

Kinetics & Mechanism of Oxidation of Butane-1,3-diol by Ce(IV) Sulphate in Aqueous Sulphuric Acid Solution: Evidence for Ce(IV) Dimer

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The kinetics of oxidation of butane-1,3-diol by Ce(IV) in dil. H_2SO_4 indicates a fractional order dependence in the [diol]² consistent with the complex formation between Ce(IV) and diol prior to its rate limiting disproportionation. The linear dependence of the observed first order rate constant (k_1) on the inverse [Ce(IV)] indicates the presence of dimeric Ce(IV) and its participation in the reaction mechanism. The data also indicate that the association constant of the dimeric Ce(IV) is appreciable and its significance cannot be minimized in view of the dependence of the rate on the initial [Ce(IV)]. The diol is oxidized to crotonaldehyde via an intermediate free radical. The mechanism is discussed and the activation parameters at a given [Ce(IV)] are reported.

THE kinetics of oxidation of diols, with the exception of glycols by Ce(IV) sulphate has been reported earlier by us¹⁻³. These oxidations exhibited a first-order dependence in [diol]; the plot of observed first-order rate constant k_1 versus [diol] was linear and passed through the origin in each case. These oxidations were considered partly to proceed through Ce(IV)-diol complex formation and partly through the bimolecular mechanism. The present paper reports the necessary kinetics evidence for the formation of the intermediate complex and a different dependence, unlike the one reported in the oxidation of pentane-1,5-diol³, of k_1 on [Ce(IV)]. The differing dependence of k_1 on [Ce(IV)] is considered as a possible potential tool in distinguishing the nature of the intermediate complex formed in the oxidation of pentane-1,5- and butane-1,3-diols.

Materials and Methods

The cerium(IV)-sulphate (Fisher) was used as such. The stock Ce(IV) solution was prepared in Basynt's analar sulphuric acid. The acid strength in Ce(IV) solution was determined as described earlier¹⁻³.

The stock solution of butane-1,3-diol (Fluka, purum grade) was prepared by direct weighing of the sample. Other chemicals used were of either BDH or Sarabhai-Merck grade.

The reaction was followed over two half-lives (80%) and the usual first-order plots were linear throughout the range covered. The reaction mixtures were prepared so as to have [diol] in much excess over that of [Ce(IV)]. The slope values of the plots, wherever needed, were calculated by the least squares method. Other experimental details were similar to those reported earlier¹⁻³. The rate constants, reported here, are the average values

of two to three runs and agreed within 3% with the individual values obtained from identical runs.

Results and Discussion

Although the first-order plots were linear at all [Ce(IV)], the first-order rate constant k_1 with respect to Ce(IV) was not found to be independent of initial [Ce(IV)]. It rather decreased with the increase in [Ce(IV)] (Table 1).

There was no appreciable change in k_1 at different $[H_2SO_4]$ (Table 2), except for a very small retardation and acceleration in k_1 in solutions $<1.5M$ and $>1.5M$ sulphuric acid respectively.

The k_1 measured at different $[H^+]$ but constant ionic strength did not increase proportionately with the increase in [diol] (Table 3). The ionic strength was kept constant by using mixtures of

TABLE 1 — EFFECT OF VARYING [Ce(IV)] ON k_1

{[Butane-1,3-diol] = 0.3M; $[H_2SO_4]$ = 1.5M; temp. = 40°C}

$10^2[Ce(IV)]$ M	10^5k_1 sec ⁻¹	$10^2[Ce(IV)]$ M	10^5k_1 sec ⁻¹
0.25	3.90	2.0	1.95
0.50	2.78	2.5	1.90
1.0	2.22	—	—

TABLE 2 — DEPENDENCE OF THE RATE CONSTANT (k_1) ON VARYING INITIAL $[H_2SO_4]$

{[Ce(IV)] = 0.005M; [Butane-1,3-diol] = 0.3M; temp. = 40°C}

$[H_2SO_4]$ M	10^5k_1 sec ⁻¹	$[H_2SO_4]$ M	10^5k_1 sec ⁻¹
0.3	3.3	2.5	3.1
1.0	2.9	3.0	3.2
1.5	2.8	3.5	3.3
2.0	3.0	4.0	3.6

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TABLE 3 — DEPENDENCE OF RATE CONSTANT (k_1) ON [BUTANE-1,3-DIOL] AT VARYING $[H^+]$

{[Ce(IV)] = 0.005M; $[HSO_4^-]$ = 1.5M; temp. = 40°C}

[Butane-1,3-diol] M	$10^5 k_1$ (sec ⁻¹) at			
	$[H^+] = 0.8M$	1.0M	1.2M	1.5M
0.10	0.7	0.8	0.9	1.2
0.15	1.1	1.2	1.3	1.7
0.30	1.8	2.2	2.4	2.8
0.45	2.4	2.7	3.0	3.8
0.75	3.6	—	4.6	—
1.00	—	6.0	—	7.0

 TABLE 4 — EFFECT OF VARYING $[HSO_4^-]$ ON k_1 AT CONSTANT $[H^+]$

{[Ce(IV)] = 0.005M; [Butane-1,3-diol] = 0.3M; temp. = 40°C}

$[HSO_4^-]$ M	$10^5 k_1$ sec ⁻¹	$[HSO_4^-]$ M	$k_1 \times 10^6$ sec ⁻¹
0.8	4.6	1.2	3.4
1.0	3.8	1.5	2.8

 TABLE 5 — EFFECT OF IONIC STRENGTH ON OBSERVED RATE CONSTANT (k_1)

{[Ce(IV)] = 0.005M; [Butane-1,3-diol] = 0.3M; $[H^+] = 1.5M$
 $[H_2SO_4] = 1.5M$; temp. = 40°C}

$[NaClO_4]$ M	$10^5 k_1$ sec ⁻¹	$[NaClO_4]$ M	$10^5 k_1$ sec ⁻¹
0.0	2.8	0.3	2.4
0.1	2.6	0.5	2.3

 TABLE 6 — EFFECT OF TEMPERATURE ON RATE CONSTANT (k_1) AND ACTIVATION PARAMETERS

{[Ce(IV)] = 0.005M; [Butane-1,3-diol] = 0.45M;
 $[H_2SO_4] = 1.5M$ }

Temperature (°C)	$10^5 k_1$ sec ⁻¹	Temperature (°C)	$10^5 k_1$ sec ⁻¹
40	3.75	55	23.9
50	14.3	60	41.3

$\Delta E^\ddagger = 24.6 \pm 1.6$ kcal mole⁻¹, $\Delta S^\ddagger = -4 \pm 5$ cal deg⁻¹ mole⁻¹.

sulphuric acid and sodium hydrogen sulphate. The plots between $1/k_1$ versus $1/[\text{diol}]$ were linear (Fig. 1). The intercepts on the rate axis were independent of $[H^+]$.

The rate decreased with the increase in $[HSO_4^-]$ (Table 4) at constant $[H^+]$ which was kept constant by using mixtures of sulphuric and perchloric acids in such a way that the overall $[H_2SO_4]$ was always $> [HClO_4]$. It ensured the continuity of the Ce(IV) species in this mixture. The rate also decreased with the increase in ionic strength (Table 5), which was varied using sodium perchlorate. The values of rate constant (k_1) and the activation parameters are given in Table 6.

The kinetic evidence for the existence of the Ce(IV)-diol complex was indicated by Michaelis-

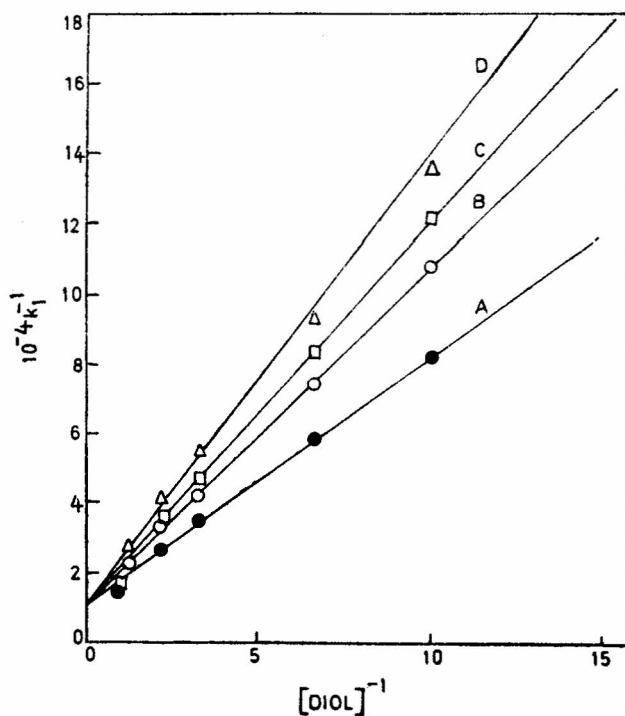


Fig. 1 — The plot between $1/k_1$ and $[\text{butane-1,3-diol}]^{-1}$ at 40° with $[\text{Ce(IV)}] = 0.005M$; $[HSO_4^-] = 1.5M$; and $[H^+] = (A) 1.5M$; (B) 1.2M; (C) 1M; (D) 0.8M

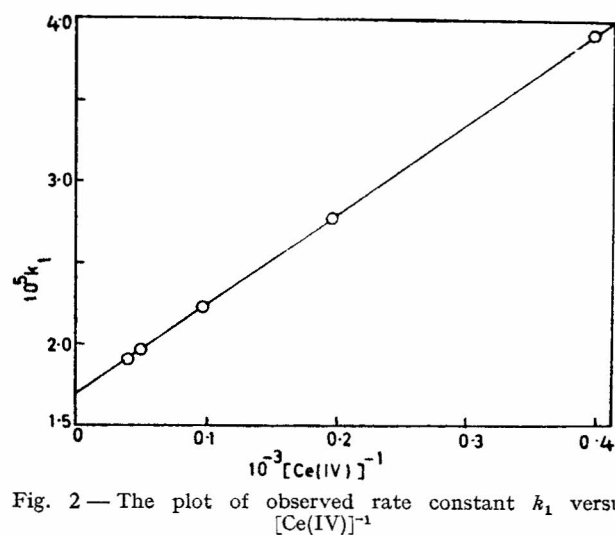


Fig. 2 — The plot of observed rate constant k_1 versus $[\text{Ce(IV)}]^{-1}$

Menten plots (Fig. 1). The assumption of the complex formation in the oxidation of propane-1,3- and butane-1,4-diols^{1,2} is thus justified and the deviation from Michaelis-Menten plot in these cases could be ascribed to the smaller or negligible value of the formation constant for Ce(IV)-diol complexes.

The data in Table 1 gives a linear plot between k_1 and $[\text{Ce(IV)}]^{-1}$ with a positive intercept on the rate axis (Fig. 2). This correlation between k_1 and $[\text{Ce(IV)}]$ is different from the one observed in the oxidation of pentane-1,5-diol³ where it was noted that the plot of $1/k_1$ versus $[\text{Ce(IV)}]$ was linear. This difference in the dependence of the

rate on [Ce(IV)] in the oxidation of butane-1,3- and pentane-1,5-diols could be ascribed to the reactivity or inactivity of some Ce(IV) species present in dil. H_2SO_4 solutions. We believe⁸ this species is dimeric Ce(IV).

Our efforts to establish the existence of dimeric Ce(IV) by spectrophotometric measurements remain inconclusive in the sense that the equation correlating the optical density with the various molar extinction coefficients corresponding to various Ce(IV) species and their concentrations is not easy to resolve. However, it should be noted that there is a shift in the maximum of absorption towards shorter wavelength with increasing $[H_2SO_4]$ (ref. 4). We have ourselves noted some kind of shift in λ_{max} with increasing [Ce(IV)] at a given [sulphuric acid].

Considering the well established existence of dimeric Ce(IV) in non-complexing perchlorate⁵ and complexing nitrate media⁶ and a trimeric Ce(IV) species in acetic acid⁷, we conclude that there should be no valid objection to such an assumption in sulphate medium, especially when the same is very much indicated and supported by the kinetics of the present reaction and oxidation of other diols such as propane-1,3-, butane-1,4-, hexane-1,6- and hexane-2,5-diols⁸. It may be added that the dependence of the rate on [Ce(IV)] in the oxidation of propane-1,3-, butane-1,4- and hexane-2,5-diols is similar to one observed in the present case, whereas in the oxidation of hexane-1,6-diol it is similar to that observed in the oxidation of pentane-1,5-diol³.

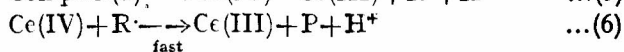
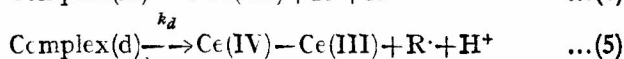
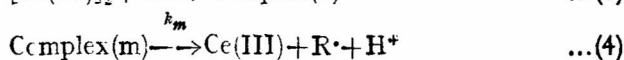
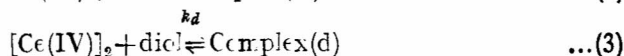
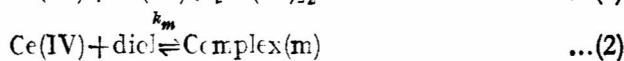
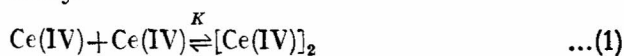
The differing dependence of k_1 on [Ce(IV)] could possibly be used as a potential tool in visualizing the nature of the intermediate complex formed between Ce(IV) and the diol. A chelate complex is indicated in the oxidation of butane-1,3-diol if one assumes the ability of the reactive Ce(IV) species including dimeric Ce(IV) in successfully bridging the gap between the two hydroxyl groups of butane-1,3-diol. An acyclic complex formation in the oxidation of pentane-1,5-diol is expected because of the inability of Ce(IV) species including dimeric species in bridging the increased gap between the two hydroxyl groups of the diol.

These conclusions based on experimental observations are however not in agreement with those of Young and Trahanovsky⁹ who believe in the formation of the acyclic complex between Ce(IV) and the diol. However, further support for our conclusions comes from a recently completed study on the oxidation of these diols by Ce(IV) in perchlorate medium¹⁰. The conclusions are in agreement with those of Hintz and Johnson¹¹ who favour the formation of a chelate complex. Also Duke *et al.*¹²⁻¹⁴ have reported the chelate formation between Ce(IV) and organic compounds having more than one hydroxyl groups.

It is interesting to note that the formation constant for dimeric Ce(IV) from monomeric Ce(IV) species has an appreciable value in nitrate⁶ (17 ± 2 at 30°), perchlorate^{5b} (16.2 at 25°) and 1.62×10^5 for the formation constant of trimeric Ce(IV) from monomeric Ce(IV) in acetic acid medium⁷. Thus it would not be erroneous to assume that in the present medium also the equilibrium constant for the equi-

librium between monomeric Ce(IV) and dimeric Ce(IV) species has an appreciable value.

Since it is not easy to identify which of the monomeric Ce(IV) species present in dilute sulphuric acid solutions¹⁵ form the dimeric Ce(IV) species, the following basic mechanism is proposed in view of the principal kinetic results obtained in the present study.



where the product P is crotonaldehyde, R is the

free radical $CH_3 \cdot CHO \cdot CH_2 \cdot \dot{C}HOH$, the formation of which is indicated by the polymerization of acrylonitrile added to the reaction mixture. There was no polymerization when the monomer was added to Ce(IV) solution in the absence of the diol. The formation of the dimer Ce(IV)-Ce(III) is again based on the existence of such dimeric species in the nitrate⁶ and perchlorate medium⁵. Blaustein and Gyde¹⁶ have examined the data of Sherill *et al.*¹⁶ and have concluded that Ce(III)-Ce(IV) dimers are present in perchloric acid medium.

The reactions (1)-(6) give the following rate Eq. (7)

$$\frac{-d[Ce(IV)]}{dt} = \frac{2(k_m K_m + k_d K_d K [Ce(IV)]) [Ce(IV)] [diol]}{(1 + K_m [diol]) + K [Ce(IV)] (1 + K_d [diol])} \quad \dots(7)$$

Now if it is assumed, as a measure of approximation, that $K [Ce(IV)] (1 + K_d [diol]) > (1 + K_m [diol])$ because of the appreciable value of K as stated earlier and K_d is expected to be $> K_m$, the Eq. (7) is reduced to Eq. (8).

$$\frac{-d[Ce(IV)]}{dt [Ce(IV)]} = k_1 = \frac{2(k_m K_m + k_d K_d K [Ce(IV)]) [diol]}{K [Ce(IV)] (1 + K_d [diol])} \quad \dots(8)$$

At a given [diol] the Eq. (8) could be expressed by Eq. (9)

$$k_1 = \frac{2k_m K_m [diol]}{K (1 + K_d [diol]) [Ce(IV)]} + \frac{2k_d K_d [diol]}{(1 + K_d [diol])} \quad \dots(9)$$

Thus Eq. (9) is consistent with the linear plot (Fig. 2) between k_1 and $[Ce(IV)]^{-1}$. Again, at a fixed [Ce(IV)], the Eq. (8) could be rearranged to give the Eq. (10) which is consistent with the linear plots between $1/k_1$ and $1/[diol]$ (Fig. 1).

$$\frac{1}{k_1} = \frac{K [Ce(IV)]}{2\{k_m K_m + k_d K_d K [Ce(IV)]\} [diol]} + \frac{K K_d [Ce(IV)]}{2\{k_m K_m + k_d K_d K [Ce(IV)]\}} \quad \dots(10)$$

It is thus seen that within the assumed approximations, the proposed mechanism and the rate equations derived therefrom are consistent with

the observed results. The existence of dimeric Ce(IV) species in sulphuric acid solutions seems likely and requires a careful reinvestigation of the equilibria between various Ce(IV) species in this acid medium. It should be pointed out that without the assumption of dimeric Ce(IV) and its formation of a chelate complex with butane-1,3-diol, it is difficult to explain the differing dependence of the rate on the initial [Ce(IV)] in the oxidation of pentane-1,5- and butane-1,3-diols.

Stoichiometry — The reaction product is repeatedly extracted with ether from the reaction mixtures having different [diol] and a known [Ce(IV)]. The extracted product (80%) formed 2,4-DNP derivative, m.p. 187-88°, identical with the 2,4-DNP derivative¹⁷ of crotonaldehyde. In a separate experiment the absence of HCHO in the extracted product is established with chromotropic acid¹⁸.

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