Kinetics and Mechanism of Redox Reactions in Aqueous Solution. Part 3.[1] Oxidation of Diols by Aquacerium(IV) Species in Perchlorate Solution

By **Aditya Prakash, Raj Narain Mehrotra,* and Ramesh C. Kapoor,*** Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

Michaelis–Menten kinetics have been observed for the oxidation of diols and 3-methoxybutan-1-ol by aquacerium(IV) ions in acid perchlorate solution of 2 mol dm^{-3} ionic strength. The reaction has a first-order dependence on cerium(IV) concentration and the rate is accelerated by increasing acidity. An analysis of the equilibrium constants for complex formation between Ce^{IV} and the substrates, the rates of disproportionation of the intermediate complexes, and the entropy values associated with the latter suggests the formation of chelate complexes in the oxidation of propane-1,3-, butane-1,3-, and butane-1,4-diols, whereas in the oxidation of pentane-1,5- and hexane-1,6-diols and 3-methoxybutan-1-ol the substrate is believed to act as a unidentate ligand.

THERE are differing opinions as to the nature of intermediate complexes formed in the oxidation of diols by cerium(IV). Strong and convincing evidence has been put forward to support the formation of intermediate complexes containing both chelate [2-4] and unidentate [5-7] ligands. In this context we have studied the oxidation of some diols, hitherto not investigated, by aquacerium(IV) ions in perchlorate media. The perchlorate medium was chosen to avoid interfering complex formation between Ce^{IV} and the anions of nitric and sulphuric acids. Such complex formation was, perhaps, the reason why the previous studies [8] in aqueous sulphuric acid solution gave inconclusive results about the nature of the complex formed between Ce^{IV} and the diols. The present results indicate that the formation of an intermediate complex containing chelate or unidentate ligands depends on the distance between the two hydroxyl groups in the diol reductant.

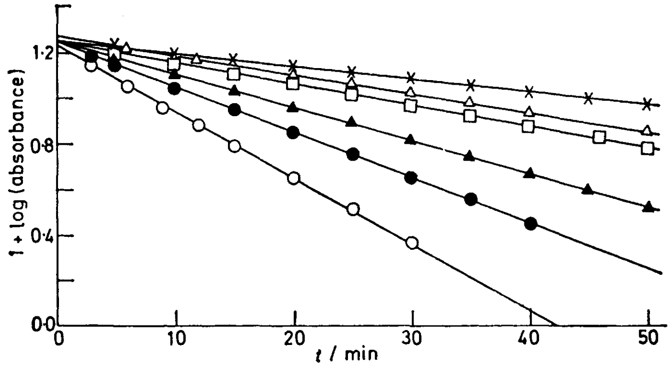


FIGURE 1 First-order plots at 15 °C and [H$^+$] = 1 mol dm^{-3} (I = 2 mol dm^{-3}) for the disappearance of Ce^{IV} in the presence of different substrates. The $k_{obs.}$ values were calculated from the gradients of such plots. Substrate = butane-1,3-diol (×), propane-1,3-diol (□), butane-1,4-diol (▲), pentane-1,5-diol (●), hexane-1,6-diol (○), and 3-methoxybutan-1-ol (△)

EXPERIMENTAL

Stock solutions of the diols and 3-methoxybutan-1-ol (Fluka products) were prepared by direct weighing of the samples. The water used was redistilled in the presence of permanganate in an all-glass still. Cerium(IV) perchlorate was prepared by electrolytic oxidation of cerium(III) perchlorate. The cerium(IV) content of the solution was estimated by titration against a freshly prepared standard iron(II) solution. The acid concentration of the stock solution was determined with standard alkali after reducing Ce^{IV} with sodium oxalate and removing the insoluble cerium(III) oxalate. Other solutions, as and when needed, were prepared from the samples as received and analysed by standard analytical methods.

Stoicheiometry and Product Analysis.—The oxidation products, recovered as 2,4-dinitrophenylhydrazones, were isolated from reaction mixtures containing a large excess of diol.[8] The m.p.s of the recovered 2,4-dinitrophenylhydrazones compared well with those of hydrazones of the respective hydroxyaldehydes reported in the literature;[9,10] it was thus concluded that in each case the diol oxidation product was the corresponding hydroxyaldehyde. The stoicheiometry of the reaction is thus as follows:

$$2Ce^{IV} + HOCH_2[CH_2]_nCH_2OH \longrightarrow HOCH_2[CH_2]_nCHO + 2Ce^{III} + 2H^+$$

Kinetic Measurements.—The kinetic measurements were made in the presence of a large excess of substrate and at constant ionic strength, 2 mol dm^{-3}, maintained with sodium perchlorate. The reactant solutions were thermally equilibrated in a constant-temperature bath maintained at the desired temperature ±0.1 °C. The reaction was initiated by mixing reactant solutions of appropriate concentrations. At known intervals of time aliquots were withdrawn and transferred to the spectrophotometer cell immediately. The absorbance of the unchanged cerium(IV) solution was recorded at 300 nm (ref. 11) on a Beckman DU-2 spectrophotometer using matched silica cells (pathlength 1 cm).

The observed first-order rate constant $k_{obs.}$, with respect to Ce^{IV}, was calculated from the gradients of linear plots (Figure 1) of log (absorbance) against time. The reaction was generally followed beyond two half-lives. The values of $k_{obs.}$ reported are the means obtained from duplicate or triplicate runs. Values obtained from repeated runs agreed within 2—3%. The gradients and intercepts of such plots were calculated by the method of least squares.

RESULTS

The first-order dependence on the cerium(IV) concentration was indicated not only by the linearity of the plots illustrated in Figure 1 but also by the observed independence of the first-order rate constant $k_{obs.}$ on different initial [Ce^{IV}] values, varied from 0.000 22 to 0.003 3 mol dm^{-3} in a number of steps at constant concentrations of other reagents ([Propane-1,3-diol] = 0.02 mol dm^{-3}, [$HClO_4$] = 2 mol dm^{-3}, 20 °C).

The dependence of the $k_{obs.}$ values on the substrate was consistent with Michaelis-Menten kinetics in each case. Reciprocal Michaelis-Menten plots are illustrated in Figure 2. It was further noted that the gradients of these plots were dependent on [H^+] whereas the intercepts were independent of acidity at constant ionic strength. These conclusions are illustrated in Figure 3 with the rate data obtained in the oxidation of butane-1,4-diol.

The effect of Ce^{III} on the rate of reaction was investigated in the oxidation of propane-1,3-diol at constant ionic strength (2.2 mol dm^{-3}) and constant concentrations of the other reagents ([Ce^{IV}] = 0.001 mol dm^{-3}, [Diol] = 0.02 mol dm^{-3}, [$HClO_4$] = 2 mol dm^{-3}; 20 °C). The observed rate, however, increased with increasing ionic strength, which was varied with sodium perchlorate, in the range 2—3.5 mol dm^{-3} ([Ce^{IV}] = 0.001 mol dm^{-3}, [Propane-1,3-diol] = 0.02 mol dm^{-3}, [$HClO_4$] = 2 mol dm^{-3}; 20 °C).

FIGURE 2 Plots of $k_{obs.}^{-1}$ against [Substrate]$^{-1}$ ([H^+] = 0.5 mol dm^{-3} and 20 °C) indicating the formation of cerium(IV)-substrate complexes. Such plots were also obtained at other temperatures. Key as in Figure 1

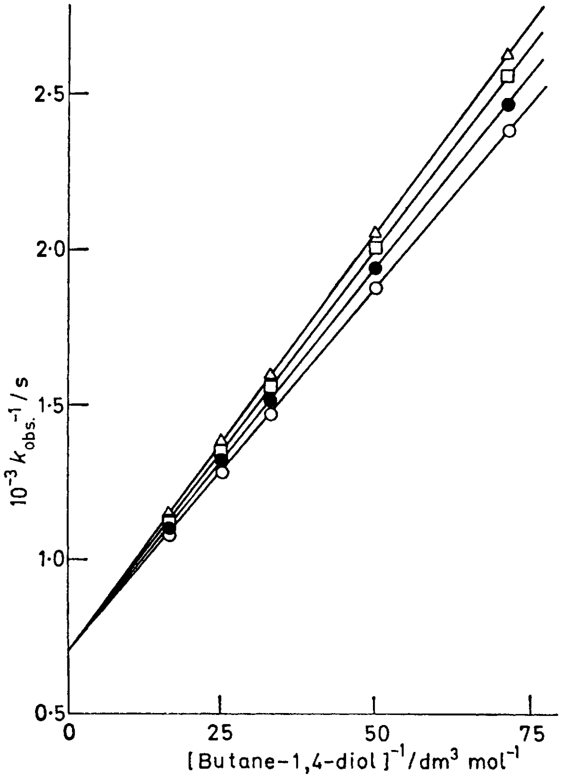


FIGURE 3 Representative Michaelis-Menten plots for butane-1,4-diol at 15 °C. Such plots were obtained at other temperatures and substrates. These plots, at different [H^+], show that the intercepts are independent, whereas the gradients are dependent, of the initial [H^+]. Initial [H^+] = 0.5 (△), 1.0 (□), 1.5 (●), and 2.0 mol dm^{-3} (○)

DISCUSSION

The increase in the rate with increasing [H^+] at constant ionic strength (2 mol dm^{-3}) indicates that the species Ce^{4+}(aq) and [$Ce(OH)]^{3+}$(aq), that exist in aqueous perchloric acid solutions of Ce^{IV},[12] are both reactive. The formation of cerium(IV)-substrate complexes, prior to the rate-limiting step, is indicated by the Michaelis-Menten plots and by the dependence of the initial absorbance, obtained by extrapolation of log (absorbance)-time plots to $t = 0$, on the initial concentrations of the substrates. Since the absorbance was obtained using a spectrometer having no thermostatting assembly, no precise data on the absorbance could be compiled to identify the nature of the complex, *i.e.* whether it contains a chelate or unidentate ligand. This problem, however, has been resolved by considering some of the kinetic parameters evaluated in the present study. A detailed discussion is presented after considering the mechanism and the rate law for the reactions.

Because of the similar kinetics, a general mechanism consisting of reactions (1)—(7) is suggested for the oxidation of diols and 3-methoxybutan-1-ol. Equilibria (1)—(4) are considered to be established rapidly and reactions (5) and (6) are the rate-limiting steps with the assumption that $k_0 \gg k$ and $k_0 \gg k_1$. Here R =

$$Ce^{4+}(aq) \xrightleftharpoons{K_h} [Ce(OH)]^{3+}(aq) + H^+ \quad (1)$$

$$Ce^{4+}(aq) + R[CH_2]_nCH_2OH \xrightleftharpoons{K} [Ce\{HOCH_2(CH_2)_nR\}]^{4+} \quad (2)$$

$$[Ce(OH)]^{3+}(aq) + R[CH_2]_nCH_2OH \xrightleftharpoons{K_1} [Ce\{OCH_2(CH_2)_nR\}]^{3+} \quad (3)$$

$$[Ce\{HOCH_2(CH_2)_nR\}]^{4+} \xrightleftharpoons{K_2} [Ce\{OCH_2(CH_2)_nR\}]^{3+} + H^+ \quad (4)$$

$$[Ce\{HOCH_2(CH_2)_nR\}]^{4+} \xrightarrow{k} R[CH_2]_n\dot{C}H_2O + H + Ce^{III} \quad (5)$$

$$[Ce\{OCH_2(CH_2)_nR\}]^{3+} \xrightarrow{k_1} R[CH_2]_n\dot{C}H_2O + Ce^{III} \quad (6)$$

$$Ce^{IV} + R[CH_2]_n\dot{C}H_2O \xrightarrow{k_0} R[CH_2]_nCHO + Ce^{III} + H^+ \quad (7)$$

CH_2OH for diols and MeCH(OMe) for 3-methoxybutan-1-ol and n has the appropriate value for each of the diols. The formation of the free radical was confirmed by the polymerisation of acrylonitrile added to partially oxidised reaction mixtures. The monomer, however, did not polymerise when it was added to solutions of Ce^{IV} and the substrates taken separately. Reactions (1) and (3), and (2) and (4), are alternate paths for the formation of the $[Ce\{OCH_2(CH_2)_nR\}]^{3+}$ complex. These paths cannot be distinguished from the kinetics because $K_1K_h = KK_2$. The hydrolytic equilibrium (1) is well established[12] in aqueous perchloric acid solutions containing Ce^{IV}. Values of the hydrolytic constant K_h, at different temperatures, were obtained by extrapolation from the data reported by Baker *et al.*[13], *viz.* 11.88, 13.49, 15.31, and 16.44 mol dm^{-3} at 12, 15, 18, and 20 °C respectively.

Consideration of reactions (1)—(7) gives rate law (8) in terms of the disappearance of Ce^{IV} where $[Ce^{IV}]_T$ is the total concentration of Ce^{IV}. The observation that the intercepts of the Michaelis–Menten plots (Figure 3) are

$$\frac{-d[Ce^{IV}]}{dt} = \frac{2K(k + k_1K_2[H^+]^{-1})[Ce^{IV}]_T[Diol]}{1 + K_h[H^+]^{-1} + K(1 + K_2[H^+]^{-1})[Diol]} \quad (8)$$

independent of the initial $[H^+]$ is not in agreement with this rate law. It was therefore appropriate, in the first instance, to consider that the reaction proceeded through the formation and disproportionation of only one of the two complexes, *i.e.* either $[Ce\{HOCH_2(CH_2)_nR\}]^{4+}$ or $[Ce\{OCH_2(CH_2)_nR\}]^{3+}$. Considering that the reactions (3), (4), and (6) are not involved and that reaction (5) is rate limiting, the rate law could now be expressed by equation (9) or (9a). Equation (9a) is consistent with the observation that the intercepts of the Michaelis–Menten plots are independent of $[H^+]$. However, a

$$\frac{-d[Ce^{IV}]}{dt} = \frac{2kK[Ce^{IV}][Diol]}{1 + K_h[H^+]^{-1} + K[Diol]} \quad (9)$$

$$\frac{1}{k_{obs.}} = \frac{[H^+] + K_h}{2kK[H^+][Diol]} + \frac{1}{2k} \quad (9a)$$

plot of $([H^+] + K_h)/S$ against $[H^+]$, Figure 4, does not pass through the origin as is required by (9a); S is the gradient of the Michaelis–Menten plot. This indicates that steps (2) and (5) do not constitute the mechanism of the reaction.

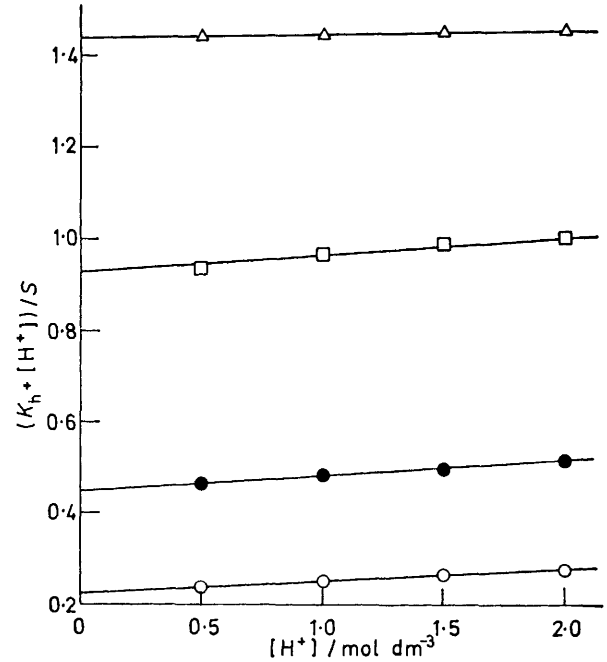


FIGURE 4 Representative plots of $(K_h + [H^+])/S$ against $[H^+]$ for hexane-1,6-diol at different temperatures. Such plots were obtained for other substrates too. The gradient value, S, used here was obtained from plots such as those illustrated in Figure 3. Temperature = 25 (△), 18 (□), 15 (●), and 12 °C (○)

Next, reactions (2) and (5) were eliminated and (6) was considered to be rate limiting. The new rate law is given by (10) and its rearrangement gives (10a). Equation (10a) is consistent with the observation that

$$\frac{-d[Ce^{IV}]}{dt} = \frac{2k_1K_1K_h[Ce^{IV}][Diol][H^+]^{-1}}{1 + K_h[H^+]^{-1} + K_1K_h[H^+]^{-1}[Diol]} \quad (10)$$

$$\frac{1}{k_{obs.}} = \frac{[H^+] + K_h}{2k_1K_1K_h[Diol]} + \frac{1}{2k_1} \quad (10a)$$

the intercepts of the plots of $1/k_{obs.}$ against $[Diol]^{-1}$, Figure 3, are independent of the acidity, but not with Figure 4 because (10a) indicates that plots of $([H^+] + K_h)/S$ against $[H^+]$ should be linear and parallel to the $[H^+]$ axis. The plots in Figure 4 have definite gradients. It is thus concluded that the remaining reactions, except (2) and (5), also do not constitute the mechanism, and therefore it is clear that a mechanism based on only one of the cerium(IV) species or on only one complex formed with this particular cerium(IV) species is not tenable.

Wells and Husain [14] have concluded that if $k = k_1$ the intercept of plots of k_{obs}^{-1} against $[\text{Substrate}]^{-1}$ will be independent of acidity, and a slight variation in the intercepts will be observed if $k \sim k_1$. Assuming that $k = k_1$ in (8), one can write equation (11) after suitable rearrangements. This equation is consistent with the observations (*i*) that the intercepts of plots of $k_{obs.}^{-1}$

$$\frac{1}{k_{obs.}} = \frac{[\text{H}^+] + K_h}{2kK([\text{H}^+] + K_2)[\text{Diol}]} + \frac{1}{2k} \qquad (11)$$

against $[\text{Diol}]^{-1}$ are independent of acidity and (*ii*) that plots of $([\text{H}^+] + K_h)/S$ against $[\text{H}^+]$, Figure 4, have intercept $= 2kKK_2$ and gradient $= 2kK$, where S is the gradient $\{= ([\text{H}^+] + K_h)/2kK([\text{H}^+] + K_2)\}$. The method adopted for evaluation of the parameters in equation (8) was similar to that described by Wells and Husain.[14,15] The values of the constants obtained for each of the substrates are reported in Table 1. (Complete kinetic data are available from Professor R. C. Kapoor.[16]) Because of the errors inherent in this analysis, the values of the constants K, K_1, and K_2 have been rounded off to the nearest whole number and the standard deviation is given in Table 1 for each parameter.

TABLE 1

Values of the constants K, K_1, K_2 (equilibrium constants) and k (rate of disproportionation) as these appear in the proposed mechanism

Substrate	θ_c	K	K_1	K_2	10^4k
	°C		mol dm^{-3}		s^{-1}
Propane-1,3-diol	12	60	30	7	4.2
	15	60	30	7	5.8
	18	65	27	6	8.0
	20	68	30	5	10.0
	Average	63	29	6	
		±4	±1.5	±1	
Butane-1,3-diol	12	69	23	4	2.5
	15	75	26	5	3.0
	18	78	25	4	3.6
	20	66	29	7	6.0
	Average	72	25.8	5	
		±5.5	±2.5	±1.4	
Butane-1,4-diol	12	57	22	5	5.3
	15	60	24	5	7.0
	18	58	23	6	9.8
	20	55	28	7	12.5
	Average	57.5	24	5.7	
		±2	±2.6	±1	
Pentane-1,5-diol	12	7	31	55	4.0
	15	10	37	50	7.6
	18	6	34	85	11.9
	20	9	36	65	16.7
	Average	8	34.5	64	
		±1.8	±2.6	±15.5	
Hexane-1,6-diol	12	19	16	10	6.2
	15	10	18	23	9.9
	18	17	17	17	16.7
	20	15	18	20	23.8
	Average	15	17	17.5	
		±4	±1	±5.5	
3-Methoxy-butan-1-ol	12	16	14	10	8.0
	15	22	8	5	11.1
	18	20	11	8	15.9
	20	17	9	9	20.0
	Average	18.7	10.5	8	
		±2.7	±2.6	±2.2	

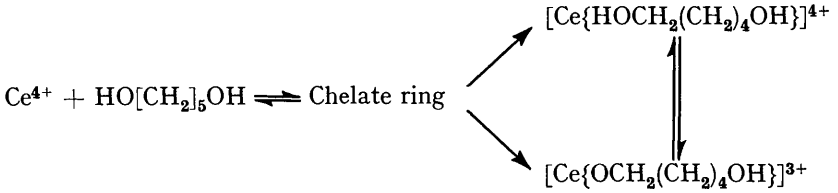
Standard deviations are given for the average values.

The point of the present study was to investigate the nature of the cerium(IV)–substrate complexes which could either contain chelate or unidentate ligands corresponding to co-ordination of two or only one hydroxyl group(s) respectively by the metal ion. Since no direct methods are available for this purpose, an indirect approach was adopted. The co-ordination of two hydroxyl groups increases the stability of a complex and thus a higher value of the equilibrium constant for the formation of the complex is expected in comparison with the value obtainable when only one hydroxy-group is co-ordinated. Hintz and Johnson,[3] adopting this approach, favoured a chelated complex between Ce^{IV} and *cis*- and *trans*-cyclohexanediols but the ligands *trans*-2-methoxycyclohexanol and cyclohexanol were unidentate.

Comparison of Equilibrium Constants.—The magnitude of K. The K values (Table 1) for propane-1,3-, butane-1,3-, and butane-1,4-diols are much higher than those of pentane-1,5- and hexane-1,6-diols and 3-methoxybutan-1-ol. The value for pentane-1,5-diol is the lowest. Since 3-methoxybutan-1-ol can only act as a unidentate ligand towards Ce^{4+}(aq), it can be inferred that hexane-1,6-diol behaves similarly, but chelated complexes are formed with propane-1,3-, butane-1,3-, and butane-1,4-diols. The significantly low K value for pentane-1,5-diol suggests that the formation of a chelated complex is not favoured. This is understandable because there is a sharper decrease in equilibrium constant in the case of formation of an eight-membered ring.[17] Thus the formation of a complex with unidentate pentane-1,5-diol is also favoured.

The magnitude of K$_1$. The K_1 values, like the K values, for propane-1,3-, butane-1,3-, and butane-1,4-diols are definitely higher than those of hexane-1,6-diol and 3-methoxybutan-1-ol. The earlier inference, based on the K values, is thus confirmed. However, the K_1 value for pentane-1,5-diol is even higher than those for propane-1,3-, butane-1,3-, and butane-1,4-diols, which seemingly form chelated complexes. This is rather surprising in view of the earlier inference from the K value that pentane-1,5-diol acts as a unidentate ligand. This anomaly seems to have no plausible explanation.

The magnitude of K$_2$. Reactions (1) and (4) are considered to be similar because both depict an equilibrium between a Lewis acid and its conjugate base. A comparison of the values of K_2 with those of K_h, indicates that complexes with substrates other than pentane-1,5- and hexane-1,6-diols are less acidic than Ce^{4+}(aq)-($K_2 < K_h$; the K_h values are given in ref. 13). The complex of pentane-1,5-diol is, however, much more markedly acidic than $\text{Ce}^{4+}(\text{aq})(K_2 > K_h)$. The probable explanation, suggested by a referee, is that pentane-1,5-diol probably initially forms a chelate complex. Since the chelate ring is not stable, because of the strain factor, it opens immediately with the release of a proton and the formation of the conjugate base. The opening of the ring also results in the formation of a complex in which the ligand is unidentate. The whole sequence could be visualised as illustrated below:



Comparison of k *Values*.—Inductive effects for the different substrates are neglected in this comparison. The rates of disproportionation of complexes of unidentate ligands are expected to be nearly the same since there is no strain of the chelate ring. The same is true for the rates of oxidation of hexane-1,6-diol and 3-methoxybutan-1-ol. The rates of oxidation of pentane-1,5-diol and hexane-1,6-diol are also comparable. All these substrates are believed to be oxidised through the formation of complexes in which they act as unidentate ligands. The conclusion that pentane-1,5-diol acts a unidentate ligand, based on the comparison of equilibrium constants and now with the rate of disproportionation of the complex formed with pentane-1,5-diol, is also consistent with the suggestion of a referee that the existence of an eight-membered chelate ring in solution has a low probability.

The rates of disproportionation of chelate complexes are expected to show variations because of the differing strains of the differently sized chelate rings. The strain factor of a ring is in the order: seven-membered > six-membered ring[17] and the same order is reflected in the k values for the diols: butane-1,4-diol > propane-1,3-diol > butane-1,3-diol. Both propane-1,3-diol and butane-1,3-diol form a six-membered chelate ring. The lowest value of k for the butane-1,3-diol [k(propane-1,3-diol) > k(butane-1,3-diol)] is attributed to the greater stability of the chelate ring formed with this substrate.

Comparison of Entropies of Activation.—Hintz and Johnson[4] have suggested that differences in the entropies of activation for closely related reactions, calculated from second-order rate constants (= $k_{obs.}$/[Substrate]), reflect differences in the nature of the transition state. In the present study the entropies of activation have been calculated from k, the rate of disproportionation of the complex.

TABLE 2

Comparison of the activation parameters calculated from the rates of disproportionation of cerium(IV)–substrate complexes

Substrate	E/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	ΔG_{293}/ kJ mol^{-1}
Propane-1,3-diol	75.2	29.3	66.6
Butane-1,3-diol	66.9	−16.7	71.8
Butane-1,4-diol	75.2	29.3	66.6
Pentane-1,5-diol	125.4	192.3	69.0
Hexane-1,6-diol	117.0	171.4	66.8
3-Methoxybutan-1-ol	87.8	66.9	68.2

The small entropies of activation associated with the disproportionation of the complexes of propane-1,3-, butane-1,3-, and butane-1,4-diols (Table 2) are consistent with a more ordered chelated transition state. These substrates are believed to form chelated complexes. The association of much larger entropies of activation with the disproportionations of the complexes formed with pentane-1,5-diol, hexane-1,6-diol and 3-methoxybutan-1-ol, perhaps supports the idea that transition states containing unidentate ligands, and with relatively more disorder than their [Ce(substrate)]$^{4+}$ complex precursors, are being formed. Thus there is some reason to believe, at least in the present system, that the nature of the transition state is the same as that of the precursor complex. Further, the effects of solvation or desolvation on the activated states were not taken into account while seeking the above correlation between the entropy of activation and the nature of the activated state.

It is believed that whether the ligand in a complex formed between a diol and a metal ion is unidentate or chelated is dependent on the relative distance between the two hydroxyl groups and the size of the metal ion bridging the gap between these two groups. This assumption rationalises the formation of complexes of unidentate ligands in the oxidation of propane-1,3-, butane-1,3-, and butane-1,4-diols by V^{V},[18,19] and of chelated complexes in the oxidations of these substrates with Ce^{IV} in perchlorate and nitrate media.[20] The formation of complexes containing unidentate ligands in the oxidations of butane-1,4-, pentane-1,5-, and hexane-1,6-diols by aquamanganese(III) ions[21] is also rationalised because the crystallographic radius of Mn^{III} is intermediate between those of Ce^{IV} and V^{V}. However, the confirmation of this general view needs more work, which is in progress.

We thank the referees for their helpful discussions and suggestions, and the U.G.C., New Delhi, for support.

[6/277 *Received*, 9*th February*, 1976]

REFERENCES

[1] Part 2, Raj N. Mehrotra, *J.C.S. Dalton*, 1978, 681.
[2] F. R. Duke and H. A. Forist, *J. Amer. Chem. Soc.*, 1949, **71**, 2790.
[3] H. G. Offner and D. A. Skoog, *Analyt. Chem.*, 1965, **37**, 1018.
[4] H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, 1969, **32**, 556.
[5] J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1960, 2767.

[6] L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1969, **91**, 5060.

[7] W. S. Trahanovsky, J. R. Gilmore, and P. C. Heaton, *J. Org. Chem.*, 1973, **38**, 760.

[8] P. S. Sankhla and Raj N. Mehrotra, *Indian J. Chem.*, 1972, **10**, 1077; 1975, **13**, 904; 1976, **A14**, 663; *J. Inorg. Nuclear Chem.*, 1973, **35**, 891.

[9] I. Heilborn, A. H. Cook, H. M. Bunbury, and D. H. Hey, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, pp. 17, 754, 1696, 1775.

[10] S. Coffey, 'Rodd's Chemistry of Carbon Compounds,' ed. E. H. Rodd, Elsevier Publishing Co., 2nd edn., vol. I, p. 48.

[11] S. B. Hanna, S. A. Attiga, W. R. Carrol, and W. H. Web, *Z. Analyt. Chem.*, 1972, **260**, 371.

[12] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, 1951, **29**, 818.

[13] F. B. Baker, T. W. Newton, and M. Kahn, *J. Phys. Chem.*, 1960, **64**, 109.

[14] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1970, **66**, 679.

[15] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1971, **67**, 1086.

[16] A. Prakash, Ph.D. Thesis, University of Jodhpur, 1976.

[17] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 198.

[18] Raj N. Mehrotra, *J. Chem. Soc. (B)*, 1968, 1563.

[19] Raj N. Mehrotra, *J. Chem. Soc. (B)*, 1970, 1722.

[20] Ratan R. Nagori, Ph.D. Thesis, University of Jodhpur, 1977.

[21] Mahendra Mehta, Ph.D. Thesis, University of Jodhpur, 1977.