Int. J. Chem. Sci. : 1 (3), 2003, 193–196

KINETICS AND MECHANISM OF OXIDATION OF PHOSPHITE BY PYRIDINIUM CHLOROCHROMATE

D.D. VIRKAR*. and G.S. GOKAVI

Department of Chemistry, Mudhoji College,
PHALTAN – 415523; Satara (Maharastra) INDIA

ABSTRACT

The pyridinium chlorochromate– H_3PO_3 reaction proceeds with the formation of a complex which decomposes in a slow step to generate Cr (IV), followed by its disproportionation. The experimental rate law is rate– $K_1 K_e [H^+] [H_3PO_3] [PCC]/ (1 + K_C [H_3PO_3] ([H^+] K_d)$ where Kc and Kd are the formation contants of the complex and the dissociation contant of phosphorous acid, respectively and K_1 is the rate constant of the decomposition of the complex. The complex formation is verified kinetically by the Michaelis–Menten plot. Added Mn (II) decreases the rate slightly and change in ionic strength does not affect the reaction. The effect of hydrogen ion concentration is due to the dissociation of the phosphorus acid.

Key words: Phosphite; Pyridinium Chlorochromate; Oxidation; Kinetics.

INTRODUCTION

Although pyridinium chlorochomates is used as a mild oxidising agent in organic synthesis[1] and their mechanisms are also reported[2], oxidation of inorganic substrates using the reagent has not received much attention. Several mechanisms have been proposed for oxidation of two electron reductants[3] by Cr (VI) with the formation of Cr (IV) and Cr (V) oxidation states. These states were found to be more stablilised[4] in presence of suitable ligands. In a recent study[5], on the oxidation of hypophosphite in solution containing 3–ethyl–2–hydroxy butanoic acid, further reduction of Cr (IV) by two electron transfer step leading to the formation of Cr (II) has been reported. On the other hand, when Cr (VI) is associated with either chloride or pyridine, the rate of oxidation was found to decrease[6]. Since, Cr (VI) oxidation of any compound containing –OH group involves an ester formation as the initial step, chloride inhibition was explained[7] due to dissociation of chlorochromic acid, which does not facilitate the decomposition of the ester. Therefore, change in the Cr(VI) environment may alter the route of the reaction. As very few Cr (VI) oxidations have been studied in hydrochloric acid[8] and therefore in view of new mechanisms suggested for Cr(VI) oxidations[4,5], the present study was carried out to understand the reactivity of pyridinium chlorochromate towards two equivalent inorganic reductants[9–11].

EXPERIMENTAL

The oxidant pyridinium chlolrochromate was synthesised according to reported producedure[12]. Its stock solultions were prepared in water and the concentration was ascertained by iodometric titration. The stock solution of reductant H_3PO_3 (BDH) was prepared by dissolving calculated quantity in water and the concentration was ascertained by titrating against iodine. The ionic strength was maintained with sodium perchlorate. The solution of Mn (II) was prepared by dissolving calculated quantity of manganese chloride (BDH) in water. The Co (III) complex $[Co(NH_3)_5 Cl] Cl_2$, for trapping any Cr (II) formed, was prepared according to the reported procedure[13].

Kinetic measurements – The solutions containing the reactants and all other constitutents were thermally equilibrated at 30 ± 0.1°C separately, and then mixed. The reaction mixture was analysed for unreacted pyridinium chlorochromate iodometrically. Since the reaction was studied under pseudo–first order conditions, the rate constants were calculated by plotting log (PCC) against time. The pseudo–first order rate constants were reproducible upto ± 5%.

RESULTS AND DISCUSSION

Stoichiometry in presence and in absencse of added Mn(II) – The stoichiometry for phosphite was studied by keeping excess of oxidant under the reaction conditions and analyzed for remaining oxidant, pyridinium chlorochromate. The stoichiometry was found to be three moles of reductant per two moles of oxidant. It was also found that there was no change in the stoichiometry in presence of added Mn(II).

Experiment of trap Cr(II) – Formation of chromium (II) has been reported[5] earlier. Therefore, in order to know whether chromium (II) is formed in the present study, the reactions were carried out in the presence of $[Co(NH_3)_5Cl] Cl_2$. The complex $[Co(NH_3)_5Cl] Cl_2$ under the present conditions will be expected to reduce to Co (II) by chromium (II) only, which can be determined spectrophotometyrically at 692 nm. But the formation of Co (II) was not observed as there was no obsorbance at 692 nm.

Effect of reactants and added product – The effect of reactants on the reaction was studied at 30°C and at an ionic strength of 1.1 mol dm^{-3}. The concentration of oxidant was varied from 0.5×10^{-4} to 5.0×10^{-3} mol.dm^{-3} at constant concentration of phosphite and hydrochloric acid of 0.15 and 1.0 mol. dm^{-3} respectively. The pseudo–first order plots of log [PCC] against time were linear upto more than three half–lives and the rate constants obtained were also faily constant indicating first order dependence on the oxidant. The effect of phosphite was studied between the concentration range of 3.0×10^{-2} to 2.7×10^{-1} mol. dm^{-3} keeping the concentration of PCC 2.5×10^{-3} mol.dm^{-3} and [HCl] 1.0 mol dm^{-3}, constant at an ionic strength of 1.1 mol dm^{-3}. at 30°C. The order in phosphite was found to be 0.6 as determined from the plot of log k_{obs} against log [Red].

Under similar conditions, the product phosphate did not affect the reaction between 3.0 x 10^{-3} to 1.5 x 10^{-2} mol dm^{-3}.

Effect of hydrogen and chloride ion concentration: Keeping the oxidant, reductant, chloride, and ionic strength constant at 1.5 x 10^{-3}, 1.5 x 10^{-2}, 1.0 and 1.1 mol.dm^{-3}, respectively, the effect of hydrogen ion concentration was studied between 0.1 to 1.0 mol dm^{-3}. The pseudo–first order rate constants increase with the increase in hydrogen ion concentration and the order in hydrogen ion as determined from the log of pseudo–first order rate constant against log $[H^+]$ was found to be 0.5, whereas change in chloride ion concentration from 0.1 to 1.0 mol dm^{-3} did not affect rate of the reaction at a hydrogen ion concentration of 1.0 mol dm^{-3} keeping all other concentrations constant.

Effect of ionic strength, added manganese (II) and temperature: The effect of ionic strength and added manganese (II) was studied by keeping the oxidant, reductant and hydrochloric acid constant, at 1.5 x 10^{-3}, 1.5 x 10^{-2} and 1.0 mol dm^{-3}. There was no effect of ionic strength between 0.1 to 1.0 mol dm^{-3} whereas the added manganese (II) decreases the pseudo–first order rate constant slightly. The activation parameters were determined by studying the reaction at four different temperatures (25, 30, 35 and 40°C). The values at activation parameters are :

$$E_a = 44.3 \text{ kJ mol}^{-1} \quad \Delta G^* = 90.75 \text{ kJ mol}^{-1} \quad \Delta H^* = 35.01 \text{ kJ mol}^{-1} \quad \Delta S^* = -187.1 \text{ JK mol}^{-1}$$

The reaction was found to be overall second order; unity in oxidant, as evidenced by the linear pseudo first order plots and fractional in phospite. It was also observed that the plot of $1/k_{obs}$ against $1/[H_3PO_3]$ was linear with a small intercept. Therefore, reaction proceeds with formation of an anhydride between phosphite and the pyridinium chlorochromate in prior equilibrium. The anhydride, thus formed, undergoes internal oxidation. The reduction of Cr (IV) was tested by studying the reaction in presence of added Mn(II) where there was slight decrease in the observed values of the rate constants. The reason for marginal decrease in the rate is due to the fact that Mn (III) produced as a result of Cr (IV)–Mn (II) reaction, is also an oxidising agent and such oxidations are catalysed by chloride ions[14].

The Cr (IV) thus produced will disroportionate to give Cr (V) in a fast step as it is thermodynamically favored[13] over its reaction with another oxidant molecule. Another possible way of Cr (IV) reaction[15] would be its reduction to Cr (II) by oxidising the substrate through a two electron transfer step. Since the trapping experiments for Cr (II) with cobalt ammine complex were negative; therefore, disproportionation of Cr (IV) into Cr (V) is considered as the probale path. The Cr (V) reacts with substrate to give a Cr (III) and the product. The detail mechanism is –

$$H_3PO_3 \xrightleftharpoons{K_d} H^+ + H_2PO_3^-$$

$$Py\,H^+\,O\,CrO_2\,Cl + H_3PO_3 \xrightleftharpoons{K_c} \text{Complex}$$

$$\text{Complex} \xrightarrow{k_1} \text{Cr (IV)} + H_3PO_4$$

$$2\,\text{Cr (IV)} \xrightarrow{\text{fast}} \text{Cr (V)} + \text{Cr (III)}$$

$$\text{Cr (V)} + H_3PO_3 \xrightarrow{\text{fast}} \text{Cr (III)} + H_3PO_4$$

$$\text{rate} = k_1 K_c\,[H^+]\,[H_3PO_3]\,[PCC] \,/\, (1 + K_c\,[H_3PO_3])\,([H^+] + K_d)$$

$$k_{obs} = k_1\,K_c\,[H^+]\,[H_3PO_3] \,/\, (1 + K_c\,[H_3PO_3])\,([H^+] + K_d)$$

There was no effect of chloride ion concentration on the reaction as there are no probable prior equilibria involving chloride ions, whereas, the hydrogen ion concentration has a slight catalysing effect, which may be due to the protonation equilibria and also due to formation of ester (complex). The mechanism represented involves formation of a ester between phosphite and pyridinium chlorochromate in prior equilibrium which has been verified kinetically by ploting $1/k_{obs.}$ against $1/[H_3PO_3]$. The change in ionic strength did not affect the reaction, and hence supports the involvement of an uncharged species.

REFERENCES

1. F. Freeman, Organic Synthesis by Oxidation with Metal Compounds, Plenum, New York, (1986) 41–108.
2. S. Mohan, M. Gopal Krishna, and M. Sekar, Tetrahedron, **50**, 10933 (1994).
3. K. Beattle and J. P. Height, Jr., Inorganic Reaction Mechanisms. Part–II, Interscience, New York (1972) p. 95.
4. S. L. Scott, A. H. Bakar and J. H. Espenson. J. Am. Chem. Soc. **114**, 4205 (1992).
5. K. Chandra, E. Gelerinter and E.S. Gould, Inorg. Chem., **34**, 4057 (1995).
6. J. K. Sengupta and Chakladar, J. Chem. Soc., Perkin Trans., **II** 929 (1973).
7. M. Cohen and W. H. Westheimer, J. Am. Chem. Soc., **74**, 4387 (1952).
8. G. S. Gokavi and J. R. Raju, Polyhedron, **6**, 1721 (1987).
9. D. D. Virkar and G. S. Gokavi : Indian J.Chem., **38A**, 1268 (1999).
10. D. D. Virkar and G. S. Gokavi : Oxid. Comm., **22**, 532 (1999).
11. D. D. Virkar and G. S. Gokavi, Pol. J.Chem., **72**, 2267 (1998).
12. G. Marr and B. W. Rockett, Practical Inorganic Chemistry, Van Nostrand Reinhold Company, London (1972) p. 266.
13. D. R. Rosseinsky and R. J. Hill, J. Chem. Soc. Dalton Trans., 715 (1972).
14. J. H. Espenson and D. F. Dustin, Inorg. Chem., **8**, 1760 (1969).
15. Swapan K.Chandra, E. Gelerinter and E. S. Gould, Inorg. Chem., **34**, 4057 (1995).

Accepted : 14.4.2003