Kinetics and Mechanism of the Oxidation of Diols by Ethyl *N*-Chlorocarbamate

Anjali Grover, Seema Varshney and Kalyan K. Banerji *
Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

The kinetics of oxidation of five vicinal and four non-vicinal diols, and two of their monoethers by ethyl *N*-chlorocarbamate (ECC) have been studied. The vicinal diols yielded products arising out of the glycol bond fission while the other diols yielded hydroxycarbonyl compounds. The reaction is first order with respect to ECC, the diol, and hydrogen ions. Addition of ethyl carbamate and acrylonitrile has no effect on the reaction. The oxidation of [1,1,2,2-$^2H_4$]ethanediol showed the absence of a primary kinetic isotope effect. The values of solvent isotope effect, $k(H_2O)/k(D_2O)$, at 303 K for the oxidation of ethanediol, propane-1,3-diol and 3-methoxybutan-1-ol are 3.51, 2.21 and 1.98 respectively. An acyclic mechanism involving glycol bond fission has been proposed for the oxidation of the vicinal diols. The other diols are oxidized by a hydride-transfer mechanism as are monohydric alcohols.

Ethyl *N*-chlorocarbamate (ECC) is a well-known chlorinating and oxidizing agent and its use in synthetic organic chemistry is well documented.[1] We have been interested in the kinetics and mechanisms of the oxidations by ECC and have reported the oxidation of alcohols and lower oxyacids of phosphorus by ECC.[2-4] However, several oxidations of monohydric and polyhydric alcohols follow different mechanistic pathways, *e.g.* oxidations by lead(IV),[5] periodic acid,[6] acid permanganate[7] and bromamine-B.[8] Therefore, we have studied the oxidation of several diols by ECC in aqueous acetic acid solution. Mechanistic aspects of the reactions are discussed.

Experimental

Materials.—The diols were commercial products and were distilled under reduced pressure before use. [1,1,2,2-$^2H_4$]Ethanediol was prepared by the reduction of diethyl oxalate with lithium aluminium deuteride.[9] ECC was prepared by the reported method.[10]

Product Analysis.—In a typical experiment ethanediol (6.2 g, 0.1 mol) and ECC (2.5 g, 0.02 mol) were dissolved in a 1 : 1 (v/v) mixture of acetic acid–water (100 cm^3), in the presence of perchloric acid. (0.5 mol dm^{-3}). The reaction mixture was allowed to stand for *ca.* 12 h to ensure completion of the reaction. It was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in HCl (2 mol dm^{-3}) and stored in a refrigerator for *ca.* 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 7.2 g (86%) and 6.7 g (80%). A similar experiment with propane-1,3-diol yielded DNP of 3-hydroxypropanal in 71% yield after recrystallization.

Kinetic Measurements.—The pseudo-first order conditions were attained by keeping an excess of the diol over ECC. The solvent was 1 : 1 (v/v) acetic acid–water, unless mentioned 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 concentration of ECC iodometrically for up to 70% reaction. Pseudo-first order rate constants, k_{obs}, were evaluated from the linear (r > 0.990) plots of log[ECC] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ±4%. The specific rate constant, k, was determined using the relation: $k = k_{obs}/[\text{diol}][H^+]$. Preliminary experiments showed that the reaction is not sensitive to changes in ionic strength (0.1–2.0 mol dm^{-3}) and, therefore, no attempt was made to keep this constant.

Simple and multivariate linear regression analyses were carried out by the least-squares method.

Results

The oxidation of vicinal diols by ECC yields arising from the glycol bond fission, *i.e.* rupture of the bond between the carbon atoms bearing the hydroxy groups, while the other diols give products of simple oxidation of one of the hydroxy groups. Analyses of products indicate the overall reactions (1) and (2).

$$R_2C(OH)C(OH)R_2 + EtO_2CNHCl \longrightarrow 2\,R_2C{=}O + EtO_2CNH_2 + HCl \quad (1)$$

$$HOCH_2[CH_2]_nCH_2OH + EtO_2CNHCl \longrightarrow HOCH_2[CH_2]_nCHO + EtO_2CNH_2 + HCl \quad (2)$$

Rate Laws.—The reactions were found to be first order with respect to ECC. Individual kinetic runs were strictly first order in ECC. Further, the first-order rate coefficients did not vary with the initial concentration of ECC. The order with respect to the diol was also found to be one. The rate increased linearly with an increase in hydrogen ion concentration. The rate constants for the oxidation of ethanediol and propane-1,3-diol are recorded in Tables 1 and 2.

Isotope Effects.—To ascertain the importance of the C–H bond cleavage in the rate-determining step, the oxidation of [1,1,2,2-$^2H_4$]ethanediol was studied. The results showed the absence of a primary kinetic isotope effect (Table 3).

The rates of oxidation of ethanediol, propane-1,3-diol, and 3-methoxybutan-1-ol were obtained in deuterium oxide (overall 95% D_2O). This set of experiments was carried out in aqueous solution. The results are summarized in Table 4.

Effect of Ethyl Carbamate.—The rates of oxidation were obtained in the presence of initially added ethyl carbamate (EC). The results showed the absence of any effect of EC on the reaction rate (Table 5).

Induced Polymerization of Acrylonitrile.—The oxidation of

Table 1 Rate constants for the oxidation of ethanediol by ECC at 303 K

10^3 [ECC]/mol dm^{-3}	[Diol]/mol dm^{-3}	[H$^+$]/mol dm^{-3}	$10^5\ k_{obs}$/s^{-1}
2.0	0.20	0.50	4.37
4.0	0.20	0.50	4.50
6.0	0.20	0.50	4.41
10.0	0.20	0.50	4.31
15.0	0.20	0.50	4.50
5.0	0.10	0.50	2.24
5.0	0.20	0.50	4.35
5.0	0.40	0.50	9.75
5.0	0.60	0.50	13.7
5.0	0.80	0.50	17.7
5.0	1.00	0.50	21.9
5.0	0.40	0.10	2.00
5.0	0.40	0.20	3.93
5.0	0.40	0.80	15.7
5.0	0.40	1.00	19.6
5.0	0.40	1.50	30.0
5.0	0.40	0.50[a]	9.60

[a] Contained 10^{-3} mol dm^{-3} acrylonitrile.

Table 2 Rate constants for the oxidation of propane-1,3-diol by ECC at 293 K

10^3 [ECC]/mol dm^{-3}	[Diol]/mol dm^{-3}	[H$^+$]/mol dm^{-3}	$10^5\ k_{obs}$/s^{-1}
2.0	0.64	0.40	18.7
5.0	0.64	0.40	19.0
8.0	0.64	0.40	18.6
12.0	0.64	0.40	20.0
15.0	0.64	0.40	19.2
5.0	0.16	0.40	4.73
5.0	0.32	0.40	9.52
5.0	0.48	0.40	14.0
5.0	0.96	0.40	28.4
5.0	1.28	0.40	37.5
5.0	0.48	0.10	3.56
5.0	0.48	0.20	7.20
5.0	0.48	0.80	28.4
5.0	0.48	1.20	42.1
5.0	0.48	1.50	54.0
5.0	0.48	0.50[a]	18.1

[a] Contained 10^{-3} mol dm^{-3} acrylonitrile.

Table 3 Kinetic isotope effect in the oxidation of ethanediol by ECC: [ECC] 0.005 mol dm^{-3}, [H$^+$] 0.50 mol dm^{-3}, [diol] 0.40 mol dm^{-3}, T 303 K

	$10^5\ k_{obs}$/s^{-1}	k_H/k_D
Ethanediol	9.75	1.01
[1,1,2,2-$^2H_4$]Ethanediol	9.68	

Table 4 Solvent isotope effect in the oxidation of ethanediol, propane-1,3-diol and 3-methoxybutan-1-ol: [ECC] 0.005 mol dm^{-3}, T 303 K

Compound	$10^4\ k(H_2O)$ mol^{-2} dm^6 s^{-1}	$10^4\ k(D_2O)$ mol^{-2} dm^6 s^{-1}	$k(H_2O)/k(D_2O)$
Ethanediol	2.42	0.69	3.51
Propane-1,3-diol	9.75	4.41	2.21
3-Methoxybutan-1-ol	17.0	8.58	1.98

diols by ECC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, an addition of acrylonitrile had no effect on the rate of reaction (Tables 1 and 2).

Table 5 Effect of ethyl carbamate (EC) on the oxidation of ethanediol and propane-1,3-diol ($10^4\ k$/mol^{-2} dm^6 s^{-1}): [ECC] 0.005 mol dm^{-3}, T 303 K

	10^3 [EC]/mol dm^{-3}				
	0.0	2.5	5.0	10.0	20.0
Ethanediol	4.37	4.51	4.55	4.20	4.28
Propane-1,3-diol	6.10	5.87	6.12	6.23	6.00

Table 6 Effect of solvent composition on the reaction rate ($10^4\ k$/mol^{-2} dm^6 s^{-1}): [ECC] 0.005 mol dm^{-3}, T 303 K

	% AcOH (v/v)				
	0	20	30	50	70
Ethanediol	2.42	3.22	3.75	4.37	6.53
Propane-1,3-diol	9.75	12.1	15.4	18.5	30.2

Table 7 Temperature dependence of the rate constants ($10^4\ k$/mol^{-2} dm^6 s^{-1})

Diol	293 K	303 K	313 K	323 K
Ethanediol	2.32	4.37	8.32	15.4
Propane-1,2-diol	3.40	6.10	11.3	20.3
Butane-2,3-diol	4.70	8.32	14.7	26.3
Butane-1,2-diol	9.00	15.4	26.2	44.9
Pinacol	9.55	15.9	26.9	46.5
Propane-1,3-diol	7.37	18.5	45.9	116
Butane-1,3-diol	12.3	29.1	63.1	159
Butane-1,4-diol	10.5	26.3	59.0	142
Pentane-1,5-diol	12.8	31.5	72.5	162
3-Methoxybutan-1-ol	14.5	33.5	70.7	175
2-Methoxyethanol	8.57	20.8	53.1	126

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 increased with an increase in the amount of acetic acid in the solvent (Table 6).

Effect of Temperature.—The rates of the oxidation of diols were obtained at different temperatures and activation parameters were evaluated (Tables 7 and 8).

Discussion

Little is known about the state of ECC in aqueous solutions. However, by analogy with structurally similar *N*-halosulfonamides,[1] one can visualize the following equilibria [eqns. (3)–(5)].

$$EtO_2CNHCl + H_2O \rightleftharpoons EtO_2CNH_2 + HOCl \quad (3)$$

$$2\,EtO_2CHNCl \rightleftharpoons EtO_2CNH_2 + EtO_2CNCl_2 \quad (4)$$

$$EtO_2CNHCl \rightleftharpoons EtO_2CNCl^- + H^+ \quad (5)$$

The probable oxidizing species in an acidified aqueous solution of ECC are, therefore, EtO_2CNHCl, EtO_2CNCl_2, EtO_2CNCl^-, HOCl, and their protonated forms. The dichloro species can be ruled out as an oxidizing species in view of the strict first-order dependence of the reaction rate on ECC. The absence of any effect of EC on the rate of reaction also precludes both HOCl and EtO_2CNCl_2 as the reactive oxidizing species. This leaves ECC and its anion as the probable oxidizing species. However, ECC is a weak acid[2] (pK 8.5) and in the acidity range

Table 8 Activation parameters of the oxidation of diols by ECC

Diol	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}	ΔG^*/kJ mol^{-1}
Ethanediol	47.2 ± 0.6	−154 ± 2.0	92.5 ± 0.4
Propane-1,2-diol	44.5 ± 0.7	−160 ± 2.0	92.1 ± 0.6
Butane-2,3-diol	42.6 ± 0.7	−164 ± 2.0	91.3 ± 0.6
Butane-1,2-diol	39.3 ± 0.5	−169 ± 1.8	89.7 ± 0.4
Pinacol	38.9 ± 0.9	−171 ± 2.7	89.6 ± 0.7
Propane-1,3-diol	69.6 ± 1.1	−68 ± 1.5	89.7 ± 0.9
Butane-1,3-diol	63.9 ± 1.0	−83 ± 1.4	88.6 ± 1.1
Butane-1,4-diol	65.3 ± 0.9	−80 ± 1.0	88.9 ± 0.8
Pentane-1,5-diol	64.0 ± 0.5	−88 ± 0.7	88.4 ± 0.4
3-Methoxybutan-1-ol	62.1 ± 1.0	−88 ± 1.4	88.2 ± 1.2
2-Methoxyethanol	67.8 ± 1.1	−73 ± 2.0	89.4 ± 0.9

Table 9 Reaction constants of the oxidation of vicinal diols by ECC

T/K	ρ_I	δ	r	sd
293	−0.97	−1.49	0.9998	0.007
303	−0.84	−1.40	0.9999	0.003
313	−0.74	−1.28	0.9997	0.006
323	−0.72	−1.19	0.9997	0.005

used almost all of ECC will be in the unionized form. Thus the most probable oxidizing species is ECC itself.

The linear increase in the rate of oxidation with an increase in the hydrogen-ion concentration suggests that (i) there is a rapid equilibrium between the protonated and unprotonated forms, (ii) the equilibrium constant has a small value, and (iii) only the protonated form is kinetically reactive.[11] It is proposed that ECC is protonated to yield a stronger oxidant and electrophile [eqn. (6)]. The value of K_p, in aqueous solution, has earlier

$$\mathrm{EtO_2CNHCl} + \mathrm{H_3O^+} \xrightleftharpoons{K_p} [\mathrm{EtOC(OH)NHCl}]^+ + \mathrm{H_2O} \quad (6)$$

been determined to be 0.034 at 298 K.[2]

The effect of solvent composition indicated that the rate increased with a decrease in the polarity of the medium. This is in accord with the proposal of an interaction between a cationic species and a neutral molecule in the rate-determining step. As the two species come together to form an activated complex, the charge density obviously decreases. This decrease in the charge density is facilitated by the decrease in the polarity of the medium.

The diverse nature of the products formed in the oxidation of vicinal diols and other diols suggests that these compounds follow different mechanistic pathways.

Oxidation of Vicinal Diols.—The absence of a primary kinetic isotope effect, in the oxidation of [1,1,2,2-^{2}H$_4$]ethanediol, confirmed that the α-C–H bond is not cleaved in the rate-determining step. In contrast, substantial primary kinetic isotope effects were observed in the oxidations of both ethanol[2] and benzyl alcohol[3] by ECC. Thus it seems that the oxidation of monohydric alcohols and vicinal diols follows different mechanisms. The rate of an acid-catalysed reaction is expected to be faster in D_2O than in H_2O when a pre-equilibrium protonation is involved.[12] In the present case an 'inverse' solvent isotope effect has been observed. Active hydrogens like those present in hydroxy and carboxyl groups undergo rapid exchange in deuterium oxide. If the cleavage of the O–H bond is involved in the rate-determining step, the O–H/O–D isotope effect may neutralize the rate-enhancing effect of D_2O or even result in an 'inverse' solvent isotope effect. Thus, in the present reaction, an O–H bond cleavage in the rate-determining step is indicated. The large magnitude of solvent isotope effect, observed in the oxidation of ethanediol, suggests that both the hydroxy groups are involved in the rate-determining step. The magnitude of the negative entropy of activation is almost double in the oxidation of vicinal diols, compared to that of the other compounds. This points to a more rigid transition state in the oxidation of the vicinal diols. This also supports the involvement of both the hydroxy groups in the rate-determining step. The only mode of oxidation available for pinacol is the fission of the bonds between alcohol carbon atoms. That the other vicinal diols follow this mechanism is confirmed by the

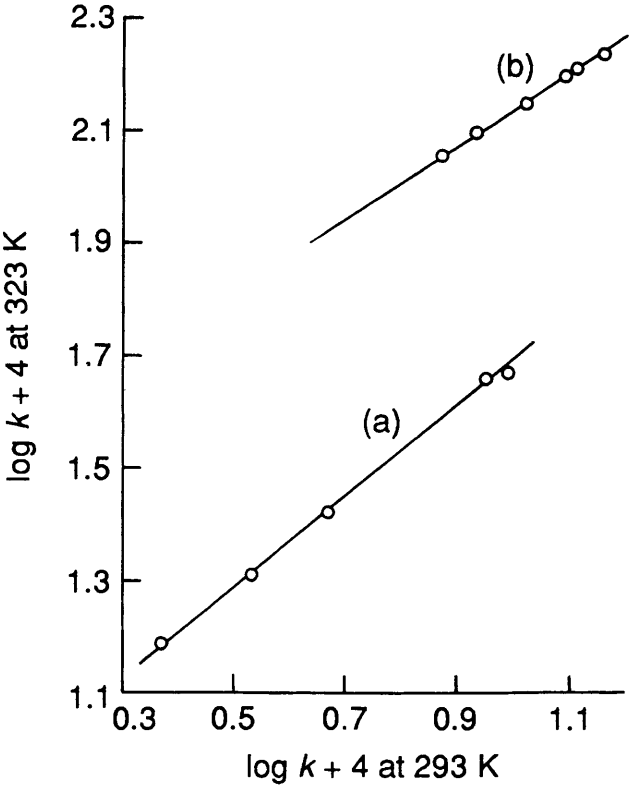
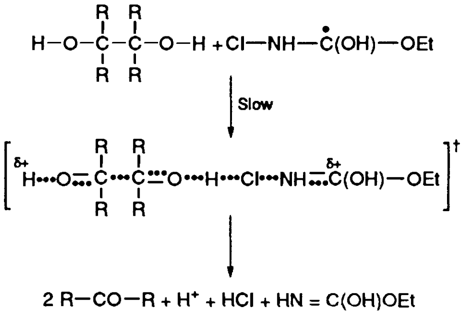


Fig. 1 Isokinetic relationship in the oxidation of vicinal and other diols by ECC: (a) vicinal diols, (b) other diols



(7)

isolation of products formed by the C–C bond fission. The mechanism in eqns. (7) and (8) accounts for the experimental results.

$$HN{=}C(OH)OEt \xrightarrow{\text{fast}} H_2NCO_2Et \qquad (8)$$

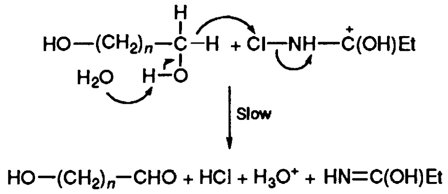
Correlation of Structure and Reactivity.—The rates of oxidation of the vicinal diols failed to show satisfactory correlation with either the polar or steric substituent constants.[13] Therefore, the rates were analysed in terms of the dual substituent-parameter, eqn. (9). The results recorded in Table 9, show that

$$\log k = \rho_I \Sigma\sigma_I + \delta \Sigma E_s + \log k_0 \qquad (9)$$

the rates exhibited an excellent correlation with polar and steric substituent constants. There is no significant collinearity between $\Sigma\sigma_I$ and ΣE_s (r 0.5224).

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

Oxidation of Other Diols.—The similar values of solvent isotope effect obtained in oxidations of propane-1,3-diol, 3-methoxybutan-1-ol and ethanol,[2] suggest that the non-vicinal diols are oxidized by a mechanism similar to that operative for monohydric alcohols. The oxidation of ethanol[2] exhibited a substantial kinetic isotope effect confirming the cleavage of the α-C–H bond in the rate-determining step. Therefore, a mechanism, similar to one proposed earlier[2] for monohydric alcohols, accounts the experimental results obtained in the oxidation of non-vicinal diols.



(10)

$$HN{=}C(OH)Et \xrightarrow{\text{fast}} H_2NCOOEt \qquad (11)$$

Acknowledgements

Thanks are due to University Grants Commission (India) for the financial support.

References

1 M. M. Campbell and G. Johnson, *Chem. Rev.*, 1978, **78**, 65.
2 S. Mittal, V. Sharma and K. K. Banerji, *Int. J. Chem. Kinet.*, 1986, **18**, 689.
3 S. Jain and K. K. Banerji, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1767.
4 R. Asopa, A. Mathur and K. K. Banerji, *Indian J. Chem.*, 1991, **30A**, 784.
5 C. A. Bunton, in *Oxidation in Organic Chemistry, Part A*, ed. K. B. Wiberg, Academic Press, New York, 1966, ch. 6.
6 F. R. Duke, *J. Am. Chem. Soc.*, 1947, **69**, 3054.
7 I. Bhatia and K. K. Banerji, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1577.
8 A. Mathur and K. K. Banerji, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1645.
9 T. J. Kemp and W. A. Waters, *Proc. R. Soc. London, Ser. A*, 1963, **274**, 480.
10 C. Bachand, D. Hughes, J. M. Paton, T. Daniel and J. Lessard, *J. Org. Chem.*, 1974, **39**, 3137.
11 Y. K. Gupta and K. S. Gupta, *J. Chem. Educ.*, 1984, **61**, 972.
12 C. J. Collins and M. S. Bowman, *Isotope Effects in Chemical Reactions*, Van Nostrand, New York, 1970, p. 267.
13 C. D. Johnson, *The Hammett Equation*, Cambridge University Press, Cambridge, 1973, pp. 78–80.

Paper 3/03788F
Received 1*st July* 1993
Accepted 22*nd September* 1993