

## Kinetics and mechanism of oxidation of diols by *bis*(2,2'-bipyridyl) copper(II) permanganate

KAVITA MOHNOT, PRADEEP K SHARMA and  
KALYAN K BANERJI\*

Department of Chemistry, J N V University, Jodhpur 342 005, India

MS received 10 May 1995; accepted 20 July 1996

**Abstract.** Kinetics of oxidation of five vicinal, four non-vicinal diols, and one of their monoethers by *bis*(2,2'-bipyridyl) copper(II) permanganate (BBCP), has been studied. The vicinal diols yielded the products arising out of the glycol bond fission, while the other diols yielded the hydroxycarbonyl compounds. The reaction is first-order with respect to BBCP. Michaelis–Menten type kinetics were observed with respect to the diol. There is no effect of added 2,2'-bipyridine on the reaction. The oxidation of [1,1,2,2- $^2\text{H}_4$ ] ethanediol showed the absence of a primary kinetic isotope effect. A mechanism involving a glycol bond fission has been proposed for the oxidation of the vicinal diols. The other diols are oxidised by a hydride-transfer mechanism as are monohydric alcohols.

**Keywords.** Diols; *bis*(2,2'-bipyridyl) copper(II) permanganate; oxidation kinetics.

### 1. Introduction

*Bis*(2,2'-Bipyridyl)copper(II)permanganate (BBCP) is a well-known oxidizing reagent and its use in synthetic organic chemistry is well documented (Firouzabadi *et al* 1983, 1984). We have been interested in the kinetics and mechanism of the oxidation by BBCP and have reported the oxidation of monohydric alcohols (Satsangi *et al* 1994), thioacid (Kothari 1991), and aliphatic aldehydes (Kothari *et al* 1992) by BBCP. However, several oxidations of monohydric and polyhydric alcohols are known to follow different mechanistic pathways, e.g. oxidations by lead (IV) (Bunton 1966), periodic acid (Duke 1947), acid permanganate (Bhatia and Banerji 1983) and bromamine-B (Mathur and Banerji 1987). Therefore, we have studied the oxidation of several diols by BBCP in aqueous acetic acid solution. The mechanistic aspects are discussed.

### 2. Experimental

#### 2.1 Materials

The diols were commercial products and were distilled under reduced pressure before use. (1,1,2,2- $^2\text{H}_4$ )-Ethanediol was prepared by the reduction of diethyl oxalate with lithium aluminium deuteride (Kemp and Waters 1963). Its isotopic purity, determined by its NMR spectrum, was  $90 \pm 4\%$ . BBCP was prepared by the reported method (Firouzabadi *et al* 1983) and its purity checked by iodometry.

\*For correspondence

## 2.2 Product analyses

Product analyses were carried out under kinetic conditions. In a typical experiment, ethanediol (6.2 g, 0.1 mol) and BBCP (12.3 g, 0.02 mol) were dissolved in 100 ml of 1:1 (v/v) acetic acid–water and kept in the dark for  $\approx 12$  h to ensure completion of reaction. The solution was then treated with an excess (200 cm<sup>3</sup>) of a saturated solution of 2,4–dinitrophenylhydrazine in 2 mol dm<sup>-3</sup> HCl and kept in a refrigerator for  $\approx 15$  h. The precipitated 2,4–dinitrophenylhydrazone (DNP) was filtered off, weighed, recrystallized from ethanol and weighed again. The product was identical (m.p. and mixed m.p.) with an authentic sample of the DNP of formaldehyde. The yield of DNP before and after recrystallization was 7.4 g (88%) and 6.8 g (81%). A similar experiment with propane-1,3-diol yielded DNP of 3-hydroxypropanal in 73% yield after recrystallization. Iodometric determinations of the oxidation state of manganese in a spent reaction mixture indicated it to be  $4.03 \pm 0.11$ .

## 2.3 Kinetic measurements

The pseudo-first-order conditions were attained by keeping a large excess ( $\times 15$  or greater) of the diols over BBCP. The solvent was 1:1 (v/v) acetic acid–water, unless specified otherwise. The reactions were carried out in flasks blackened from the outside to avoid any photochemical reactions and were followed by monitoring the decrease in the [BBCP] at 358 nm for up to 70% reaction. The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were evaluated from the linear least-squares plots of  $\log [\text{BBCP}]$  against time. Duplicate kinetic runs showed that the rate constants are reproducible to within  $\pm 3\%$ . Simple and multivariate linear regression analyses were carried out by the least-squares method.

**Table 1.** Rate constants for the oxidation of ethanediol and propane-1,3-diol at 293 K and  $[\text{H}^+] = 0.24 \text{ mol dm}^{-3}$ .

$10^3 [\text{BBCP}]$ (mol dm <sup>-3</sup> )	[Diol] (mol dm <sup>-3</sup> )	$10^5 k_{\text{obs}} (\text{s}^{-1})$	
		Ethanediol	Propane-1,3-diol
1.0	0.05	3.02	16.1
1.0	0.10	5.01	25.9
1.0	0.20	7.70	38.3
1.0	0.40	10.2	49.0
1.0	0.80	12.1	58.0
1.0	1.00	13.0	60.4
1.0	1.30	13.3	61.8
1.0	1.60	13.8	63.4
1.0	1.00	12.9 <sup>a</sup>	60.4 <sup>a</sup>
1.0	1.00	13.2 <sup>b</sup>	60.0 <sup>b</sup>
1.0	2.00	14.0	64.7
2.0	0.80	12.5	56.7
4.0	0.80	11.9	57.8
6.0	0.80	12.3	59.1
8.0	0.80	12.0	58.6

<sup>a</sup>Contained 0.05 mol dm<sup>-3</sup> acrylonitrile; <sup>b</sup>contained 0.02 mol dm<sup>-3</sup> 2,2'-bipyridyl

**Table 2.** Formation constants and thermodynamic parameters of the diol-BBCP complexes.

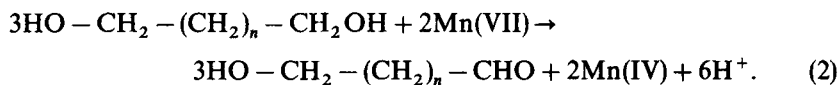
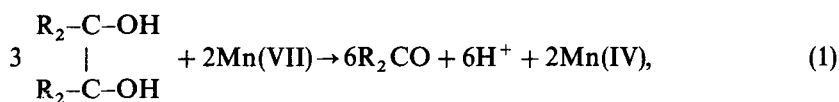
Diol	$K(\text{dm}^{-3}\text{mol}^{-1})$ at temp. (K)				$\Delta H$	$\Delta S$	$\Delta G$
	283	293	303	313	( $\text{kJ mol}^{-1}$ )	( $\text{J mol}^{-1}\text{K}^{-1}$ )	( $\text{kJ mol}^{-1}$ )
Ethane-1,2-diol	6.52	4.84	3.55	2.58	$-24.1 \pm 0.4$	$-67 \pm 1$	$-4.30 \pm 0.3$
Propane-1,2-diol	7.21	5.48	4.20	3.12	$-21.8 \pm 0.5$	$-58 \pm 2$	$-4.50 \pm 0.4$
Butane-2,3-diol	6.93	4.87	3.42	2.38	$-28.0 \pm 0.5$	$-80 \pm 2$	$-4.30 \pm 0.4$
Butane-1,2-diol	6.41	4.50	3.30	2.30	$-26.6 \pm 0.5$	$-76 \pm 2$	$-4.20 \pm 0.3$
Pinacol	7.03	5.11	3.82	2.79	$-24.1 \pm 0.4$	$-66 \pm 1$	$-4.40 \pm 0.3$
Propane-1,3-diol	8.75	5.95	4.00	2.77	$-30.2 \pm 0.4$	$-85 \pm 3$	$-4.90 \pm 0.4$
Butane-1,3-diol	9.21	6.00	3.89	2.60	$-33.2 \pm 0.3$	$-95 \pm 2$	$-5.00 \pm 0.5$
Butane-1,4-diol	8.32	5.12	3.15	1.92	$-38.4 \pm 0.6$	$-114 \pm 3$	$-4.60 \pm 0.5$
Pentane-1,5-diol	9.56	5.80	3.50	2.11	$-39.6 \pm 0.6$	$-117 \pm 4$	$-5.00 \pm 0.5$
3-Methoxybutan-1-ol	10.4	7.31	5.20	3.50	$-28.3 \pm 0.8$	$-78 \pm 3$	$-5.40 \pm 0.6$
2-Methoxyethanol <sup>a</sup>	10.2	6.75	4.80	3.22	$-32.4 \pm 0.6$	$-83 \pm 2$	$-7.70 \pm 0.4$

<sup>a</sup>Data from Satsangi *et al* (1994)

### 3. Results

#### 3.1 Stoichiometry

The oxidation of vicinal diols by BBCP yields products arising out of glycol bond fission, i.e. rupture of the bond between the carbon atoms bearing the hydroxy groups, while the other diols give products by simple oxidation of one of the hydroxy-groups. Analyses of products indicate the overall reactions



BBCP is reduced to Mn(IV). To confirm that Mn(IV) is indeed formed as a result of the oxidation of diols by BBCP, the rates were determined by monitoring the increase in [Mn(IV)] at 418 nm also (Freeman and Kappos 1985; Lee and Perez-Benito 1988). The results showed that the rates of decay at 529 nm and of increase at 418 nm agreed within  $\pm 8\%$ . BBCP has virtually no absorption at 418 nm.

**Table 3.** Rate constants and activation parameters of the decomposition of diol-BBCP complexes.

Diol	$10^4 k_2 (\text{s}^{-1})$ at temp. (K)				$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
	283	293	303	313	(kJ mol <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )	(kJ mol <sup>-1</sup> )
Ethane-1,2-diol	0.80	1.55	2.79	5.76	45.8 ± 0.6	-162 ± 2	93.9 ± 0.5
Propane-1,2-diol	1.15	2.12	3.95	7.55	43.6 ± 0.6	-167 ± 3	93.1 ± 0.7
Butane-2,3-diol	1.60	2.87	5.50	10.0	42.7 ± 0.9	-167 ± 3	92.3 ± 0.7
Butane-1,2-diol	2.70	5.11	9.30	16.5	41.6 ± 0.4	-165 ± 2	91.0 ± 0.5
Pinacol	3.12	5.41	9.80	17.2	39.5 ± 0.7	-173 ± 3	90.9 ± 0.6
Propane-1,3-diol	2.53	7.00	19.4	60.2	65.7 ± 0.9	-82 ± 5	89.8 ± 1.2
Butane-1,3-diol	4.32	12.0	30.9	93.5	63.3 ± 1.4	-85 ± 4	88.6 ± 1.1
Butane-1,4-diol	3.78	10.3	27.8	83.4	64.0 ± 1.5	-84 ± 5	88.9 ± 1.2
Pentane-1,5-diol	4.43	12.7	32.0	105	65.1 ± 1.0	-79 ± 3	88.5 ± 0.8
3-Methoxybutane-1-ol	5.07	14.1	35.2	116	64.3 ± 0.7	-81 ± 2	88.2 ± 0.6
2-Methoxyethanol <sup>a</sup>	3.02	8.00	20.3	67.4	64.0 ± 0.4	-86 ± 1	89.6 ± 0.3

<sup>a</sup>Data from Satsangi *et al* (1994)

### 3.2 Rate laws

The reaction was found to be first-order with respect to the BBCP. The individual kinetic runs were strictly first-order in BBCP. Further, the first-order rate coefficients did not vary with the initial concentration of BBCP. The order with respect to diol is less than one (table 1). A plot of  $1/k_{\text{obs}}$  versus  $1/[\text{diol}]$  is linear with an intercept on the rate ordinate. Thus, Michaelis–Menten type of kinetics are observed with respect to diols. This leads to the postulation of the following overall mechanism ((3) and (4) below) and the rate law ((5) below).



$$\text{rate} = k_2 K [\text{diol}] [\text{BBCP}] / (1 + K [\text{diol}]). \quad (5)$$

Dependence on the concentration of the diol was studied at different temperatures and the values of  $K$  and  $k_2$  were calculated from the double reciprocal plots. The thermodynamic parameters of the complex formation and the activation parameters of

**Table 4.** Dependence of the rate of oxidation of ethanediol on hydrogen ion concentration<sup>a</sup>.

[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	0.03	0.06	0.12	0.24	0.40	0.50	0.98	1.2	1.60	2.00
10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )	2.90	4.00	6.11	10.2	15.6	19.0	70.2	105	185	290

<sup>a</sup>[Diol] = 0.40 mol dm<sup>-3</sup>; [BBCP] = 0.001 mol dm<sup>-3</sup>; T = 293 K

**Table 5.** Dependence of k<sub>obs</sub> on the concentration of ethanediol in solvents of different compositions.

[BBCP] 0.001 mol dm<sup>-3</sup>; [H<sup>+</sup>] = 0.24 mol dm<sup>-3</sup>; T = 293 K

[Diol] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> ) [at % AcOH (v/v)]				
	72	60	50	40	25
0.05	9.92	5.75	3.02	2.05	1.15
0.10	17.0	9.82	5.01	3.50	1.90
0.20	25.3	14.6	7.70	5.10	2.79
0.40	33.2	20.5	10.2	6.94	3.82
0.80	41.0	24.0	12.1	8.20	4.55
1.00	42.0	25.5	13.0	8.72	4.70
K/dm <sup>3</sup> mol <sup>-1</sup>	4.82	4.54	4.84	4.91	5.16
10 <sup>5</sup> k <sub>2</sub> /s <sup>-1</sup>	51.4	31.1	15.6	10.4	5.60

the decomposition of the complexes were calculated from the values of *K* and *k*<sub>2</sub> respectively at different temperatures (tables 2 and 3). The oxidation of ethanediol in an atmosphere of nitrogen failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (table 1).

### 3.3 Isotope effects

To ascertain the importance of the cleavage of the α-C-H bond in the rate-determining step, the oxidation of [1, 1, 2, 2-<sup>2</sup>H<sub>4</sub>] ethanediol was studied. The results showed the absence of a primary kinetic isotope effect.

### 3.4 Effect of 2, 2'-bipyridine

The rate of oxidation were not affected by an addition of 2, 2'-bipyridine (up to 0.02 mol dm<sup>-3</sup>).

### 3.5 Effect of acidity

The reaction rate increases with an increase in the concentration of hydrogen ions (table 4). A plot of rate versus [H<sup>+</sup>] is a curve concave to the rate axis and intercepts it. The dependence of the reaction rate on the concentration of ethanediol and propane-1, 3-diol was studied at [H<sup>+</sup>] = 0.20, 0.45 and 1.5 mol dm<sup>-3</sup>. It was observed that the formation constant, *K*, does not vary appreciably with the hydrogen ion concentration. This led us to conclude that the changes in the hydrogen ion concentration affect only the decomposition of the complex.

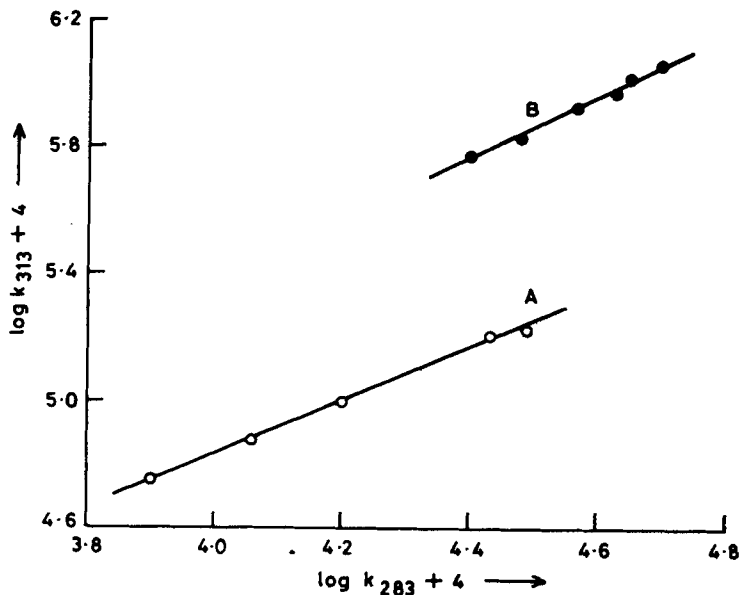


Figure 1. Isokinetic relationship in the oxidation of diols by BBCP (A) vicinal diols, (B) other compounds.

### 3.6 Effect of solvent composition

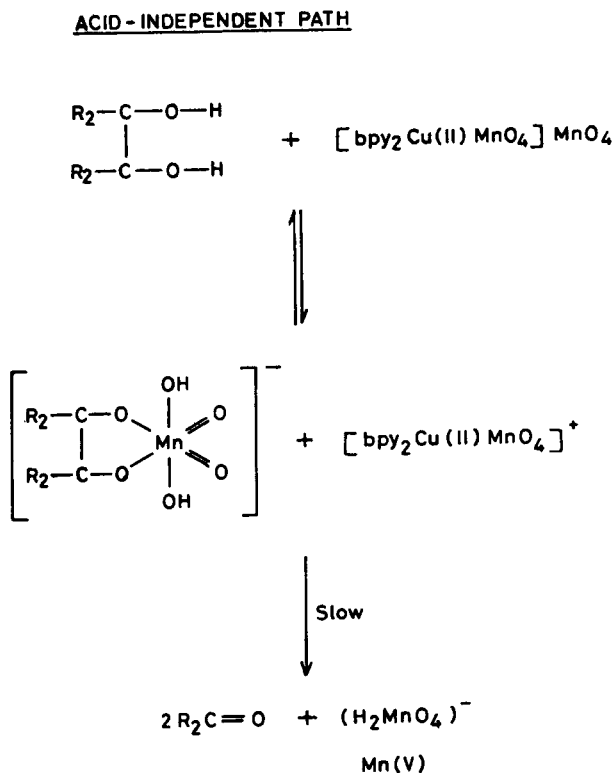
The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increases with an increase in the amount of acetic acid in the solvent.

To ascertain whether the changes in solvent composition affect the formation constant of the complex and/or the rate of its decomposition, the dependence of the reaction rate on the concentration of ethanediol was studied in solvents of different compositions. Results recorded in table 5 show that the rate constant for the decomposition of the complex increases with an increase in the amount of acetic acid in the solvent. The formation constant,  $K$ , remains practically constant.

## 4. Discussion

Not much is known about the structure of BBCP. In particular, the nature of the bonding of the permanganate anions with the  $[\text{Cu}^{\text{II}}(\text{bpy})_2]^{+2}$  is not certain. However, in the corresponding halide complexes, it has been shown that one halide is joined to the central metal atom by a covalent bond and the other by an electrovalent bond (Barclay *et al* 1963). Based on this analogy, BBCP may also be represented as  $[\text{Cu}(\text{bpy})_2(\text{MnO}_4)\text{MnO}_4]$ .

Linear regression analysis of the data on  $[\text{H}^+]$  dependence revealed that at moderate proton concentrations ( $[\text{H}^+] \leq 0.50$  mol), the rate law takes the form  $k_{\text{obs}} = a + b[\text{H}^+]$  ( $a = 2.05 \times 10^{-5}$ ;  $b = 3.39 \times 10^{-4}$ ;  $r = 0.9997$ ) and at higher concentrations ( $[\text{H}^+] \geq 0.50$  mol), it has the form  $k_{\text{obs}} = c + d[\text{H}^+]^2$  ( $c = 8.40 \times 10^{-6}$ ;  $d = 7.22 \times 10^{-4}$ ;  $r = 0.9998$ ). This observation leads us to propose that the reaction follows an acid-independent path and two acid-dependent paths, involving singly



Scheme 1.

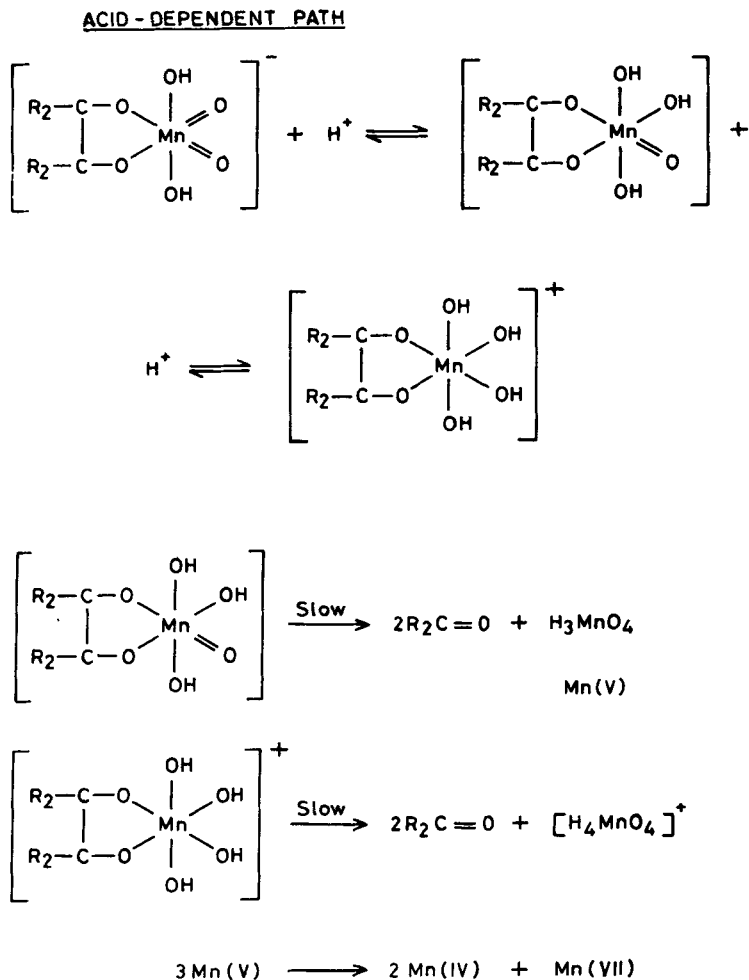
protonated and doubly protonated forms of a reactant as the reactive species at moderate and higher concentrations of hydrogen ion respectively. Similar results were also observed in the oxidation of alcohols and methionine (Satsangi *et al* 1994, 1995) by BBCP. Comparison of rate constants of the two acid-independent paths in moderate and higher proton concentrations suggests that the contribution of the acid-independent path, at higher acidity, is much less.

Wiberg and Evans (1958) have determined Hammett's acidity function,  $H_0$ , for low concentrations of acid in a series of acetic acid-water mixtures. They observed that the acidity increases as the water concentration decreases. Since the reaction under investigation is acid catalysed, increase in the proportion of acetic acid in the solvent results in an increase in the rate.

The diverse nature of the products formed in the oxidation of vicinal diols and other diols suggests that these compounds follow different mechanistic pathways. This is further supported by the two linear plots obtained between  $\log(\text{rate})$  at 283 K and at 313 K, one for vicinal diols and another for the rest (figure 1).

#### 4.1 Oxidation of vicinal diols

The linear correlation between  $\log(\text{rate})$  at 283 K and 313 K for the oxidation ( $r = 0.9978$ ; slope =  $0.9437 \pm 0.0261$ ) shows that an isokinetic relationship exists in the oxidation of vicinal diols by BBCP (Exner 1973). The values of the isokinetic temperature is  $777 \pm 56$  K.



Scheme 2.

An isokinetic relationship is a necessary condition for the validity of linear free-energy relationships. It also implies that all the diols are oxidized by a similar mechanism.

The absence of a primary kinetic isotopic effect confirms that the  $\alpha$ -C-H bond is not cleaved in the rate-determining step. In contrast, substantial primary kinetic isotopic effect was observed in the oxidation of ethanol by BBCP (Satsangi *et al* 1994). Thus, it seems that the oxidation of monohydric alcohols and vicinal diols follows a different mechanism.

The magnitude of the negative entropy of activation is almost double in the oxidation vicinal diols as compared to that of the other compounds (cf. table 3). This points to a more rigid transition state in the oxidation of the vicinal diols. Thus, involvement of both the hydroxyl groups in the rate-determining step is indicated. The only mode of oxidation available for pinacol is the fission of the bonds between the carbinol carbon atoms. That the other vicinal diols follow this mechanism is confirmed by the isolation of products from C-C bond fission and the isokinetic relationship.



**Table 6.** Reaction constants of the oxidation of vicinal diols by BBCP.

T(K)	$\rho_I$	$\delta$	$R^2$	sd*
283	$-1.18 \pm 0.05$	$-1.26 \pm 0.02$	0.9997	0.006
293	$-0.90 \pm 0.02$	$-1.29 \pm 0.01$	0.9999	0.003
303	$-0.88 \pm 0.06$	$-1.23 \pm 0.01$	0.9995	0.007
313	$-0.78 \pm 0.04$	$-1.14 \pm 0.02$	0.9999	0.002

sd – standard deviation

In view of the absence of any effect of the radical scavenger, acrylonitrile, on the reaction rate, it is unlikely that a one-electron reaction, giving rise to free radicals, is operative in this oxidation. The observed Michaelis–Menten kinetics with respect to the diol lead us to suggest the formation of a 1:1 complex of BBCP and diol in a rapid pre-equilibrium. Thus, on the basis of all the above experimental facts, the following mechanism has been proposed (scheme 1). Littler (1971) has shown that the formation of a cyclic permanganate ester, in the oxidation of 1,2-diol, is an allowed (Huckel-type, ten-electron) process. Acid catalysis may well be due to the successive protonation of the permanganate ester prior to its decomposition (scheme 2).

*Correlation of structure and reactivity:* A perusal of data in tables 3 and 4 showed that the formation constants of the BBCP–diol complexes are not sensitive to the structure of the diol. However, the rate constants of the decomposition show considerable variation. The rates of decomposition were, therefore, subjected to correlation analyses.

The rates of the decomposition of the complexes failed to show satisfactory correlation with either the polar or the steric substituent constants (Johnson 1987). Therefore, the rates were analysed in terms of the dual substituent-parameter (DSP) equation of Pavelich and Taft (1957),

$$\log k = \rho_I \sum \sigma_I + \delta \sum E_s + \log k_0. \quad (6)$$

The results recorded in table 6, show that the rates exhibited an excellent correlation with polar and steric substituent constants. Though the number of compounds (five) is rather small for correlation analysis by a DSP equation, the correlations are excellent and the results can be used qualitatively.

The values of the reaction constants support the proposed mechanism. The small negative polar reaction constant accords with the net flow on electrons towards the oxidant, while the negative steric reaction constant implies a steric acceleration of the reaction. This is probably due to increase in the steric relief on going from tetragonal ( $sp^3$ ) carbon atoms to trigonal ( $sp^2$ ) ones, with increasing substitution at the carbon atoms.

#### 4.2 Oxidation of other diols

The linear correlation between  $\log k$  at 283 K and 313 K ( $r = 0.9890$ , slope =  $0.9640 \pm 0.0721$ ) for the oxidation of four non-vicinal diols, 3-methoxybutan-1-ol, and 2-methoxyethanol shows that all the compounds are oxidized by the same mechanism (Exner 1973). The value of the isokinetic temperature is  $801 \pm 45$  K. 3-Methoxybutan-1-ol and 2-methoxyethanol are typical monohydric alcohols and, therefore, it is highly

likely that these diols are oxidized by a mechanism similar to that operative for monohydric alcohols. The oxidation of ethanol (Satsangi *et al* 1994) exhibited a substantial kinetic isotopic effect confirming the cleavage of the  $\alpha$ -C-H bond in the rate-determining step. Therefore, a mechanism, similar to one proposed earlier (Satsangi *et al* 1994) for monohydric alcohols, accounts for the experimental results obtained in the oxidation of non-vicinal diols.

### Acknowledgements

Thanks are due to University Grants Commission, New Delhi and the Council of Scientific and Industrial Research, New Delhi for financial support.

### References

- Barclay G A, Hokins B F and Kennard C H L 1963 *J. Chem. Soc.* 5691  
Bhatia I and Banerji K K 1983 *J. Chem. Soc., Perkin Trans.* **2** 1577  
Bunton C A 1966 *Oxidation in organic chemistry* (ed.) K Wiberg (New York: Academic Press) ch. 6  
Duke F R 1947 *J. Am. Chem. Soc.* **69** 3054  
Exner O 1973 *Prog. Phys. Org. Chem.* **10** 411  
Firouzabadi H, Naderi M, Sardarian A R and Vessel B 1983 *Synth. Commun.* **13** 611  
Firouzabadi H, Naderi M, Sardarian A R and Vessel B 1984 *Tetrahedron* **40** 5001  
Johnson C D 1987 *The Hammett equation* (Cambridge: University Press) p 54  
Freeman F and Kappos J C 1985 *J. Am. Chem. Soc.* **107** 6628  
Kemp T J and Waters W A 1963 *Proc. R. Soc. London A* **274** 480  
Kothari S 1991 *Proc. Indian Acad. Sci. (Chem. Sci.)* **103** 747  
Kothari S, Sharma V, Sharma P K and Banerji K K 1992 *Proc. Indian Acad. Sci. (Chem. Sci.)* **105** 583  
Lee D G and Perez-Benito J F 1988 *J. Org. Chem.* **53** 5728  
Littler J S 1971 *Tetrahedron* **27** 81  
Mathur A and Banerji K K 1987 *J. Chem. Soc., Perkin Trans.* **2** 1645  
Pavelich W A and Taft R W 1957 *J. Am. Chem. Soc.* **79** 4935  
Satsangi B K, Kothari S and Banerji K K 1994 *J. Chem. Res. (S)* 208  
Satsangi B K, Kothari S and Banerji K K 1995 *Transition Met. Chem.* **20** 288  
Wiberg K B and Evans R 1958 *J. Am. Chem. Soc.* **80** 3019