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Oxidation of butane-1,3-, butane-1,4-, 2-methyl pentane-2,4- and 3-methyl pentane-2,4-diols by cerium(IV) in aqueous acidic medium catalyzed by rhodium(III)

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Abstract The oxidation kinetics of butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol with cerium(IV) catalyzed by rhodium(III) in aqueous sulfuric acid showed a peculiar nature with respect to the variation in oxidant concentration, such that the reaction follows first-order kinetics in [Ce(IV)] at low [Ce(IV)] and then reaches a maximum with increasing [Ce(IV)], beyond which further increase in the oxidant concentration retards the rate. The rate shows direct proportionality with respect to [diol] at low concentrations, becoming independent of [diol] at higher concentrations. The rate is first order in catalyst. Retarding effects are observed when [H^+] and [Ce(III)] are increased, while [Cl^-] and hence ionic strength have a positive effect on the rate. Spectroscopic studies confirmed that the primary hydroxyl groups in butane-1,3-diol and butane-1,4-diol resulted in the formation of 3-hydroxy butanal and 4-hydroxy butanal, respectively. In the case of oxidation of the secondary hydroxyl groups in 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, the products of oxidation were 4-hydroxy-4-methyl pentan-2-one and 4-hydroxy-3-methyl pentan-2-one, respectively.

Introduction

The uncatalyzed oxidation of aliphatic compounds by cerium(IV) has been frequently reported from the kinetic point of view. However, catalysis of these oxidations by transition metal ions has been less well studied. We have reported a kinetic study of the catalyzed oxidation of various aliphatic organic compounds such as cyclic ketones by cerium(IV) [1]. We have also reported on the catalytic activity of rhodium(III) in the oxidation of cyclic ketones by alkaline hexacyanoferrate(III), in which it was observed that the catalytically active species of rhodium(III) depends on the pH of the medium [2, 3]. Rhodium(III) proved to be more effective than iridium(III) and palladium(II) in catalyzing organic oxidations with hydrogen peroxide from a synthetic point of view [4]. In the present work, we have studied the oxidation of four diols, namely butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol by cerium(IV) sulfate in aqueous acidic medium catalyzed by rhodium(III) chloride. These diols were chosen in order to investigate the potential of rhodium(III) in catalyzing the oxidation of non-vicinal diols; to confirm whether a C–H or C–C bond is broken during the oxidation; to see whether the methyl group instead of hydrogen has any effect on the oxidation of the hydroxyl group; and to confirm whether the secondary or tertiary alcoholic group is oxidized under these conditions.

Results and discussion

For all the four diols, initially, the first-order rate constant k values are constant but decrease at higher [Ce(IV)] (Table 1). The rate values ($-dc/dt$) initially increase with increasing [Ce(IV)] and then reach a maximum beyond which further increase in [Ce(IV)] decreases the rate (Fig. 1). Plots of rate versus [diol] for all substrates gave a straight line passing through the origin at low [diol], but at higher organic substrate concentrations, the trend of the

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Table 1 Effect of variation in [Cerium(IV)] and [Diols] on the rate at 32 °C

$[Ce^{IV}] \times 10^4$ M	$k \times 10^2$ min^{-1}				[Diol] $\times 10^3$ M	k^* (M^{-1} min^{-1})			
	A	B	C	D		A	B	C	D
2.00	2.80	0.50	0.50	0.32	2.00	4.20	0.96	0.86	0.86
3.00	2.67	0.47	0.57	0.33	2.50	4.32	0.96	0.80	–
4.00	2.92	0.40	0.50	0.36	3.00	4.26	0.89	0.85	0.89
5.00	2.84	0.46	0.50	0.33	4.00	4.16	0.83	0.80	0.90
6.00	2.78	0.45	0.50	0.33	5.00	4.33	0.72	0.73	0.80
7.00	2.14	0.47	0.31	0.21	6.00	4.44	0.66	0.71	0.83
8.00	1.66	0.31	0.25	0.17	8.00	4.00	0.55	0.67	0.81
10.0	1.00	0.14	0.15	0.13	10.0	3.50	0.50	0.64	0.80

A-butane-1,3-diol; B-butane-1,4-diol; C-2-methyl pentane-2,4-diol; D-3-methyl pentane-2,4-diol

Variation in cerium(IV) sulfate concentrations**:** [Diol] $\times 10^{-3}$ M = 5.0 (A to D); [H_2SO_4] $\times$ M = 0.50 (A, D), 1.00 (B), 0.35 (C); [$RhCl_3$] $\times 10^{-5}$ M = 2.39 (A, B), 1.40 (C, D)

Variation in diol concentrations: [$Ce(SO_4)_2$] $\times 10^{-4}$ = 5.00 M (A to D), [H_2SO_4] $\times$ M = 0.50 (A), 1.00 (B), 0.20 (C), 0.25 (D). [$RhCl_3$] $\times 10^{-5}$ M = 2.39 (A, B), 1.40 (C and D)

$k^* = -dc/dt/[Ce(IV)][diol]$

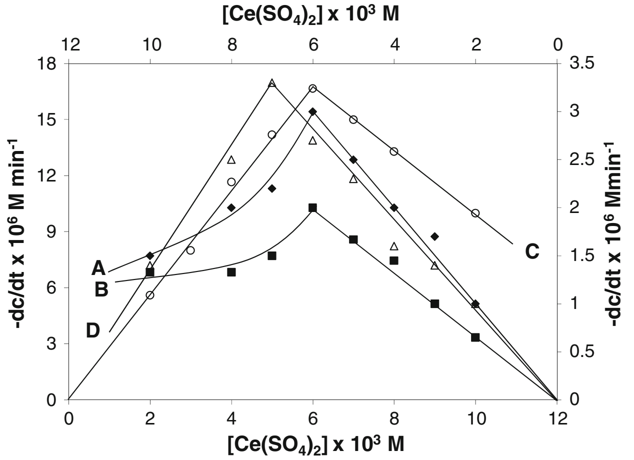


Fig. 1 Effect of variation in [$Ce(SO_4)_2$] on the rate at 32 °C. [Diol] $\times 10^{-3}$ M = 5.0 (*A–D*); [H_2SO_4] $\times$ M = 0.50 (*A*, *D*), 1.00 (*B*), 0.35 (*C*); [$RhCl_3$] $\times 10^{-5}$ M = 2.39 (*A*, *B*), 1.40 (*C*, *D*). A-butane-1,3-diol; B-butane-1,4-diol; C-2-methyl pentane-2,4-diol; D-3-methyl pentane-2,4-diol

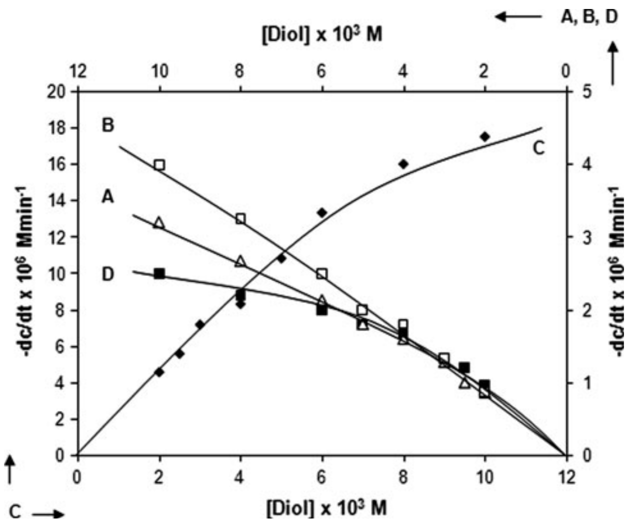


Fig. 2 Effect of variation in [Diol] on the rate at 32 °C. [$Ce(SO_4)_2$] $\times 10^{-4}$ = 5.00 M (*A–D*), [H_2SO_4] $\times$ M = 0.50 (*A*), 1.00 (*B*), 0.20 (*C*), 0.25 (*D*). [$RhCl_3$] $\times 10^{-5}$ M = 2.39 (*A*, *B*), 1.40 (*C* and *D*). A-butane-1,3-diol; B-butane-1,4-diol; C-2-methyl pentane-2,4-diol; D-3-methyl pentane-2,4-diol

line to become parallel to the x-axis becomes apparent (Fig. 2). This is confirmed by the trend in the second-order rate constant k^* values (Table 1). The rate increases proportionally with increasing concentrations of rhodium(III) for all substrates. The second-order rate constant k^* values were determined as 1.16 ± 0.13, 1.67 ± 0.05, 1.65 ± 0.25 and 2.22 ± 0.23 for butane-1, 3-diol, butane-1, 4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively (Table 2). Straight lines passing through the origin were obtained on plotting $-dc/dt$ versus [$RhCl_3$], indicating first-order kinetics in [$RhCl_3$]. This was further confirmed from plots of log ($-dc/dt$) versus log [$RhCl_3$], which gave slopes of 0.96, 0.98, 0.97 and 0.98 for butane-1, 3-diol, butane-1, 4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively. The rate of reaction decreases with increasing concentrations of sulfuric acid (Table 2) and also on addition of $Ce_2(SO_4)_3$ to the reaction mixture (Table 3). On plotting rate values against [H_2SO_4] or [$Ce_2(SO_4)_3$], an initial sharp fall in the rate becomes less prominent at higher concentrations of both acid and cerium(III). These observations suggest that the reduction of cerium(IV) to cerium(III) along with the removal of H^+ takes place before the rate determining step in the mechanism. Where the dielectric constant of the medium was increased by addition of a standard solution of potassium chloride, the rate was found to increase (Table 3).

Table 2 Effect of variation in [$RhCl_3$] and [H^+] on the rate at 32 °C

[$RhCl_3$] x 10^5 M	$k^* \times 10^{-2}$ (M^{-1} min^{-1})				[H_2SO_4] × M	$-dc/dt \times 10^6$ (M min^{-1})			
	A	B	C	D		A	B	C	D
0.47	1.44	–	–	2.68	0.30	–	8.28	19.80	6.66
0.75	–	1.60	1.78	–	0.50	–	3.96	13.20	4.98
0.95	1.17	1.68	2.09	2.09	0.60	–	–	12.48	–
1.70	–	1.76	–	–	0.70	2.49	3.96	–	3.00
1.90	1.05	–	1.40	2.11	0.80	–	–	–	–
2.39	1.11	1.67	1.46	2.09	1.00	1.99	2.82	9.00	2.49
3.10	1.13	1.61	1.61	2.15	1.20	–	2.46	–	–
3.58	1.11	1.68	1.58	2.23	1.30	–	–	–	1.26
4.70	–	1.70	–	–	1.50	–	1.50	8.28	0.71
–	–	–	–	–	1.60	1.65	–	–	–
–	–	–	–	–	1.75	1.39	–	–	–
–	–	–	–	–	1.85	1.39	–	–	–
–	–	–	–	–	2.00	1.29	–	–	–

A-butane-1,3-diol; B-butane-1,4-diol; C-2-methyl pentane-2,4-diol; D-3-methyl pentane-2,4-diol

Variation in $RhCl_3$ concentrations: [$Ce(SO_4)_2$] × 10^{-4} M = 5.00 (A to D); [Diol] × 10^{-3} M = 5.0 (A to D); [H_2SO_4] × M = 0.30 (A), 1.0 M (B), 0.30 (C), 0.50 (D)

Variation in H_2SO_4 concentrations: [$Ce(SO_4)_2$] × 10^{-4} M = 5.00 (A to B); [Diol] × 10^{-3} M = 5.0 (A to B); [$RhCl_3$] × 10^{-5} M = 2.39 (A, B), 1.40 (C, D)

$k^* = -dc/dt/[Ce(IV)][diol]$

Table 3 Effect of variation in [Ce^{III}] and [Cl^-] on the rate at 32 °C

[$Ce_2(SO_4)_3$] × 10^4 M	$-dc/dt \times 10^6$ (M min^{-1})				[KCl] M	$-dc/dt \times 10^6$ (M min^{-1})			
	A	B	C	D		A	B	C	D
2.00	1.67	1.17	8.33	1.50	0.70	2.75	1.67	6.25	0.71
2.50	1.00	1.00	7.50	–	0.85	4.00	3.00	7.50	–
3.50	1.00	0.75	7.50	1.33	1.00	4.30	4.38	7.50	1.00
5.00	0.75	0.67	6.67	1.00	1.15	–	5.00	8.30	–
7.00	–	0.44	–	–	1.30	4.50	5.00	10.00	1.50
7.50	0.60	–	5.00	0.71	1.50	5.00	6.25	12.50	1.75
10.00	0.33	0.33	4.00	–	–	–	–	–	–

A-butane-1,3-diol; B-butane-1,4-diol; C-2-methyl pentane-2,4-diol; D-3-methyl pentane-2,4-diol

Variation in $Ce_2(SO_4)_3$ concentrations: [$Ce(SO_4)_2$] × 10^{-4} M = 5.00 (A to D); [Diol] × 10^{-3} M = 5.0 (A to B); [$RhCl_3$] × 10^{-5} M = 2.39 (A, B), 1.40 (C and D); [H_2SO_4] × M = 0.30 (A); 0.50 (B), 0.30 (C), 0.70 (D)

Variation in KCl concentrations: A-[$Ce(SO_4)_2$] × 10^{-4} M = 5.00 (A to D); [Diol] × 10^{-3} M = 5.0 (A to D); [$RhCl_3$] × 10^{-5} M = 2.39 (A, B), 1.40 (C and D); [H_2SO_4] × M = 1.00 (A, B), 0.30 M (C, D)

Reactive species of rhodium(III)

The rhodium(III) aqua ion $[Rh(H_2O)_6]^{3+}$ is quite stable, and exchange between the inner sphere H_2O protons and bulk water is highly pH dependent [5]. It is also known that this species is extensively hydrolyzed in water [6]. Between the species $RhCl_6^{3-}$, which is obtained in excess hydrochloric acid, and $[Rh(H_2O)_6]^{3+}$, which is formed in boiling aqueous solutions of rhodium(III) chloride, there are several intermediate species, as follows;

$$Rh(H_2O)_6^{3+} + OH^- \rightleftharpoons Rh(OH)(H_2O)_5^{2+} + H_2O$$

$$Rh(OH)_2(H_2O)_4^{+} + OH^- \rightleftharpoons Rh(OH)_3(H_2O)_3 + H_2O$$

$$Rh(OH)_3(H_2O)_3 + Cl^- \rightleftharpoons RhCl(OH_2)(H_2O)_3 + OH^-$$

$$RhCl_2(OH)(H_2O)_3 + Cl^- \rightleftharpoons RhCl_3(H_2O)_3 + OH^-$$

Fritz [7] identified only one complex, $[RhCl_5(H_2O)]^{2-}$, in 40% hydrochloric acid. On diluting the solution, after 24 h, $[RhCl_4(H_2O)_2]^-$ and $[RhCl_3(OH)(H_2O)_2]^-$ were also observed. Capillary zone electrolysis has revealed the existence of three species of rhodium, namely $[RhCl_4(H_2O)_2]^-$, $[RhCl_3(H_2O)_3]$ and $[RhCl_2(H_2O)_4]^+$, on changing the pH of the solution from 1.0 to 3.50 with hydrochloric acid, along with a decrease in the cationic form and increase in the uncharged complex with the formation of two negatively charged chlorocomplexes [8]. The present study was carried out in acidic medium, and the positive effect of chloride ions on the rate indicates that both $[RhCl_4(H_2O)_2]^-$ and $[RhCl_5(H_2O)]^{2-}$ may be present in the reaction mixture. The absence of saturation kinetics even at high concentrations of catalyst indicates that the catalyst is not forming a complex with the organic substrate. The positive effect of chloride ions on the rate suggests that $[RhCl_4(H_2O)_2]^-$converts into $[RhCl_5(H_2O)]^{2-}$, which ultimately catalyzes the reaction.

Oxidative cleavage of diols and related compounds

Many oxidants readily cleave 1,2-glycols [9, 10]. Cleavage of 1,2-glycols by lead(IV) probably involves the formation of a bidentate metal glycol complex which then breaks down to products via a two-electron process, which gets support from the failure to trap radical intermediates and the fact that cis diols and threo diols are more readily oxidized than the trans diols and erythro diols, respectively [11]. On the other hand, cleavage of 1,2-glycols by cerium(IV) seems to involve coordination of only one hydroxy group followed by a one-electron oxidation to give an intermediate radical. This is supported by the similar rates of oxidation of 1,2-glycols and their monomethyl ethers and also by trapping experiments [10, 12]. Moreover, based on orbital symmetry considerations, the former cyclic mechanism is a forbidden process for one-electron oxidants such as cerium(IV) [13]. The cleavage of 1,2-glycols by cerium(IV) is just a special case of the general oxidative cleavage of alcohols by cerium(IV) [14, 15]. The same mechanism seems to operate for all these oxidative cleavages, and as expected, the α-hydroxy radicals are sufficiently stable that alcohols which can form them (i.e., 1,2-glycols) undergo rapid cleavage. The polar nature of the transition state [14] also favors the cleavage of α-hydroxy radicals. In the uncatalyzed oxidation of diols, in which hydroxyl groups are not at the vicinal position, only the corresponding hydroxy aldehydes were obtained as oxidation products [16]. It has been suggested that oxidation of diols is followed by the scission of a C–H bond instead of C–C bond [17], which has been reported previously in the case of glycols [18].

Reactive species of cerium(IV) sulfate

Cerium(IV) forms a number of complexes in sulfuric acid solution. Hardwick and Robertson [19] have reported the following equilibria in sulfuric acid solutions of 2 M ionic strength;

$$Ce^{4+} + HSO_4^- \overset{K_1}{\rightleftharpoons} CeSO_4^{2+} + H^+ \tag{1}$$

$$CeSO_4^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \tag{2}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+ \tag{3}$$

The equilibrium constants K_1, K_2, and K_3 for the above steps are 3,500, 200 and 20, respectively, at 25 °C. Under our experimental conditions, we deduce that total cerium(IV) is mainly present as $Ce(SO_4)_2$. The concentration of Ce^{4+} species in a solution having $[Ce(IV)] = 0.00125$ M and $[H_2SO_4] = 1.0$ M may be calculated from Eq. 4, which has been derived from Eqs. 1 and 2. The value was found to be 1.0×10^{-9} M.

$$[Ce(IV)]_{Total} = \left[Ce^{4+}\right]\left(1+K_1\left[HSO_4^-\right]/[H^+]+K_1K_2\left[HSO_4^-\right]^2/[H^+]^2\right) \tag{4}$$

The range of concentration of acid in which the present study was carried out and the steep fall in rate with increasing concentration of sulfuric acid indicates that the concentration of other species would be negligible. Thus, $Ce(SO_4)_2$ has been taken as the reactive species of Ce^{IV} in aqueous sulfuric acid medium, as considered by other workers also [17].

Mechanism

Cerium(IV) forms a complex with the organic substrate, which then decomposes to a free radical. Transfer of the electron of the radical to the catalyst initiates breaking of the C–H bond, resulting in the formation of the organic product plus rhodium(II). Rhodium(II) is quickly oxidized back to rhodium(III) by cerium(IV).

According to the rate determining step of Scheme 1, the rate in terms of $[Ce^{IV}]$ is given as

$$-\frac{d[Ce^{IV}]}{dt} = k[C] \tag{5}$$

where [C] is concentration of the complex. The total concentration of catalyst in the reaction mixture may be given as

$$[Rh^{III}]_T = [RhCl_4(H_2O)_2]^- + [RhCl_5(H_2O)]^{2-} + [C] \tag{6}$$

where $[Rh^{III}]_T$ is the total concentration of the catalyst. The concentrations of $[RhCl_4(H_2O)_2]^-$, $[S^{\cdot}]$ and $[RhCl_5(H_2O)]^{2-}$ calculated from Scheme 1 may be given as

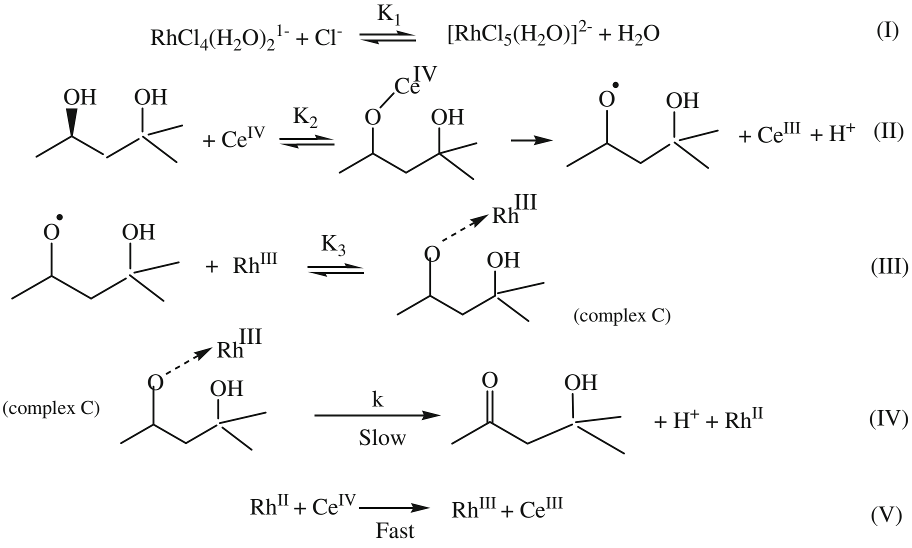
$$[RhCl_4(H_2O)_2^-] = [RhCl_5(H_2O)^{2-}][H_2O]/K_1[C] \tag{7}$$

$$[S^{\cdot}] = K_2[S][Ce^{IV}]/[Ce^{III}][H^+] \tag{8}$$

$$[RHCl_5(H_2O)^{2-}] = [C]/K_3[S^{\cdot}] \tag{9}$$

Substituting the value of $[S^{\cdot}]$ from Eq. 8 into Eq. 9,

Scheme 1 Probable oxidation path for 2-methyl pentane-2,4-diol



$$[RhCl_5(H_2O)^{2-}=\frac{[C][Ce^{III}][H^+]}{K_2K_3[S][Ce^{IV}]} \tag{10}$$

Substituting the values of $[RhCl_4(H_2O)_2^-]$ from Eq. 7 and $[RhCl_5(H_2O)^{2-}]$ from Eq. 9 into Eq. 6, the total concentration of catalyst in terms of [C] may be given as

$$[Rh(III)]_T=\frac{[C][H_2O][Ce^{III}][H^+]}{K_1K_2K_3[Cl^-][S][Ce^{IV}]}+\frac{[C][Ce^{III}][H^+]}{K_2K_3[S][Ce^{IV}]}+[C] \tag{11}$$

From this equation, the concentration of complex C comes out to be

$$[C]=\frac{K_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]\{[H_2O]+K_1[Cl^-]\}+K_1K_2K_3[S][Ce^{IV}][Cl^-]} \tag{12}$$

Now, on putting the concentration of the complex C as obtained from Eq. 12 into Eq. 5, the rate in terms of concentration of cerium(IV) may be given by Eq. 13. This equation includes a factor of 2 because two moles of oxidant are consumed to regenerate the catalyst in its original state, thus

$$-\frac{d[Ce^{IV}]}{dt}=\frac{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]\{[H_2O]+K_1[Cl^-]+K_1K_2K_3[S][Ce^{IV}][Cl^-]\}} \tag{13}$$

As the study was carried out in aqueous medium, the inequality $[H_2O] \gg K_1[Cl^-]$ may be considered valid and we get

$$-\frac{d[Ce^{IV}]}{dt}=\frac{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]+K_1K_2K_3[S][Ce^{IV}][Cl^-]} \tag{14}$$

At low concentrations of oxidant and the organic substrate, the inequality $[Ce^{III}][H^+] \gg K_1K_2K_3[S][Ce^{IV}][Cl^-]$ is valid and the rate law Eq. 14 becomes

$$-\frac{d[Ce^{IV}]}{dt}=\frac{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]} \tag{15}$$

This rate law explains the nature shown by all the reactants at their low concentrations, i.e., first-order kinetics with respect to oxidant, organic substrate, catalyst and the chloride ions. The retarding effects of cerium(III) and H^+ are also explained by this equation. At higher concentrations of oxidant and organic substrate, the reverse inequality $[Ce^{III}][H^+] \ll K_1K_2K_3[S][Ce^{IV}][Cl^-]$ becomes valid, and Eq. 14 may be written as

$$-\frac{d[Ce^{IV}]}{dt}=2k[Rh^{III}]_T \tag{16}$$

Equation 16 explains the observed first-order kinetics with respect to catalyst over a very wide range of concentrations. This equation also predicts that at higher concentrations of H^+ or cerium(III), the rate becomes independent of concentration. However, contrary to the experimental findings, according to Eq. 16, the rate with respect to both oxidant and chloride should also become independent of concentration at higher concentrations. Here, it is important to note that the effect of chloride on the rate was studied by adding these ions externally in the form of a solution of potassium chloride. Thus, the effect of further increase in chloride concentration could not be studied because the reaction becomes too fast to be studied conveniently. It may be possible that had the study been conducted at still higher chloride concentrations, the rate would have become independent of $[Cl^-]$. Further, the effect of the oxidant concentration is somewhat surprising because at higher concentrations instead of showing zero-order kinetics, the rate starts decreasing. It is interesting to note that the decrease in rate starts only when the concentration of oxidant exceeds 6.0×10^{-4} M in all the cases. It is possible that the decrease may be due to formation of some dimeric species of Ce(IV) in the reaction mixture. Formation of dimeric species of Ce(IV) has been reported by a number of workers in sulfuric, nitric [16, 20] and perchloric acids [21], while the existence of a trimeric cerium species has been reported in acetic acid medium [22]. In a number of studies, it has been reported that the first-order rate constant decreases with increasing cerium(IV) concentrations due to the formation of dimeric species [23–25]. The retarding trend shown by the oxidant at higher concentrations may also be due to the formation of a complex between the oxidant and sulfuric acid, according to the following equilibria;

$$Ce(SO_4)_2 + HSO_4^- \overset{K'}{\rightleftharpoons} HCe(SO_4)_3^- \qquad (17)$$

$$HCe(SO_4)_3^- + HSO_4^- \overset{K''}{\rightleftharpoons} H_2Ce(SO_4)_4^{2-} \qquad (18)$$

$$Ce(SO_4)_2 = [H_2Ce(SO_4)_4]^{2-}/[HSO_4^-]^2 \qquad (19)$$

$[H_2Ce(SO_4)_4]^{2-}$, a well-known unreactive species of cerium(IV) sulfate in sulfuric acid medium [26, 27], would retard the rate as given in Eq. 19. Similar behavior has been reported in the oxidation of hydrocarbons by cerium(IV) [28].

Further verification of the final rate law Eq. 14 may be given by rewriting the equation as

$$\frac{1}{-d[Ce^{IV}]/dt} = \frac{[Ce^{III}][H^+]}{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T} + \frac{1}{2k[Rh^{III}]_T} \qquad (20)$$

From this equation, values of k calculated from the intercepts of the graphs of 1/rate versus 1/[S] and $[H^+]$ were obtained as 38.02 (±0.04) and 20.90 (±0.00); 90.90 (±0.02) and 93.45 (±0.09); 27.77 (±0.12) and 24.63 (±0.10); 25.51 (±0.07) and 10.20 (±0.00) for butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively. Similarly, the values of $kK_1K_2K_3$ from the slopes of the graphs between 1/rate versus 1/[S] and $[H^+]$ were calculated as 6.27 (±0.07) and 6.15 (±0.06); 4.74 (±0.31) and 5.03 (±0.00); 4.58 (±0.10) and 4.16 (±0.03); 5.81 (±0.02) and 5.71 (±0.11) for butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively. Since the rates were measured at the beginning of the reaction, the concentration of the product cerium(III) at the point where the rates were measured will be negligible. Similarly, in the absence of externally added chloride, the concentration of chloride will be only due to the traces of catalyst present in the reaction mixture (in the range of 10^{-5} M) and this may also be ignored while calculating the rate constants. The kinetic measurements were carried out at four temperatures. The values of activation energies 18.30 (±0.03), 14.82 (±0.05), 11.44 (±0.44) and 20.52 (±0.01) (kJ mol^{-1}), calculated with the help of the Arrhenius plots, were used to calculate entropy of activation and free energy of activation values which were found to be −44.08, −44.51, −45.03 and −43.86 (JK^{-1} mol^{-1}); and 31.74, 28.39, 25.13 and 33.90 for butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively.

Experimental

Cerium(IV) sulfate, diols (CDH), sulfuric acid, acetic acid, ferroin (Merck) and cerium(III) sulfate (Fluka) were used as supplied by preparing their solutions in double distilled water. The concentration of rhodium(III) chloride (Johnson Matthay) was 4.78×10^{-3} M, which was prepared by dissolving the sample in a minimum amount of AR HCl (5.0×10^{-2} M). Ferrous ammonium sulfate solution was standardized against a standard solution of potassium dichromate (Merck). Cerium(IV) sulfate was prepared by dissolving the sample in 17.0 N sulfuric acid and was standardized with standard ferrous ammonium sulfate. All other chemicals used were either AR or chemically pure substances. The progress of the reaction was measured (constant temperature ± 0.1 °C) at different time intervals by transferring aliquots to a fixed amount of ferrous ammonium sulfate solution (in slight excess to cerium (IV) sulfate initially taken) and estimating the remaining ferrous ammonium sulfate, with standard cerium(IV) sulfate solution using ferroin as indicator. In this way, the remaining amount of ferrous ammonium sulfate directly corresponds to the amount of cerium(IV) consumed in the reaction mixture. In all kinetic runs, diol concentration was kept in excess.

Determination of kinetics

In all the kinetic runs, [diol] ≫ [oxidant] as per Ostwald's isolation method, and thus, the calculated orders are given with respect to oxidant concentrations. In all the cases, the rate values ($-dc/dt$) were calculated at a fixed initial concentration of oxidant except in the case of oxidant variation, where the rate values were calculated at a fixed initial time from the individual plots. Rate values ($-dc/dt$), obtained from the initial slopes of individual plots of the residual concentrations of cerium(IV) at various time intervals, were finally plotted against the concentration of the particular reactant for which the order of the reaction was to be obtained. Orders, with respect to various reactants, were confirmed by plotting log (a–x) versus time (oxidant variation), by plotting $-dc/dt$ values versus concentration of the reactant, by calculating the slope of the double logarithmic graphs of rate versus concentration and by calculating the rate constant for concentration (catalyst variation). The effects of change of the concentration of Ce(III) and Cl^- on the reaction velocity were studied by external addition of these ions. The tables and figures give the initial concentrations of the reactants. Studies could not be made at constant ionic strength, due to large volumes of KCl required to keep the ionic strength constant. However, the effect of change of ionic strength on the rate was studied separately using a standard solution of KCl.

Product study and stoichiometry

Separation of the products to check whether the system can be used for synthetic purposes and stoichiometry of the reaction were studied by taking cerium(IV) sulfate in large excess compared to the organic substrate in different ratios. These reaction mixtures were kept overnight at room temperature. After completion of the reaction, the solution was extracted with diethyl ether (3 × 25 mL). After evaporating the solvent, the hydrazone of the organic product was prepared by standard methods [29]. Yellowish-red precipitates of the corresponding 2,4-dinitrophenyl hydrazones of 3-hydroxy butanal, 4-hydroxy butanal, 4-hydroxy-4-methyl pentan-2-one and 4-hydroxy-3-methyl pentan-2-one were dried and weighed, giving 22 and 18% yields of corresponding hydroxy ketones. The final oxidation products were confirmed by spot tests [30], chromatography [31] and spectroscopy (Supplementary Material 1 to 4). A broad $C_{O\text{–}H\ str}$ was observed at 3,550–3,200 cm^{-1}, indicating associated O–H due to hydrogen bonding, while hydrogen bonded carboxyl peaks ($\upsilon_{C=O\ str}$. peaks at 1,631, 1,634, 1,632 and 1,631 Cm^{-1} [32]. The $\upsilon_{C\text{–}Ostr}$. bands were at 1,197, 1,193, 1,200 and 1,202 Cm^{-1}, while $\upsilon_{\text{-}CH3str}$. (C–H asymmetric and symmetric) were observed at 1,343, 1,350; 1,348, 1,382; 1,348, 1,387 and 1,343, 1,383 for butane-1,3-diol, butane-1,4-diol, 2-methyl pentane-2,4-diol and 3-methyl pentane-2,4-diol, respectively. The stoichiometry of the reaction as determined by estimating the unconsumed cerium(IV) in the reaction mixture after complete oxidation of the calculated quantity of the organic substrate may be given by Eq. 21 where R = H or Me;

$$\begin{aligned}&\mathrm{MeCH(OH)CH(R)CR(OH)Me + 2Ce^{IV}}\\&\quad\rightarrow \mathrm{MeCOCHRCR(OH)Me + 2Ce^{III} + 2H^+}\end{aligned} \tag{21}$$

Conclusion

In the rhodium(III)-catalyzed oxidation of non-vicinal diols, scission of a C–H bond instead of a C–C bond takes place, as in the case of their uncatalyzed oxidations. The corresponding hydroxy ketone is found to be the oxidation product. This is not the case in vicinal diols where the C–C bond is broken [33]. The present study also shows that rhodium(III) chloride which is a sluggish catalyst in alkaline medium can act as an efficient catalyst in acidic medium.

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