amount of sample in hot water and it was kept for 24 hours. Its concentration was ascertained iodometrically<sup>12</sup> at neutral pH by phosphate buffer. KOH and KNO<sub>3</sub> (BDH, AR) were employed to maintain the required alkalinity and ionic strength, respectively in reaction solutions.

**Kinetic procedure:** The oxidation of allyl alcohol by DPC was followed under pseudo-first order conditions where [AA] was excess over [DPC] at 25°C unless stated otherwise. The progress of reaction was followed by measuring the absorbance of unreacted [DPC] in the reaction mixture in 1 cm cell in a thermostated compartment of a HITACHI 150–20 spectrophotometer at 415 nm. The first-order rate constants were calculated from the slopes of log [DPC] vs time plots. The plots were linear up to 80% completion of the reaction and rate constants were reproducible within  $\pm 5\%$ .

## RESULTS AND DISCUSSION

**Stoichiometry:** Different sets of reaction mixtures containing different concentrations of DPC and allyl alcohol with constant OH<sup>-</sup> and KNO<sub>3</sub> were kept for 6 hours in closed vessels under nitrogen atmosphere. Under the condition [DPC] > [AA], the remaining concentration of DPS was estimated spectrophotometrically at 415 nm. And also when [AA] > [DPC], the excess allyl alcohol was estimated<sup>12</sup> by the addition of an excess chloramine-T, followed by iodometric titration. The results indicated a 1:2 stoichiometry. Stoichiometric ratio suggests the main product as acrolein, which was identified by spot test<sup>13</sup>. The nature of aldehyde was confirmed by its IR spectrum, which showed a carbonyl stretching at 1715 cm<sup>-1</sup> and -CH stretching at 1392 cm<sup>-1</sup> thus confirming the presence of acrolein.

**Reaction orders:** The oxidant (DPC) concentration was varied in the range of  $2.0 \times 10^{-5}$  to  $2.0 \times 10^{-4}$  mol cm<sup>-3</sup> and the fairly constant  $k_{\text{obs}}$  values indicates that order with respect to [DPC] was one (Table 1). The substrate allyl alcohol was varied in the range of  $5.0 \times 10^{-4}$  to  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> at 25°C and the order with respect to [AA] was found to be less than unity. The rate constants decreased with increase in the concentration of alkali, indicating an apparent less than unit order dependence on [alkali] as given in the Table 1.

**Effect of ionic strength and dielectric constant:** It was found that ionic strength and dielectric constant of the medium have no effect on the rate of reaction.

**Effect of periodate and added products:** It was found that periodate has no significant effect on the rate of reaction. The externally added product such as Cu (III) and acrolein did not show any significant effect on the rate of the reaction.



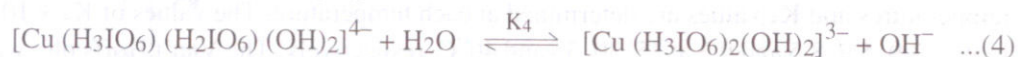
**Free radicals test:** The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hrs in inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals.

**Effect of temperature:** The kinetics were studied at four different temperatures under varying allyl alcohol concentration, keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constants ( $k$ ) of the slow step were obtained from the intercept of  $1/k_{\text{obs}}$  vs  $1/[\text{allyl alcohol}]$  ( $r \geq 0.998$  &  $s \leq 0.00298$ ) plot at four different temperatures and were used to calculate the activation parameters. The value of  $k \times 10^2$  ( $\text{s}^{-1}$ ) were  $1.40 \pm 0.05$ ,  $1.54 \pm 0.06$ ,  $1.66 \pm 0.08$  and  $1.95 \pm 0.08$  at 25, 30, 35 and  $40^\circ\text{C}$ , respectively. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of  $\log k$  vs  $1/T$  and activation parameters  $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  were calculated as  $17.0 \pm 0.5$ ,  $14.5 \pm 0.5$ ,  $-231 \pm 20$  and  $85.7 \pm 4.0$ , respectively.

**Mechanism:** The water soluble Cu (III) periodate complex is reported<sup>14</sup> to be  $[\text{Cu}(\text{HIO}_6)_2(\text{OH})_2]^{7-}$ . However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as  $\text{HIO}_6^{4-}$  (as present in the complex) as is evident from its involvement in the multiple equilibria<sup>15</sup> (1)–(3) depending on the pH of the solutions.



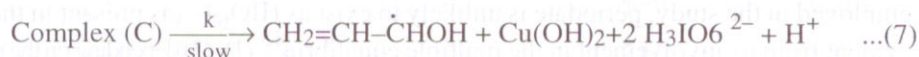
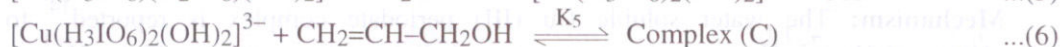
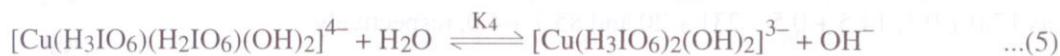
Periodic acid ( $\text{H}_5\text{IO}_6$ ) exists in acid medium and also as ( $\text{H}_4\text{IO}_6^-$ ) at pH 7. Thus, under alkaline conditions, the main species are expected to be  $\text{H}_3\text{IO}_6^{2-}$  and  $\text{H}_2\text{IO}_6^{3-}$ . At higher concentrations, periodate also tends to dimerise. Hence, at the pH employed in this study, the soluble copper (III) periodate complex exists as diperiodatocuprate (III),  $[\text{Cu}(\text{H}_3\text{IO}_6)_2(\text{OH})_2]^{3-}$  in aqueous alkaline medium. This conclusion is also supported by earlier work<sup>7,8</sup>. In most of the reports<sup>7,8</sup> on DPC periodate, it had retarding effect and order in the  $[\text{OH}^-]$  was found to be less than unity and monoperoiodatocuprate (III) is considered to be the active species. However, in the present kinetic study, different observations have been obtained i.e., periodate has totally no effect on the rate of the reaction. The rate of reaction decreased with increase in the concentration of alkali. The negative fractional order in  $\text{OH}^-$  can be explained in terms of prevailing equilibrium of formation of  $[\text{Cu}(\text{HIO}_6)_2(\text{OH})_2]^{3-}$  from  $[\text{Cu}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)(\text{OH})_2]^{4-}$  hydrolysis as given in the following equation.



Because of this reaction and fact that  $k_{\text{obs}}$  values are inverse function of hydroxyl ion concentration with fractional order in  $\text{OH}^-$  concentration, the main oxidant species is likely to be  $[\text{Cu}(\text{HIO}_6)_2(\text{OH})_2]^{3-}$  and its formation by the above equilibrium is important in the present study. The fractional order in allyl alcohol presumably results from the complex formation

between the oxidant and substrate prior to the formation of products. Indeed, it is to be noted that a plot of  $1/k_{\text{obs}}$  vs  $1/[\text{AA}]$  (Michaelis–Menten plot) shows an intercept, in agreement with complex formation. Attempts to obtain uv–vis spectra for complex between substrate and oxidant were not successful at room temperature due to weak interaction, since there is no change in uv–vis spectra of DPC and mixture of DPC and allyl alcohol. However, at lower temperature (nearly 5°C), hypsochromic shift in  $\lambda_{\text{max}}$  of about 5 nm from 416 to 411 nm of DPC and hyperchromicity at 411 nm was observed for the spectra of DPC and allyl alcohol. Such complex formation between oxidant and substrate has been already reported earlier<sup>16</sup>.

The complex (C) decomposes in the rate determining step to form a free radical derived from allyl alcohol, which further reacts with one more molecule of DPC species in a fast step to yield the products. These results indicate a mechanism of the type as in Scheme 1.



### Scheme 1

Scheme 1 leads to the rate law (9) where  $K_4$  and  $K_5$  are the equilibrium constants of different equilibria and  $k$  is rate of decomposition of the complex C, which explains all the observed orders.

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = \frac{k K_4 K_5 [\text{AA}] [\text{DPC}] [\text{OH}^-] [\text{OH}^-]}{[\text{OH}^-] ([\text{OH}^-] + K_4 K_5 [\text{DPC}])([\text{OH}^-] + K_4 + K_4 K_5 [\text{AA}])} \quad \dots(9)$$

The term  $[\text{OH}^-] + K_4 K_5 [\text{DPC}]$  in the denominator of eq. (9) approximates to  $[\text{OH}^-]$  in view of low concentration of DPC used. Therefore eq. (9) becomes eq. (10)

$$\frac{\text{Rate}}{[\text{DPC}]} = k_{\text{obs}} = \frac{k K_4 K_5 [\text{AA}]}{[\text{OH}^-] + K_4 + K_4 K_5 [\text{AA}]} \quad \dots(10)$$

The thermodynamic quantities for the second equilibrium step in Scheme 1 can be evaluated as follows. The hydroxyl ion concentration and allyl alcohol were varied at different temperatures and  $K_5$  values are determined at each temperature. The values of  $K_5 \times 10^{-2}$  ( $\text{dm}^3 \text{mol}^{-1}$ ) 3.9, 5.9, 8.5 and 9.3 at 25, 30, 35 and 40°C, respectively. The Van't Hoff's plot was made for variation of  $K_5$  with temperature i.e. ( $\log K_5$  vs  $1/T$ ) ( $r \geq 0.988$  and  $s \leq 0.0191$ ) and the values of enthalpy of reaction  $\Delta H$ , entropy of reaction  $\Delta S$ , and free energy of reaction  $\Delta G$  were calculated as  $45.5 \pm 0.5 \text{ kJ mol}^{-1}$ ,  $202 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $-16.5 \pm 0.5 \text{ kJ mol}^{-1}$ , respectively. A comparison of latter values with those obtained for slow step of the reaction shows that these



values mainly refer to rate limiting step, supporting the fact that the reaction before the rate determining step are fairly slow and involves higher activation energy<sup>17</sup>.

Further, the eqn. (10) can be rearranged to eq. (11), which is suitable for verification

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{OH}^-]}{kK_4K_5[\text{AA}]} + \frac{1}{kK_5[\text{AA}]} + \frac{1}{k} \quad \dots(6)$$

According to eq (11), the plots  $1/k_{\text{obs}}$  vs  $1/[\text{AA}]$  ( $r \geq 0.998$  and  $\leq 0.025$ ) and  $1/k_{\text{obs}}$  vs  $[\text{OH}^-]$  ( $r \geq 0.998$  and  $s \leq 0.028$ ) should be linear, which was verified in Fig. 1. The intercepts and slopes of such plots lead to the values of  $K_4$ ,  $K_5$  and  $k$  at 25°C as  $0.27 \pm 0.01 \text{ dm}^3$ ,  $3.93 \pm 0.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$  and  $1.4 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$ , respectively.

Using these values, the rate constants at different conditions were calculated by eq. (10) and were compared with experimental data. There is a good agreement between experimental and calculated values (Table 1). The negligible effect of ionic strength and dielectric constant might be due to involvement of neutral substrate in the reaction.

The proposed mechanism is also supported by the moderate values of thermodynamic parameters. The fairly high positive values of the free energy of activation and enthalpy of activation indicate that the transition state is highly solvated, while  $\Delta S^\ddagger$  suggests that the intermediate complex is more ordered than the reactants. The modest value of the enthalpy of activation and the higher rate constant of the slow step of the mechanism indicate that the oxidation presumably occurs by an inner – sphere mechanism. This conclusion was supported by earlier work<sup>18</sup>.

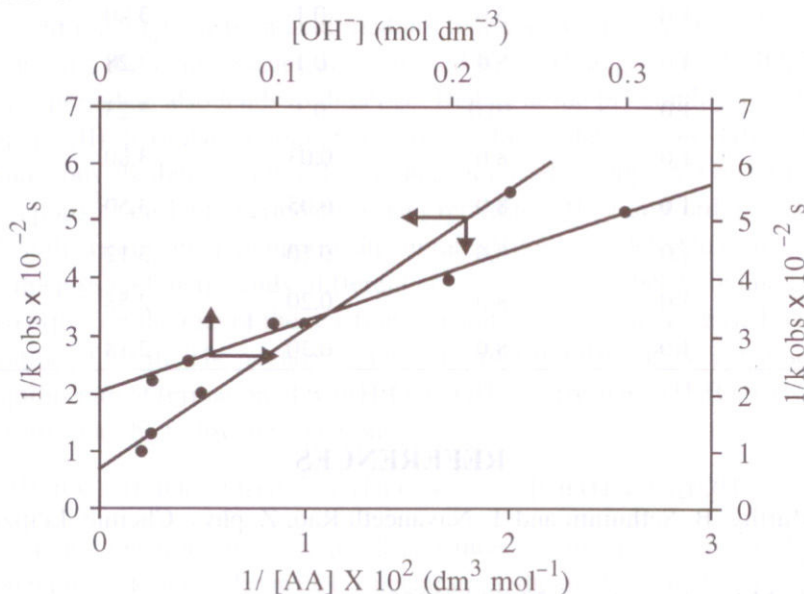


Fig. 1 Verification of rate law (11) by plotting the graph  $1/k_{\text{obs}}$  vs  $1/[\text{AA}]$  and  $1/k_{\text{obs}}$  vs  $[\text{OH}^-]$

**Table 1. Effect of variation of [DPC], [AA], [IO<sub>4</sub><sup>-</sup>] and [OH<sup>-</sup>] on oxidation of allyl alcohol by DPC at 25°C, I = 0.40 mol dm<sup>-3</sup>**

[DPC] × 10 <sup>4</sup> (mol dm <sup>-3</sup> )	[AA] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[IO <sub>4</sub> <sup>-</sup> ] × 10 <sup>5</sup> (mol dm <sup>-3</sup> )	[OH <sup>-</sup> ] (mol dm <sup>-3</sup> )	k <sub>obs</sub> × 10 <sup>3</sup> (s <sup>-1</sup> )	
				Found	Calcd.
0.2	1.0	8.0	0.1	3.15	3.40
0.5	1.0	8.0	0.1	3.24	3.40
1.0	1.0	8.0	0.1	3.12	3.40
1.5	1.0	8.0	0.1	3.19	3.40
2.0	1.0	8.0	0.1	3.28	3.40
1.0	0.5	8.0	0.1	1.80	1.77
1.0	1.0	8.0	0.1	3.12	3.40
1.0	2.0	8.0	0.1	5.30	5.20
1.0	3.0	8.0	0.1	7.60	7.50
1.0	5.0	8.0	0.1	8.35	8.26
1.0	0.1	1.0	0.1	3.18	3.40
1.0	1.0	2.0	0.1	3.12	3.40
1.0	1.0	5.0	0.1	3.20	3.40
1.0	1.0	8.0	0.1	3.28	3.40
1.0	1.0	10.0	0.1	3.23	3.40
1.0	1.0	8.0	0.03	3.80	3.60
1.0	1.0	8.0	0.05	3.50	3.50
1.0	1.0	8.0	0.10	3.12	3.40
1.0	1.0	8.0	0.20	2.58	2.60
1.0	1.0	8.0	0.30	2.18	2.20

Error ± 4%

**REFERENCES**

1. C. P. Murthy, B. Sethuram and T. Navaneeth Rao, *Z. phys. Chemie. Leipzig.*, **262**, 336 (1981).
2. B. Beck, *Mikrochem. Acta.*, **39**, 313 (1952).
3. Z. Kovat, *Acta. Chim. Hung.*, **22**, 313 (1960).

4. M. G. Ram Reddy, B. Sethuram and T. Navaneeth Rao, Indian J. Chem., **16A**, 313 (1978).
5. S. T. Nandibewoor and J. R. Raju., J. Indian Chem. Soc., **55**, 1284 (1978).
6. S. M. Tuwar, S. T. Nandibewoor and J. R. Raju., J. Indian Chem. Soc., **69**, 651 (1992).
7. K. Bal Reddy, B. Sethuram and T. Navaneeth Rao, Indian J. Chem., **20A**, 395 (1981).
8. J. Padmavati and K. Yusiff., Transition Met. Chem., **6**, 315 (2001).
9. D. S. Mahadevappa and H. M. K. Naidu, Talanta, **20**, 349 (1973).
10. P. K. Jaiswal and K. L. Yadava, Indian J. Chem, **11**, 837 (1973).
11. K. Bal Reddy, B. Sethuram and T. Navaneeth Rao, Z. Phys. Chem., **268**, 706 (1987).
12. G. P. Panigrahi and P. K. Misro, Indian J. Chem., **16A**, 201 (1978).
13. F. Feigl., Spot Tests in Organic Analysis, Elsevier, New York, (1975) p. 58.
14. G. Beck, Mikrochem. Acta., **43**, 977 (1956).
15. J. C. Bailar, Jr, H. J. Emeleus, S. R. Nyholm and A. F. Trotman-Dikenson, Comprehensive Inorganic Chemistry, Vol.2, Pergamon Press, Oxford (1975) p. 1456.
16. J. Devi, S. Kothari and K. K. Banerjee, Indian J. Chem., **34A**, 116(1995).
17. K. S. Rangappa, M. P. Ragavendra, D. S. Mahadevappa and D. Channegouda, J. Org. Chem., **63**, 531 (1998).
18. N. N. Halligudi, S. M. Desai and S. T. Nandibewoor, Int. J. Chem. Kinet, **31**, 789 (1999).
19. F. M. Moore and K. W. Hicks, J. Inorg. Nucl. Chem., **38**, 1381 (1976).

Accepted : 24.3.04