

KINETICS AND MECHANISM OF OXIDATION OF DIOLS BY BARIUM MANGANATE IN ALKALI MEDIUM

SUBAS C. PATI*, B. R. DEV and RAMESH CHANDRA MAHAPATRO

Department of Chemistry, Berhampur University, Berhampur 760 007, Orissa, India

(Received 11 August 1980; after revision 10 November 1980)

The kinetics of oxidation of some aliphatic diols by barium manganate in aqueous alkaline medium is reported. The reaction is first order in manganate and first order in the substrate. The dependence on alkali is unity.

The rate law is given by

$$-\frac{d[\text{MnO}_4^{2-}]}{dt} = k [\text{MnO}_4^{2-}] [\text{S}] [\text{OH}^-]$$

The order of reactivity is 1,2 propanediol > ethylene glycol > 1,4 butandiol > 1,3 butandiol.

Effect of temperature on the reaction kinetics has been studied and different thermodynamic parameters are computed. Suitable mechanisms are discussed.

Keywords: Barium Manganate; Diols; Kinetics; Oxidation Mechanism; Manganate Ion.

INTRODUCTION

THOUGH permanganate ions have been used extensively in the oxidation of organic substrates, oxidation by manganate ions has not received considerable attention. Pode and Waters (1956) reported the use of manganate as an oxidant. Recently, Firouzabadi and Ghaderi (1978) have reported the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds. Mehrotra *et al.* (1979) have studied the kinetics of oxidation of some diols using aquamanganese(III) as an oxidant in perchloric acid medium. A survey of the literature reveals that no systematic study of the kinetics of oxidation of organic substrates by barium manganate as an oxidant has been made under homogeneous condition. In order to investigate the oxidising ability of manganate ion, the oxidation of four diols viz., ethylene glycol, 1,2 propanediol 1,3 butandiol and 1,4 butandiol by barium manganate in aqueous alkaline medium has been studied from the kinetic point of view. According to our knowledge, this is the first kinetic report on oxidation by barium manganate.

MATERIALS AND METHODS

All the diols used were of BDH(AR) grade and redistilled before use. Sodium hydroxide used was of BDH(AR) grade.

*For correspondence.

Preparation of Barium Manganate

Barium manganate was prepared by the method of Firouzabadi and Ghaderi (1978) by mixing separate solutions of potassium permanganate (1 mole), barium chloride (1 mole), sodium hydroxide (1 mole) and potassium iodide (0.12 mole) in distilled water. The reaction mixture was stirred while being heated for 15 minutes, it was then filtered with suction, and the solid material was washed until the colour of potassium permanganate was not observed in the filtrate. The resulting dark green crystals were dried in a dessicator (CaCl_2) for 24 hours and was then dried by azeotropic removal of water with dry benzene.

Preparation of Homogeneous Barium Manganate Solutions : 2.5 gms by part weight of barium manganate is taken in (IM) alkali and heated in water bath at 40°C . Then resultant solution was allowed to cool and settle down. Then it was filtered through G_4 crucible and transferred to a flask along with washings and made up to the volume and used as "stock solution," from which required concentration of barium manganate was prepared. Each day, the solution was prepared and was used in the experiments. The solution is homogeneous and stable at and above 0.5 M alkali.

The reaction kinetics has been followed by using standard sodium arsinite solution. It has been observed that manganese dioxide is precipitated after 80 per cent completion of the reaction, but upto 80 per cent of the reaction, the reaction mixture is perfectly homogeneous. The kinetic runs were followed in duplicate and the rate constants were reproducible within ± 3 per cent error.

Product Analysis

Under the experimental conditions of excess of substrate the products are the corresponding carbonyl compounds which have been identified by the 2,4-dinitrophenyl hyrazine test. The carbonyl compounds obtained have been estimated gravimetrically and found to be approximately 70 per cent.

RESULTS AND DISCUSSION

The kinetics of oxidation of four diols viz., ethylene glycol, 1,2 propanediol, 1,4 butandiol and 1,3 butandiol have been studied in aqueous alkaline medium by barium manganate.

Effect of Varying [Oxidant] on the Reaction Rate

The effect of varying oxidant concentration on the reaction has been observed at different initial oxidant concentrations. The reaction has a first order dependence on the oxidant as seen from the values of rate constants obtained with different initial oxidant concentrations Table I(A). The plots of $\log(a - x)$ vs. time are linear Table I(B) (Fig. 1) indicating the first order dependence on the oxidant concentration. The values of the rate constants have been calculated from the initial slopes of the curves obtained by plotting the unreacted manganate against time as the initial rates will be devoid of any competing oxidation, if any.

TABLE I(A)

Effect of varying [oxidant] on the reaction rate

[OH ⁻] = 1M				Temp. = 35 °C
Substrate	10 ² [S] M	10 ⁴ [Oxidant] M	10 ² k ₁ min ⁻¹	k ₂ lit mole ⁻¹ min ⁻¹
1,2 Propanediol	0.1007	3.34	4.32	42.91
	0.1007	5.52	4.28	42.87
	0.1007	10.09	4.22	41.95
Etheylene glycol	0.1	2.0	3.5	34.2
	0.1	3.6	3.8	37.6
	0.1	5.7	3.7	35.9
	0.1	7.6	3.7	35.6
1,4 Butandiol	0.1004	3.34	0.927	9.24
	0.1004	5.52	0.920	9.17
	0.1004	10.09	0.925	9.22
1,3 Butandiol	1.0	1.8	5.9	5.9
	1.0	3.6	5.8	5.8
	1.0	4.9	6.0	6.0
	1.0	7.6	5.9	5.9

TABLE I(B)

Oxidation of diols by manganate

Substrate	t _m	[S] = 0.001M,	[OH ⁻] = 1M
		a = [MnO ₄ ²⁻] = 0.000334M,	Temp. = 35°C
		10 ⁴ (a - x) M	
1,4 Butandiol	5.5	3.17	
	11.5	3.01	
	17.5	2.84	
	24	2.67	
	31	2.50	
	38.5	2.34	
	46.5	2.17	
	55	2.00	

Effect of Varying [Substrate] on the Reaction Rate

It is observed that the reaction has a first order dependence on diol concentration. The plots of $\log k_1$ vs. $\log [S]$ (Fig. 2), are linear with unit slope indicating first order dependence of the reaction on [substrate]. The second order rate constants calculated as $k_2 = k_1 [S]$ (Table II) give consistent values and thus establish a first order dependence on the concentration of substrate.

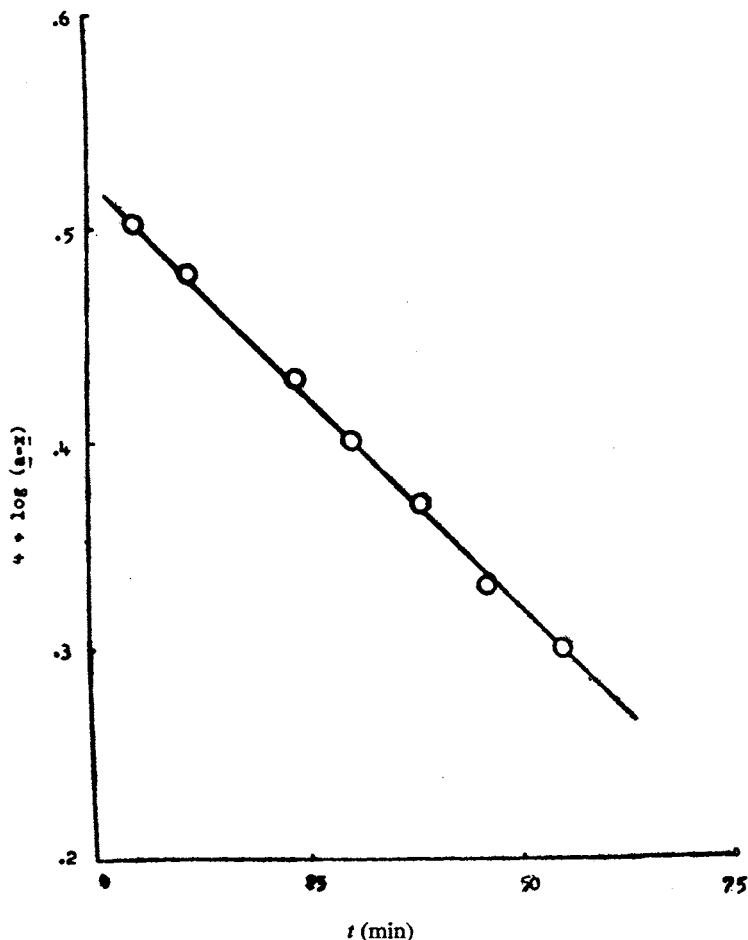


FIG. 1. 1, 3 Butandiol \sim MnO_4^{2-} $\log(a-x)$ vs. time $[\text{S}] = 0.001004 \text{ M}$ $[\text{OH}^-] = 1 \text{ M}$
Temp. = 35°C

Effect of Varying [Alkali] on the Reaction Rate

The oxidation of diols by manganate ion was found to be dependent on alkali concentration. The reaction is studied at different alkali concentrations. It is found that an increase in alkali concentration increases the rate constants linearly (Table III). The plots of $\log k_2$ vs. $\log [\text{OH}^-]$ is linear (Fig. 3) with unit slope, thereby proving first order dependence on alkali.

Effect of Catalysts

The effect of catalysts like Ru(III) and Os(VIII) on the reaction kinetics has been studied. It is found that in the present conditions the catalyst has got a marginal effect on the rate of the reaction, however, the oxidant does not disproportionate in the presence of catalysts.

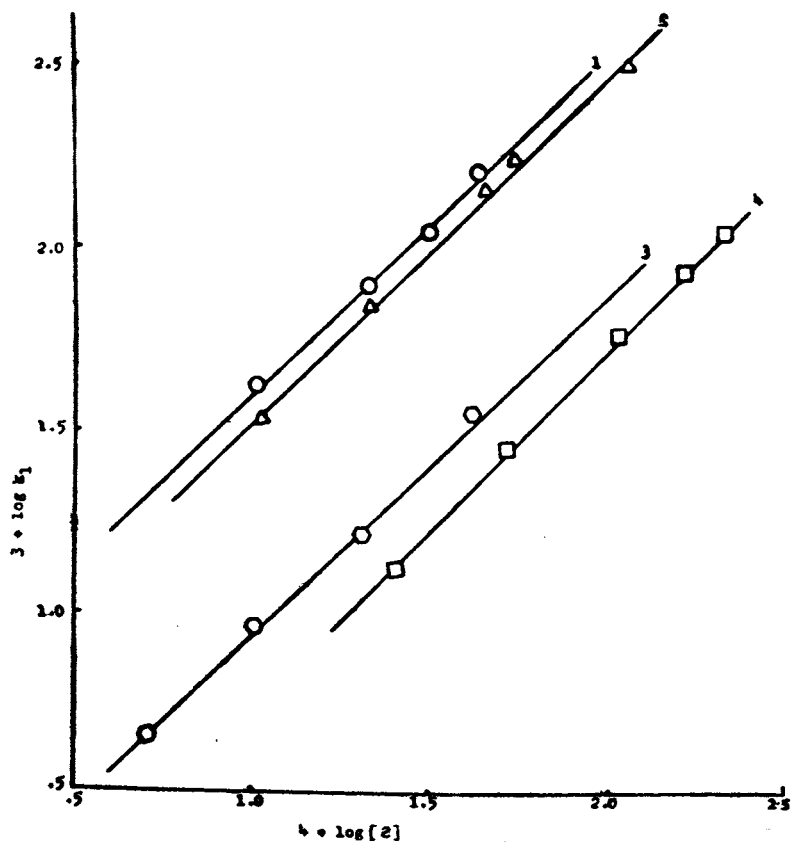


FIG. 2. Plot of $\log k_1$ vs. $\log [S]$ (Substrate variation) $[\text{MnO}_4^{2-}] = 0.0002 \text{ M}$ $[\text{OH}^-] = 1 \text{ M}$, Temp. = 35°C . (1) 1,2 Propanediol (2) Ethylene glycol (3) 1:4 Butandiol (4) 1:3 Butandiol.

Effect of Temperature

The reaction has been studied at three different temperatures i.e., 30°C , 35°C and 40°C . The rate constants are recorded in Table IV. The plots of $\log k_2$ vs. $1/T$ are linear. The different thermodynamic parameters are evaluated and given in Table V. From these data it is observed that the 1,2 propanediol and 1,3 butandiol (with one primary hydroxyl group and one secondary hydroxyl group) have almost equal entropy value and ethylene glycol and 1,4 butandiol (which have both primary hydroxyl groups) have similar values of entropy of activation, which is distinct from above series. The $\log_{10} PZ$ values lower than 11.3 indicate that the rate is much lower than calculated one from collision theory, P values being lower than unity ($P : A/Z$). This shows that at least one of the following factors is at work :—

- (i) Endothermic formation of a complex prior to the reaction proper.
- (ii) The necessity for the ionisation of either or both of the reactants.

TABLE II
Effect of varying [substrate] on the reaction rate

Substrate	10^2 [Substrate] M	$10^2 k_1 \text{ min}^{-1}$	$k_2 \text{ lit mole}^{-1} \text{ min}^{-1}$
1,2 Propanediol	0.1007	4.32	42.91
	0.2014	8.33	40.85
	0.3021	11.2	37.08
	0.4028	17.05	42.24
Ethylene glycol	0.1	3.5	34.2
	0.21	7.3	35.5
	0.41	15.2	36.7
	0.50	18.2	36.2
	1.03	32.3	31.2
1,4 Butandiol	0.0500	0.448	8.96
	0.1004	0.927	9.24
	0.2008	1.68	8.37
	0.4016	3.66	9.11
1,3 Butandiol	0.25	1.3	5.3
	0.5	2.8	5.8
	1.0	5.9	5.9
	1.5	8.9	5.9
	2.0	11.4	5.7

TABLE III
Effect of varying [alkali] on the reaction rate

Substrate	10^2 [S] M	[OH ⁻] M	$10^2 k_1 \text{ min}^{-1}$	$k_2 \text{ lit mole}^{-1} \text{ min}^{-1}$
1,2 Propanediol	0.1007	0.5	2.19	21.68
	0.1007	1.0	4.32	42.91
	0.1007	2.0	8.6	85.11
	0.1007	4.0	17.93	168.1
Ethylene glycol	0.103	1.0	3.5	34.2
	0.103	1.5	5.1	49.3
	0.103	2.0	8.0	77.9
	0.103	2.5	8.6	85.1
	0.103	3.0	9.8	95.1
1,4 Butandiol	0.1004	0.5	0.52	5.18
	0.1004	1.0	0.927	9.24
	0.1004	2.0	1.87	18.62
1,3 Butandiol	0.500	1.0	2.8	5.8
	0.522	1.5	4.3	8.3
	0.500	2.0	6.2	12.4
	0.522	2.5	7.5	14.4
	0.500	3.0	8.9	17.7

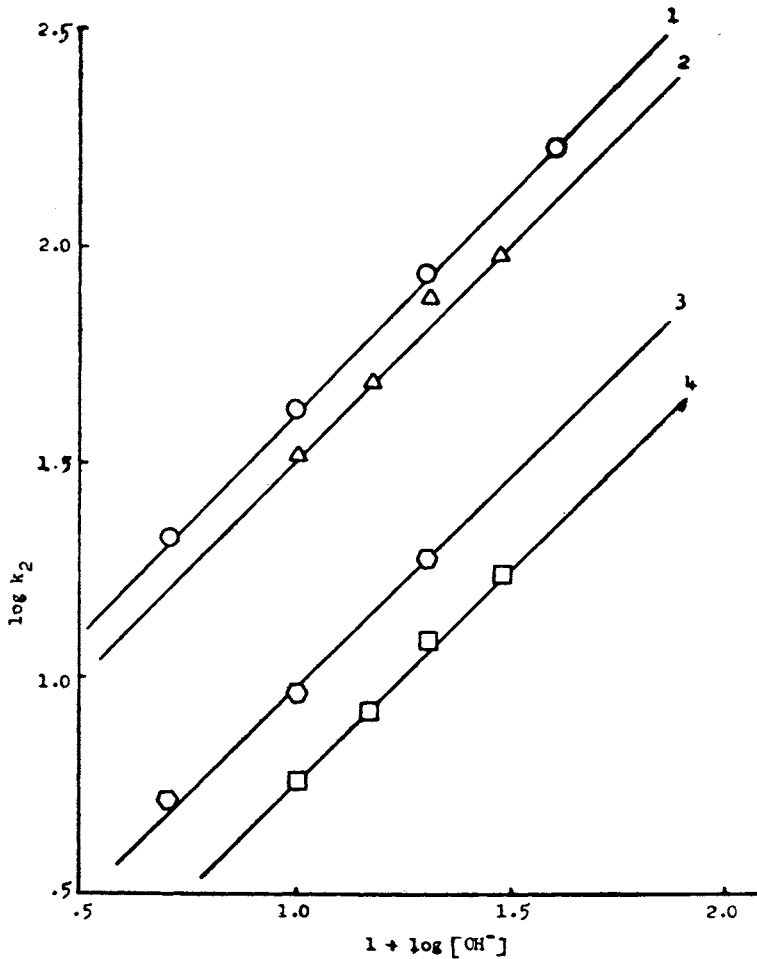


FIG. 3. $\log k_2$ vs. $\log [\text{OH}^-]$ $[\text{MnO}_4^{2-}] = 0.0002 \text{ M}$, $[\text{S}] = 0.001 \text{ M}$, $\text{Temp.} = 35^\circ \text{C}$
 (1) 1:2 Propanediol (2) Ethylene glycol (3) 1:4 Butandiol (4) 1:3 Butandiol.

TABLE IV
 Effect of varying the temperature on the reaction rate

$[\text{MnO}_4^{2-}] = 0.0002\text{M}$

$[\text{OH}^-] = 1\text{M}$

Substrate	k_2 lit mole ⁻¹ min ⁻¹ at		
	30 °C	35 °C	40 °C
1,2 Propanediol*	35.89	42.91	48.45
Ethylene glycol*	29.52	34.2	48.41
1,4 Butandiol*	7.42	9.24	12.47
1,3 Butandiol**	4.45	5.8	8.31

*[Substrate] = 0.001M
 **[Substrate] = 0.005M

TABLE V
Thermodynamic parameters

Substrate	ΔE^\ddagger kcal/mole	ΔH^\ddagger kcal/mole	$\log_{10} A$	ΔS^\ddagger e.u.
1,2 Propanediol	6.53	5.92	4.49	-25.27
Ethylene glycol	9.53	8.92	6.52	-30.78
1,4 Butandiol	9.53	8.92	6.76	-32.84
1,3 Butandiol	12.72	12.10	8.0	-23.97

- (iii) Deactivation by solvent molecules.
- (iv) Stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact.
- (v) The existence of strong forces of repulsion (Moelwyn-Hughes, 1947).

All the factors are possibly present. The energy stored up in different parts of the molecules, perhaps, is not able to redistribute itself during the short interval of impact, the molecule being thus in a condition of incorrect orientation, leading to low P factors.

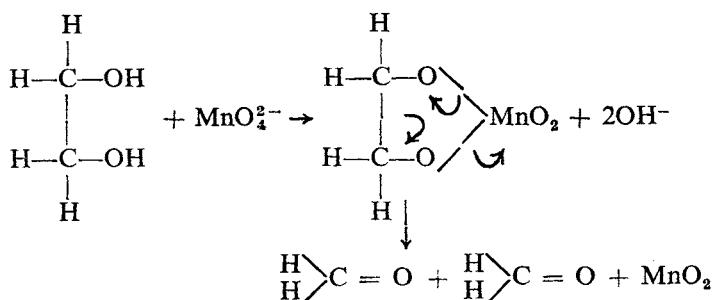
Anantkrishnan and Venkataraman (1946) have shown for the olefine-bromine reaction the low P factor could be satisfactorily accounted for by assuming that only a restricted area of the surface of the reacting molecules is available for reaction. This suggestion has been worked up by Nair and Anantkrishnan (1950) for the hydrolysis of esters the lower $\log_{10} PZ$ values being satisfactorily explained by inclusion of an orientation correction term.

Mechanism

In general, the vicinal diols undergo C-C bond cleavage depending upon the nature of the oxidant to give corresponding carbonyl compounds. Pode and Waters (1956) have reported that alkaline manganate oxidations are similar to those of alkaline permanganate oxidations. They have postulated a cyclic mechanism in the oxidation of olefins by manganate ions. According to them manganate oxidation of 1,2 glycols occurs much more rapidly than the manganate oxidation of monohydric alcohols and does not seem to pass through hypomanganate ester.

It is seen from the kinetic data that the vicinal diols viz., 1,2 propandiol and ethylene glycol react faster than the non-vicinal diols like 1,3 butandiol and 1,4 butandiol. This seems to point that in case of compounds having vicinal hydroxyl groups a cyclic mechanism is operating. The product in case of the vicinal diols are the corresponding aldehydes, which is in agreement with the postulated cyclic mechanism. This leads us to believe that C-C bond cleavage through a cyclic mechanism is taking place. Such cyclic mechanism in case of vicinal has been reported earlier by Duke (1947) and Buist *et al.* (1959) in case of oxidation by periodate ion and by Criegee *et al.* (1933) in the oxidation by lead tetra acetate (LTA).

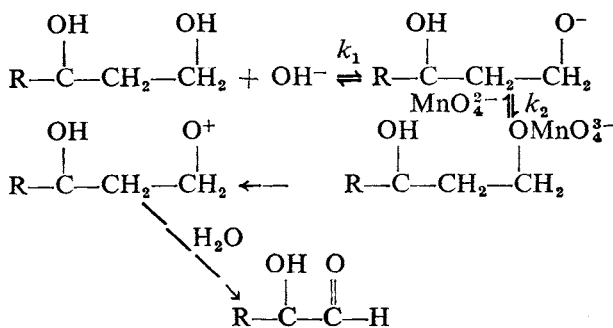
Thus the cyclic mechanism in case of vicinal diols can be depicted as follows (Scheme I) :



SCHEME I

The rates of oxidation of non-vicinal diols are lower than those of vicinal diols. In case of non-vicinal diols like 1,3 butandiol and 1,4 butandiol, obviously it does not go through cyclic mechanism. The process in these cases is mainly an acyclic process through the hypomanganate ester, followed by rate determining C-H bond fission.

It is not very appropriate to compare the relative rates of 1,3 butandiol and 1,4 butandiol on the basis of structure only, as the site of attack may be different in these two oxidation processes. It seems that the primary reaction is essentially a C-H bond fission under these conditions leading to hydroxy aldehydes or hydroxy ketones at the first instance. Such acyclic mechanisms have been postulated earlier in the oxidation of glycols by aqueous CrO_3 and in the oxidation of diols by hexacyanoferrate (Radhakrishnamurti *et al.*, 1971, 1973). Thus the following mechanism is postulated for non-vicinal diols (Scheme II) :



SCHEME II

The common rate law for both the mechanism is

$$V = k [\text{MnO}_4^{2-}] [\text{S}] [\text{OH}^-]$$

ACKNOWLEDGEMENT

The authors are thankful to Professor P. S. Radhakrishnamurti, Professor & Head of the Department of Chemistry, Berhampur University, for his valuable suggestions and keen interest in the work. One of us (BRD) thanks the UGC, New Delhi for the award of teacher fellowship and Godavaris Mahavidyalaya, Banpur (Puri) for sanctioning study leave.

REFERENCES

- Anantkrishnan, S. V., and Venkataraman, G. (1946) *Proc. Indian Acad. Sci.*, **23**, 319.
- Buist, G. J., Buton, C. A., and Miles, J. H. (1959) The mechanism of oxidation of α -glycols by periodic acid, Part V : Cyclo-hexane-1:2-diols. *J. chem. Soc.*, 743.
- Criegee, R., Kraft, L., and Rank, B. (1933) Oxidation of ethylene glycols by lead tetracetate. *Ann.*, **507**, 159.
- Duke, F. R. (1947) Theory and kinetics of specific oxidation II. The periodate glycol reaction. *J. Am. chem. Soc.*, **69**, 3054.
- Firouzabadi, H., and Ghaderi, E. (1978) Barium manganate, an efficient oxidizing reagent for oxidation of primary and secondary alcohols to carbonyl compounds. *Tetrahedron Lett.*, 839.
- Mehrotra, R. N., Nagori, R. R., and Mehta, M. (1979) Kinetics and mechanism of redox reactions in aqueous solution, Part 4 : Oxidation of diols by aquamanganese(III) ions in aqueous perchloric acid. *J. chem. Soc. Dalton Trans.*, 211.
- Moelwyn-Hughes (1947) *Kinetics of Reactions in Solution*. Oxford.
- Nair, P. M., and Anantkrishnan, S. V. (1950) Kinetic studies in ester hydrolysis IV. Alkaline hydrolysis of ethyl acetate in mixed solvents. *Proc. Indian Acad. Sci.*, **32(A)**, 187.
- Pode, J. S. F., and Waters, W. A. (1956) Stages of oxidations of organic compounds by potassium permanganate, Part VII : Characteristic features of oxidation involving the manganate, MnO_4^{2-} and hypo-manganate, MnO_4^{3-} anions. *J. chem. Soc.*, 717.
- Radhakrishnamurti, P. S., and Behera, T. Ch (1971) Kinetics of oxidation of glycols by CrO_3 in aqueous organic media. *Indian J. Chem.*, **9**, 41.
- Radhakrishnamurti, P. S., and Mahanty, M. K. (1973) Oxidation of alcohols by hexacyanoferrate (III). *Indian J. Chem.*, **11**, 762.
- Wiberg, K. B., and Stewart, R. (1955) The mechanisms of permanganate oxidation, I : The oxidation of some aromatic aldehydes by potassium permanganate in acid and alkali media. *J. Am. chem. Soc.*, **77**, 1786.