Asian Journal of Chemistry Vol. 6, No. 3 (1994), 493–497

A Comparative Study on the Kinetics of Oxidation of Thiodiglycollic Acid by Pyridinium Chlorochromate and Ceric Ammonium Nitrate

K.P. ELANGO* and N. BHAVANI
Department of Chemistry,
Annamalai University, Annamalainagar-608 002, India.

The rate of reaction of thiodiglycollic acid (TDA) with the oxidants pyridinium chlorochromate (PCC) and ceric ammonium nitrate (CAN) have been measured at different temperatures in acetic acid-water mixtures. In both the cases of study the order of the reaction is found to be one each with respect to oxidant and substrate, decrease of dielectric constant favours the rate, variation of ionic strength not affected the rate and increases of $[H^+]$ favours the rate, while addition of acrylonitrile shows dissimilar observation. Suitable mechanisms and rate laws have been proposed for both the cases.

INTRODUCTION

A great variety of new chromium(VI) oxidants[1–8] together with special reaction condition have been introduced for the chemospecific, regiospecific and stereospecific oxidative degeneration of functional groups in highly sensitive systems. The exact form of chromium(VI) in acetic acid is still under discussion, it may well be in the form of dimers, trimers or large units.[9] Kinetics of oxidation of several substrates by pyridinium chlorochromate (PCC)[10–16] gave a good idea that anhydrous conditions are more conductive to complexation of substrate with Cr(VI) and hence to mild oxidation. Kinetics of oxidation of sulphur containing substrates by (ceric ammonium nitrate) CAN[17,18], involving complex formation. The unhydrolysed Ce(IV) was found to be oxidising species. The use of these two oxidants towards thiodiglycollic acid (TDA) has not been made earlier.

EXPERIMENTAL

Thiodiglycollic acid was prepared by known procedure[19] and its melting point was checked. PCC was prepared by known procedure[1]. Then purity was determined by iodometric assay. AR sample of ceric ammonium nitrate was used. Other reagents used were of analytical grade. In both the cases the experiment was carried out by mixing the substrate and oxidant solution under pseudo-first order condition (always substrate in excess) in requisite quantity of aqueous acetic acid. PCC was estimated by iodometric titration. CAN was estimated by adding excess of known ferrous ammonium sulphate and back titrated against standard ceric ammonium nitrate using ferroin indicator.

---

*For correspondance: 24-G, Indra Nagar, Vedasandur-624 710, India.

Product analysis under knietic conditions gave sulphinyl diacetic acid and dithiodiglycollic acid for PCC and CAN respectively, identified with IR spectrum. Stoichiometry procedure should observed a reaction of 1 : 1 stoichiometry in each of the study.

TABLE 1

RATE DATA ON THE OXIDATION OF THIODIGLYCOLLIC ACID WITH PCC AND CAN AT TEMPERATURE (308 K)

S. No.	[TDA] $\times 10^2$ M	[PCC] $\times 10^3$ M	[CAN] $\times 10^3$ M	% AcOH-H_2O (v/v)	[$HClO_4$] $\times 10^4$ M	[$NaClO_4$] $\times 10^4$ M	$k_{obs} \times 10^4$ sec.	$k_2 \times 10^2$ M sec.
1.	1.0	1.0–5.0	—	50	2.0	—	4.65–3.04	—
2.	1.0–3.0	1.0	—	50	2.0	—	4.65–17.16	4.90
3.	1.0	1.0	—	50	2.0–4.0	—	4.65–30.17	—
4.	1.0	1.0	—	40–75	2.0	—	3.26–16.17	—
5.	1.0	1.0	—	50	2.0	1.0–3.0	3.86–4.24	—
6.	1.5	—	1.0–3.0	50	—	—	6.55–4.14	—
7.	1.0–3.0	—	1.0	50	—	—	4.38–13.33	4.33
8.	1.5	—	1.0	50	0.2–1.0	—	12.07–39.44	—
9.	1.5	—	1.0	40–75	—	—	6.83–8.31	—
10.	1.5	—	1.0	50	—	0.2–1.0	5.41–5.52	—

RESULTS AND DISCUSSION

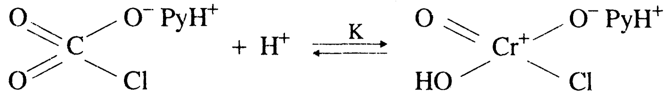
The rate constants for the reaction of thiodiglycollic acid with the oxidants PCC and CAN are given in Table 1. The change in the experimental conditions are also incorporated in the same Table. The relevant thermodynamic parameters are shown in Table 2.

TABLE 2

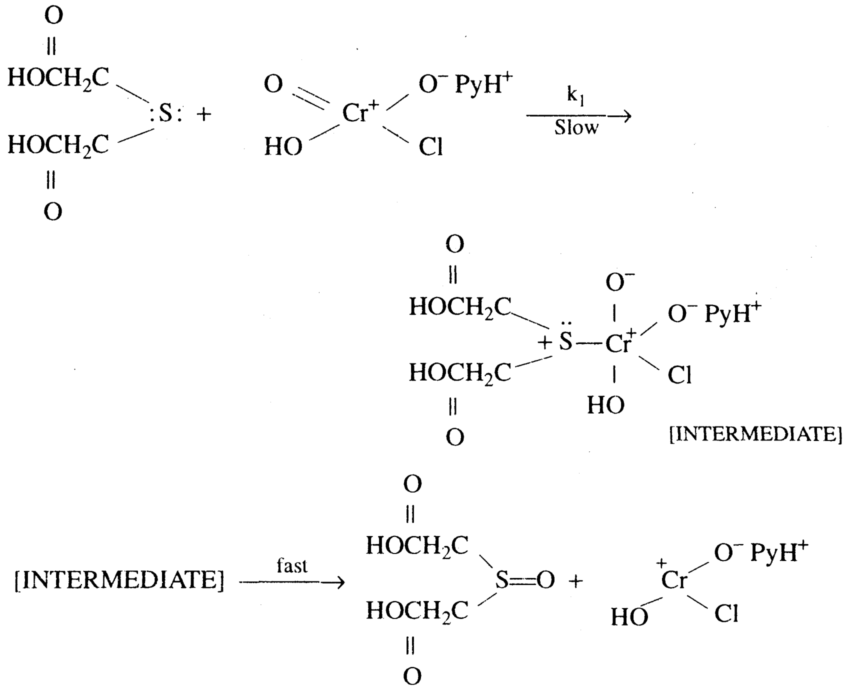
	PCC oxidation Solvent: Acetic acid-water 50% (v/v)			CAN oxidation Solvent: Acetic acid-water 50% (v/v)		
	E_a kJ mol^{-1}	$-\Delta H^*$ kJ mol^{-1}	ΔS^* Jk^{-1} mol^{-1}	E_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ Jk^{-1} mol^{-1}
TDA	40.46	37.94	147.42	58.25	55.73	90.42

The reactions were carried out under unimolecular conditions, keeping the concentrations of substrate always high. The reaction was found to be first order with respect to thiodiglycollic acid in each case of study, as evidenced by the linear plot of log k_1 *vs* log [TDA] with a slope of unity. Keeping [TDA] in excess, plot of log [oxidant] vs time was linear with a slope of unity [columns 1,2,6 and 7 of Table 1]. The order with respect to $HClO_4$ is unity and fractional (0.69) for PCC (column 3 of Table 1) and CAN (column 8 of Table 1) respectively. As concentration of PCC increases, there is a slight decrease in rate constant. This may be due to the decrease in acidity with increase in [PCC]. Increase of percentage of acetic acid increases the rate (column 4 of Table 1). This might probably be due to the ion-dipole interaction of the reactants in the slow step. Using PCC, added salt ($NaClO_4$) has no effect (column 5 of Table 1). Addition of acrylonitrile, no visible polymerisation occurs during the reaction.

The protonated form of PCC is found to be an effective oxidising species in acid medium.[11,20,21]



The protonated PCC attacks the substrate to form an Etard type of complex, decomposes to give products. The large negative entropy of activation (Table 2) suggests the complex formation. The probable mechanism is



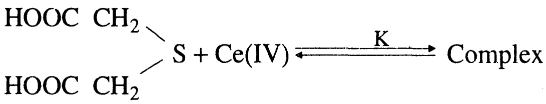
This proposed scheme envisages an oxygen atom transfer from oxidant and that is in agreement with earlier observations.[13,22]

$$\text{Hence rate} = \frac{-d\,[\text{PCC}]}{dt} = Kk_1[\text{TDA}][\text{PCC}][\text{H}^+]$$

In CAN oxidation, there is slight decrease in rate constant with increase in [CAN]. This may be due to the decrease in acidity with increase in [CAN]. Increase of percentage of acetic acid increases the rate. This is due to the increase of unhydrolysed CAN, which is the effective oxidizing species in this reaction. The variation in ionic strength of the medium by $NaClO_4$ had no effect on the reaction rate. Addition of a drop of acrylonitrile to the reaction mixture become tubrid within a few minutes, the entire mixture turned viscous, showing that the oxidation process involves a free-radical mechanism.

Rate constants were found to increase with increase of $[H^+]$ (Column 8 of Table 1). A plot of k^{-1} vs $[H^+]^{-1}$ gives a straight line. This is in agreement with the general observation that increase of $[H^+]$ increases the concentration of the effective oxidant[23] *viz.*, unhydrolysed Ce(IV), aq. $[Ce(H_2O)_8)]^{4+}$.

$$\mathrm{Ce(IV) + H_2O \xrightleftharpoons{K_h} Ce(OH)^{3+} + H^+}$$



$$\mathrm{(HOOC\ CH_2)_2S + Ce(IV) \xrightleftharpoons{K} Complex}$$

$$\mathrm{Complex \xrightarrow[Slow]{k_1} HOOC{-}CH_2{-}\dot{S} + Ce(III) + \overset{+}{C}H_2COOH}$$

$$\mathrm{2\,HOOC{-}CH_2{-}\dot{S} \xrightarrow{fast} HOOC{-}CH_2{-}S{-}S{-}CH_2{-}COOH}$$

$$\mathrm{\overset{+}{C}H_2COOH + CH_3COO^- \xrightarrow{fast} CH_3COOCH_3 + CO_2}$$

The disulphide obtained as the product finds support from the observation of McAuley[17] in the oxidation of α-mercaptocarboxylic acids by CAN.

$$\text{Hence Rate} = \frac{-d[\mathrm{CAN}]}{dt} = \frac{k_1[\mathrm{Ce(IV)}]_{\mathrm{Total}}}{\dfrac{1}{K[S]} + \dfrac{K_h[H_2O]}{K[S][H^+]} + 1}$$

$$K_{obs} = \frac{k_1}{\dfrac{1}{K[S]} + \dfrac{K_h[H_2O]}{K[S][H^+]} + 1}$$

$$\frac{1}{K_{obs}} = \frac{1}{k_1} + \frac{K_h[H_2O]}{k_1K[S][H^+]} + \frac{1}{k_1K[S]}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{k_1K[S]}\left[\frac{K_h[H_2O]}{[H^+]} + 1\right]$$

The rate law in its form accounts for the observed kinetics. The plot of $1/K_{obs}$ vs 1/[Sub] gives a straight line ($r = 0.998$) with a positive intercept suggests the formation of a complex before the rate determining step.

REFERENCES

1. E.J. Corey and J.W. Suggas, Tetrahedron Lett., 2647 (1975).
2. M.N. Bhattacharjee., M.K. Chaudri, H.S. Dasgupta and N. Roy, Synthesis, 588 (1982).
3. N. Narayanan and T.R. Balasubramanian, *Indian J. Chem.*, **25B**, 228. (1986).

4. H. Firouzabadi, A.R. Sardarine, H. Moosaripour and G.M. Afshari, Synthesis, 285 (1986).
5. Sunggak Kim and Dong Chul Ihim, *Bull. Chem. Soc.* Japan, **59**, 3297 (1986).
6. N. Bhavani and K.M. Tajun Meera Begum, M.Phil, Thesis, Annamalai University (1988).
7. K. Balasubramanian and V. Prathiba, *Indian J. Chem.*, **25B**, 326 (1986).
8. F. Anderson and B. Samuelson. Carbohydrate Res., 129 (1984).
9. K.B. Wiberg, Oxidation in Organic Chemistry, Part A Academic Press, New York, p.99 (1965).
10. H.C. Brown, C. Gundurao and S.V. Kulkarni, *J. Org. Chem.*, **44**, 2809 (1979).
11. K.K. Banerji, *Indian J. Chem.*, **17A**, 300 (1979).
12. ________, *J. Chem. Res(s),* 193 (1978).
13. G.P. Panigrahi and D.D. Mahapatro, *Int. J. Chem. Kinet.*, **13**, 85 (1981).
14. ________, *Bull. Soc. Chem. Belg.*, **90,** 927 (1982).
15. K.K. Banerji, *Indian J. Chem.*, **22B**, 413 (1983).
16. K. Rajasekaran, T. Baskaran and C. Gnanansekaran, *J. Chem. Soc.* Perkin Trans II, 1183, (1984).
17. A. McAuley and J. Hill, *J. Chem. Soc.*, (A), 156 (1968).
18. M. Gopalakrishnan, Ph. D. Thesis, Annamalai University (1988).
19. V. Baliah and T. Rangarajan, *J. Chem. Soc.*, 3068 (1954).
20. K.K. Banerji, *Bull. Chem. Soc.* (Jpn), **51**, 2732 (1978).
21. _______, *J. Chem. Soc.*, Perkin Trans II, **7**, 639 (1978).
22. G.P. Panigrahi and D.D. Mahapatro, *Indian J. Chem.*, **19A**, 579 (1980).
23. J.S. Littler, *J. Chem. Soc.*, 84, 827 (1962).

(Received: 1 January 1993; Accepted: 23 September 1993) AJC-683