Oxidation of Vicinal Diols by Cerium(IV) in Aqueous Acidic Media Catalyzed by Rhodium(III)

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Abstract: Potential of rhodium(III) chloride in catalyzing, in aqueous sulfuric acid medium, the oxidation of vicinal diols, and the kinetics of reaction of cerium(IV) with propane-1,2-diol and butane-2,3-diol catalyzed by rhodium(III) chloride was investigated. Data show that the reactions follow first order kinetics with respect to low cerium(IV) for lower concentrations, but a further increase in the oxidant concentration retards the reaction velocity. The reaction rate shows direct proportionality with respect to low concentrations of diol, which tends to become zero order at higher concentrations of the organic substrate. The Rate is first order in catalyst. Increase in the concentrations of hydrogen and cerium(III) ions show retarding effects while increase in chloride ion concentration and in turn ionic strength of the medium has a positive effect on the rate. Stoichiometry and spectral studies confirmed the formation of one molecule each of formaldehyde and acetaldehyde and two molecules of acetaldehyde as the products of oxidation in case of propane-1,2-diol and butane-2,3-diol respectively. Thermodynamic parameters like enthalpy of activation, free energy of activation and entropy values were calculated and it was found that the formation of activated complex in the case of butane-2,3-diol was easy compared to that in the case of propane-1,2-diol.

Keywords: Vicinal diols, Rhodium(III) chloride, Cerium(IV) sulfate, Aliphatic aldehydes.

1. INTRODUCTION

Cerium(IV) oxidation of aromatic compounds in the presence and absence of metal ions has been frequently reported from the synthetic point of view [1], but these oxidations have not received much attention from the kinetic point of view, when in the presence of catalytic transition metal ions. Cerium(IV) has been reported to oxidize various aromatic compounds having different functional groups, but these oxidations have been studied mainly from the synthetic point of view. Kinetic study of the catalyzed oxidation of various aliphatic organic compounds by cerium(IV) like alcohols and ketones [2-5] has been reported by us. We have also reported the oxidation of cyclic ketones by alkaline hexacyanoferrate(III) catalyzed by rhodium(III) chloride, in which it was observed that the catalytically active species of rhodium(III) depends on the pH of the medium [6,7]. We have also compared the catalytic activity of rhodium(III) chloride with iridium(III) and palladium(II) in the oxidation of various organic compounds with hydrogen peroxide from the synthetic point of view and it was observed that rhodium(III) is quite effective in catalyzing the such as organic oxidations [8]. To find out the potential of rhodium(III) chloride in catalyzing the oxidation of vicinal diols with cerium(IV) sulfate, in aqueous sulfuric acid medium, and to confirm whether scission of C-H takes place or it is the C-C bond which is broken during the course of oxidation, we have studied the oxidation of two vicinal diols viz. propane-1,2-diol and butane-2,3-diol.

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2. EXPERIMENTAL

2.1. Materials and Methodology

Cerium (IV) sulfate, diols (CDH), sulfuric acid, acetic acid, ferroin, (E. Merck) and cerium(III) sulfate (Fluka A.G.) were used as supplied without further purification by preparing their solutions in doubly distilled water. Strength of rhodium(III) chloride (Johonson Matthay & Co.) was 4.78×10^{-3} M, which was prepared by dissolving the sample in minimum amount of AR HCl (5.0×10^{-2} M). Ferrous ammonium sulfate solution was standardized by titrating it against a standard solution of potassium dichromate (E. Merck) using N-phenyl anthranilic acid as an internal indicator. Cerium(IV) sulfate, prepared by dissolving the sample in 1:1 sulfuric acid, was titrated against the standard ferrous ammonium sulfate solution using ferroin as an internal indicator. All other chemicals used were either AR or chemically pure substances. Progress of the reaction was measured (constant temperature $\pm$ 0.1° C) at different intervals of time by transferring the aliquot 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 a standard cerium (IV) sulfate solution using ferroin as an internal indicator. In this way remaining amount of ferrous ammonium sulfate directly corresponds to the amount of cerium(IV) consumed in the reaction mixture.

2.2. Kinetic Determinations

In all kinetic runs diol concentration was kept in excess. In the case of oxidant variation rate values were calculated at a fixed initial time from the individual plots, while in all other cases the values were obtained at a fixed initial concentration. Rate values (-dc/dt), obtained from the initial slopes of individual graphs between the residual

concentrations of cerium(IV) at various time intervals, were finally plotted against the changing concentrations of the particular reactant for which 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 slope of the double logarithmic graphs between rate versus concentration and by calculating rate constant for molar concentrations (catalyst variation). Effects of [cerium(III)] and Cl⁻ ions on the reaction velocity were studied by external addition of these ions. Tables and figures contain initial concentrations of the reactants. Study could not be made at constant ionic strength of the medium due to large volumes of potassium chloride required to keep the ionic strength constant. However, effect of change of ionic strength of the medium on the rate was studied separately with the help of a standard solution of potassium chloride.

3. RESULTS

3.1. Product Study and Stoichiometry

Stoichiometry of the reaction was studied by taking cerium(IV) in large excess compared to organic substrate to ensure its complete oxidation. Total amount of cerium(IV) sulfate consumed by one mole of organic substrate for its complete oxidation was determined. In case of non-vicinal diols invariably the hydroxy aldehydes are found to be the oxidation products but in the present case of vicinal diols one molecule each of formaldehyde and acetaldehyde were obtained in the case of propane-1,2-diol, while in the case of butane-2,3-diol product was found to be two molecules of acetaldehyde. Products were confirmed by preparing their hydrazones by standard method [9], by spot test methods [10] and chromatographic technique [11]. Products of the reaction were also confirmed by extracting the reaction mixture with ether (3 x 15 ml). It may be pointed out that the stretching peaks of the hydroxyl group as well as carbonyl C=O stretching peaks were shifted to lower wave numbers (Supplementary Material 1 and 2). Broad $C_{O-H \ str}$ was observed between 3500 to 3200 cm^{-1} indicating associated O-H (due to hydrogen bonding and/or complex formation), bonded carboxyl peaks ($C_{C=O \ str.}$) peaks observed at 1632 and 1626 at lower wave number than the reported range. There may be intramolecular hydrogen bonding between the hydroxyl group and the carbonyl oxygen which may be the reason for shifting of the peaks to the lower wave numbers [12]. $C_{C-O str.}$ appear in the range of 1116 and 1192. C-CH$_{3 \ str.}$ (asymmetric and symmetric) are seen at 1384, 1351 and 1377, 1348 in the case of the products of propane-1,2-diol and butane-2,3-diol respectively. Probability of cerium(IV) forming complex with product of the reaction resulting in the shifting of the peaks to the lower wave numbers seems to be small. In iridium(III) catalyzed oxidation of hydrocarbons [13] and aromatic aldehydes and phenols [14] by cerium(IV) sulfate the system [13] was proved to be so effective that it was able to oxidize cyclohexane and benzene also with 44% and 51.8% yields of corresponding carbonyl compounds. Stoichiometry of the reaction e.g. for propane-1, 2-diol may be given by equation (1).

$$CH_3CH(OH)CH_2(OH) + 2 \ Ce^{IV} \longrightarrow HCHO + CH_3CHO + 2 \ Ce^{III} + 2 \ H^+ \quad (1)$$

3.2. Reaction Orders

Table **1** shows that –dc/dt values increase steadily with increasing [oxidant] in the beginning, reach to a maximum and beyond which further increase in [oxidant] starts decreasing the rate. First order rate constant values for molar concentration of oxidant are fairly constant in the beginning but start decreasing later on. On plotting –dc/dt values versus [cerium(IV)], straight lines passing through the origin are obtained but after reaching to a maximum point negative trend in the rate values is observed (Fig. **1**). It shows that the reaction shows direct proportionality w. r. to oxidant only at its low concentrations and after a certain point increase in [oxidant] retards the rate. –dc/dt values increase proportionately with increasing [organic substrate] at low concentrations but this increase is not much prominent at higher [organic substrate] (Table **1**). On plotting rate values against [organic substrate], straight line passing through the origin is obtained in the beginning but at higher organic substrate concentrations trend of the line to becomes parallel to the x-axis becomes apparent (Fig. **2**). The second order rate constant k values are fairly constant in the beginning but as the concentration of organic substrate is increased these values start decreasing (Table **1**). These facts confirm that rate of the reaction shows direct proportionality w. r. to [organic substrate] only at low concentrations but it tends to become independent of concentration at higher [organic substrate]. Similar trend was obtained in both the cases.

On plotting –dc/dt values against [RhCl$_3$], straight lines passing through the origin were obtained (Fig. **3**), while the slope values of 0.87 and 0.85 were obtained on plotting double logarithmic graphs in case of propane-1, 2-diol and butane-1, 3-diol respectively. All these facts clearly indicate that the reaction follows first order kinetics with respect to catalyst concentrations.

To confirm the removal of hydrogen ions and reduction of cerium(IV) before the rate determining step, the effect of these ions on the rate was studied by changing the concentration of sulfuric acid and external addition of Ce$_2$(SO$_4$)$_3$ into the reaction mixture. It was observed that rate of the reaction decreases with increasing concentrations of H$^+$ (Table **2**) and Ce(III) concentrations both (Table **3**) indicating that these ions have a retarding effect on the reaction velocity. Increase in the concentration of chloride ions, with the help of a standard solution of potassium chloride, has a positive effect on the reaction velocity (Table **3**). Rate values increase proportionally with increasing concentrations of rhodium(III) chloride in both the cases. The second order rate constant k* values remain constant with average deviation of 1.29 ± 0.16 and 5.70 ± 0.55 for propane-1, 2-diol and butane-2, 3-diol respectively (Table **2**).

4. DISCUSSION

4.1. Reactive Species of Rhodium(III) Chloride

Aqua ion [Rh(H$_2$O)$_6$]$^{3+}$ is quite stable and exchange between first sphere H$_2$O protons and bulk water is highly pH dependent [15]. It is also known that its water solution is extensively hydrolyzed [16]. Between the species RhCl$_6$$^{3-}$ which is obtained in excess of hydrochloric acid and [Rh(H$_2$O)$_6$]$^{3+}$, which is formed on boiling aqueous solution of rhodium(III) chloride, there are several intermediate

Table 1.   **Effect of Variation of [Cerium(IV)] and [diols] on the Rate at 32°C (A- Propane-1,2-diol; B- Butane-2,3-diol)**

Variation of [Ce(SO₄)₂]

A- [Propane-1,2-diol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 0.70 M, [RhCl$_3$] = 1.40 x 10^{-5} M.
B- [Butane-2,3-diol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 0.30 M, [RhCl$_3$] = 1.40 x 10^{-5} M.

Variation of [Diol]

A- [Ce(SO$_4$)$_2$] = 5.00×10^{-4} M, [H$_2$SO$_4$] = 0.70 M, [RhCl$_3$] = 1.40 · 10^{-5} M.
B- [Ce(SO$_4$)$_2$] = 5.00×10^{-4} M, [H$_2$SO$_4$] = 0.30 M, [RhCl$_3$] = 1.40 × 10^{-5} M.

[Ce^{IV}] × 10^4 M	-dc/dt × 10^6 M. min^{-1}		k × 10^2 min^{-1}		[Diol] × 10^3 M	-dc/dt × 10^6 M. min^{-1}		k M^{-1}min^{-1}	
	(A)	(B)	(A)	(B)		(A)	(B)	(A)	(B)
2.00	1.00	3.57	0.50	1.78	2.00	0.85	-	0.85	-
3.00	1.20	4.17	0.40	1.39	2.50	1.14	4.40	0.91	3.52
4.00	1.33	5.83	0.37	1.46	3.00	1.25	5.00	0.83	3.33
5.00	2.00	6.67	0.40	1.33	4.00	1.50	6.00	0.75	3.00
6.00	2.67	6.67	0.44	1.12	5.00	1.83	6.25	0.73	2.50
7.00	2.50	6.25	0.35	0.89	6.00	2.25	7.50	0.75	2.50
8.00	2.25	5.50	0.28	0.69	8.00	2.67	8.33	0.6675	2.08
10.0	1.60	5.50	0.16	0.55	10.0	2.80	10.0	0.56	2.00

species. Equilibrium between various species may be shown as

$$Rh(H_2O)_6^{3+} + OH^- \rightleftharpoons Rh(OH)(H_2O)_5^{2+} + H_2O$$
$$(2)$$
$$Rh(OH)_2(H_2O)_4^{1+} + OH^- \rightleftharpoons Rh(OH)_3(H_2O)_3 + H_2O$$

$$Rh(OH)_3(H_2O)_3 + Cl^- \rightleftharpoons RhCl(OH)_2(H_2O)_3 + OH^-$$
$$(3)$$
$$RhCl_2(OH)(H_2O)_3 + Cl^- \rightleftharpoons RhCl_3(H_2O)_3 + OH^-$$

Thornton [17] revealed the existence of only one complex, [RhCl$_5$(H$_2$O)]$^{2-}$ in 40% hydrochloric acid. On diluting the solution, after 24 h, new peaks were also obtained due to hydrolysis which were attributed to [RhCl$_4$(H$_2$O)$_2$]$^-$ and [RhCl$_3$(OH)(H$_2$O)$_2$]$^-$. Capillary zone

Fig. (2). Effect of variation of [RhCl$_3$] on the rate at 32 °C. A- [Ce(SO$_4$)$_2$] = 5.00×10^{-4} M, [Propane-1,2-diol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 0.70 M. B- [Ce(SO$_4$)$_2$] = 5.00×10^{-4} M, [H$_2$SO$_4$] = 0.30 M, [Butane-2,3-diol] = 5.00×10^{-3} M.

Fig. (1). Effect of variation of [Ce(SO$_4$)$_2$] on the rate at 32 °C. A- [Propane-1,2-diol], B- [Butane-2,3-diol] = 5.0×10^{-3} M; [H$_2$SO$_4$] = 0.70 M (for A); [H$_2$SO$_4$] = 0.30 M (for B); [RhCl$_3$] = 1.40 × 10^{-5} M (for A and B).

Fig. (3). Effect of variation of [Organic substrate] on the rate at 32 °C. [Ce(SO$_4$)$_2$] = 5.00×10^{-4} M (for A and B); [H$_2$SO$_4$] = 0.70 M (for A); 0.30 M (for B); [RhCl$_3$] = 1.40 × 10^{-5} M (for A and B).

Table 2.   Effect of Variation of [RhCl$_3$] and [H$^+$] on the Rate at 32 ^{0}C (A- Propane-1,2-diol; B- Butane-2,3-diol)

Variation of [RhCl$_3$]

A-[Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Propane-1,2-diol] = 5.0 × 10^{-3} M, [H$_2$SO$_4$] = 0.70 M.
B- [Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [H$_2$SO$_4$] = 0.30 M, [Butane-2,3-diol] = 5.00 × 10^{-3} M.

Variation of [H$_2$SO$_4$]

A-[Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Propane-1,2-diol] = 5.0 × 10^{-3} M, [RhCl$_3$] = 1.40 x 10^{-5} M.
B- [Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Butane-2,3-diol] = 5.00 × 10^{-3} M, [RhCl$_3$] = 2.39 × 10^{-5} M.

[RhCl$_3$] × 10^5 M	k* × 10^{-2} M^{-1} min^{-1}		[H$_2$SO$_4$] × M	-dc/dt × 10^6 M min^{-1}	
	(A)	(B)		(A)	(B)
0.47	1.53	-	0.30	3.96	7.20
0.75	-	6.67	0.50	2.49	3.54
0.95	1.35	6.25	0.60	2.49	-
1.40	1.40	5.57	0.70	-	3.00
1.90	1.26	5.26	0.80	1.67	-
2.39	1.11	5.21	1.00	1.59	1.62
3.10	1.13	5.37	1.30	1.25	1.44
3.58	-	5.59	1.50	1.02	0.75

electrolysis method has revealed the existence of three species of rhodium [RhCl$_4$(H$_2$O)$_2$]$^-$, [RhCl$_3$(H$_2$O)$_3$] and [RhCl$_2$(H$_2$O)$_4$]$^{+1}$ on changing pH of the solution from 1.0 to 3.50 with hydrochloric acid, along with decrease in the cationic form and increase in the uncharged complex with the formation of two negatively charged chlorocomplexes [18]. Present study was performed in acidic medium and positive effect of chloride ions for their many folds variation in concentration indicates that both [RhCl$_4$(H$_2$O)$_2$]$^-$ and [RhCl$_5$(H$_2$O)]$^{-2}$ forms may be present in the reaction mixture. Conversion of [RhCl$_4$(H$_2$O)$_2$]$^-$ in to [RhCl$_5$(H$_2$O)]$^{-2}$ may increase with increasing catalyst or in other terms increasing hydrochloric acid in the system. Since saturation kinetics was not shown by the catalyst even at its higher concentration which on the one hand indicates that catalyst is not forming complex with organic substrate and on the other hand it also shows that [RhCl$_4$(H$_2$O)$_2$]$^-$ form of the catalyst converts into [RhCl$_5$(H$_2$O)]$^{-2}$ which ultimately catalyzes the reaction.

4.2. Oxidative Cleavage of Diols and Related Compounds

Many oxidants readily cleave 1,2-glycols [19, 20]. 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 [21]. On the other hand cleavage of 1,2-glycols by cerium(IV) seems to involve coordination to only one hydroxy group followed by a one-electron oxidation to give an intermediate radical. This is supported by similar rates of oxidation of 1,2-glycols and their monomethyl ethers and the successful trapping experiments [20, 22]. Moreover, based on the orbital symmetry considerations the former cyclic mechanism is a forbidden process for one-electron oxidants such as cerium(IV) [23]. The cleavage of 1,2-glycols by cerium(IV) is just a special case of the general oxidative cleavage of alcohols by cerium(IV) [24, 25]. The same

Table 3.   Effect of Variation of [Ce^{III}] and [Cl$^-$] on the Rate at 32°C (A- Propane-1,2-diol; B- Butane-2,3-diol)

Ce$_2$(SO$_4$)$_3$ Variation

A-[Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Propane-1,2-diol] = 5.0 × 10^{-3} M, [RhCl$_3$] = 1.40 × 10^{-5} M. [H$_2$SO$_4$] = 0.50 M.
B- [Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Butane-2,3-diol] = 5.00 x 10^{-3} M, [RhCl$_3$] = 2.39 × 10^{-5} M, [H$_2$SO$_4$] = 0.50 M.

KCl Variation

A-[Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Propane-1,2-diol] = 5.0 × 10^{-3} M, [RhCl$_3$] = 1.40 × 10^{-5} M. [H$_2$SO$_4$] = 0.70 M.
B- [Ce(SO$_4$)$_2$] = 5.00 × 10^{-4} M, [Butane-2,3-diol] = 5.00 x 10^{-3} M, [RhCl$_3$] = 2.39 × 10^{-5} M, [H$_2$SO$_4$] = 0.30 M.

[Ce$_2$(SO$_4$)$_3$] × 10^4 M	-dc/dt × 10^6 M min^{-1}		[KCl] × M	-dc/dt × 10^6 M min^{-1}	
	(A)	(B)		(A)	(B)
2.00	1.75	3.57	0.70	-	3.75
2.50	-	3.00	0.80	0.80	-
3.50	1.40	2.50	0.85	-	5.70
5.00	1.16	1.43	1.00	1.00	6.00
7.00	0.80	-	1.15	1.33	-
8.00	-	1.14	1.30	1.67	7.50
10.0	0.55	-	1.50	1.75	9.00

mechanism seems to operate for all these oxidative cleavages and as expected the α-hydroxy radicals are stable enough that alcohol which can form them (1,2-glycols) undergo rapid cleavage. Polar nature of the transition state for the reaction [24] also favours the cleavage of α-hydroxy radicals. In the un-catalyzed oxidation of diols, in which hydroxyl groups are not at the vicinal position, only the corresponding hydroxy aldehydes were found to be the oxidation products [26]. Formation of radical in all the cases has been reported invariably. It has been suggested that the oxidation of diols is a special case of the oxidation of alcohols in which only one hydroxy group is attacked. It has also been suggested that oxidation of diols is followed by the scission of C-H bond instead of C-C bond which has been reported previously in the case of glycols.

4.3. Reactive Species of Cerium(IV) Sulfate

Cerium(IV) forms a number of complexes in sulfuric acid solution. Hardwick and Robertson [27] have reported the following equilibrium between various complexes in sulfuric acid solutions of 2 M ionic strength at 25°C -

$$Ce^{4+} + HSO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} CeSO_4^{2+} + H^+ \quad K_1 = 3500 \tag{4}$$

$$CeSO_4^{2+} + HSO_4^- \underset{}{\overset{K_2}{\rightleftharpoons}} Ce(SO_4)_2 + H^+ \quad K_2 = 200 \tag{5}$$

$$Ce(SO_4)_2 + HSO_4^- \underset{}{\overset{K_3}{\rightleftharpoons}} Ce(SO_4)_3^{2-} + H^+ \quad K_3 = 20 \tag{6}$$

Considering the range of concentration of acid in which the present study was performed and the steep fall in rate of the reaction with increasing concentration of sulfuric acid, $Ce(SO_4)_2$ has been taken as the reactive species of Ce^{IV} in aqueous sulfuric acid medium. Existence of cerium(IV) in the form of $Ce(SO_4)_2$ under our experimental conditions has been considered by other workers also [28].

4.4. Mechanism

According to Scheme **1**, cerium (IV) forms complex with

organic substrate, which results into the formation of one molecule of formaldehyde along with formation of a radical. Transfer of the electron of the radical to the catalyst initiates the breaking of O-H bond resulting in the formation of product along with the change of rhodium(III) to rhodium(II). Rhodium(II) is quickly oxidized back to rhodium(III) by one cerium(IV) in the subsequent fast step. The rate in terms of decreasing concentrations of Ce^{IV} is given as

$$Rate = -\frac{d[Ce^{IV}]}{dt} = k[C] \tag{7}$$

Form the above mechanistic steps total concentration of the catalyst may be given as

$$[Rh^{III}]_T = [RhCl_4(H_2O)_2]^{1-} + [RhCl_5(H_2O)]^{2-} + [C] \tag{8}$$

Now putting the concentration of complex C, calculated from the concentrations of $[RhCl_4(H_2O)]^{1-}$ and $[RhCl_5(H_2O)]^{2-}$ in terms of [C] from steps I and II of the mechanism, in equation (6) the rate in terms of decreasing concentrations of Ce^{IV} is given as

$$-\frac{d[Ce^{IV}]}{dt} = \frac{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]\{[H_2O] + K_1[Cl^-]\} + K_1K_2K_3[S][Ce^{IV}][Cl^-]} \tag{9}$$

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

$$-\frac{d[Ce^{IV}]}{dt} = \frac{2kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+] + K_1K_2K_3[S][Ce^{IV}][Cl^-]} \tag{10}$$

At low concentrations of oxidant and the organic substrate, the inequality $[Ce^{III}][H^+] \gg K_1K_2K_3[S][Ce^{IV}][Cl^-]$ and the rate law (9) becomes

$$RhCl_4(H_2O)_2{}^{1-} + Cl^- \underset{}{\overset{K_1}{\rightleftharpoons}} [RhCl_5(H_2O)]^{2-} + H_2O \tag{I}$$

Scheme 1: Proposed steps in the oxidation of propane-1,2-diol by cerium(IV) sulfate in aqueous sulfuric acid medium in the presence of rhodium(III) chloride.

$$- \frac{d[Ce^{IV}]}{dt} = \frac{2 \, kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T}{[Ce^{III}][H^+]} \quad (11)$$

This rate law explains the nature shown by all the reactants at their low concentrations. At higher concentrations of oxidant and organic substrate the reverse inequality $[Ce^{III}][H^+] << K_1K_2K_3[S][Ce^{IV}][Cl^-]$ may be valid and the equation (9) may be written as

$$- \frac{d[Ce^{IV}]}{dt} = 2 \, k \, [Rh^{III}]_T \quad (12)$$

This equation explains first order kinetics with respect to catalyst for its many folds variation in concentrations. However, according to rate law (11), the rate with respect to oxidant and the chloride ions should also become independent of concentration at higher concentrations of both the reactants. Here it is important to note that the effect of chloride ions on the rate was studied by adding these ions externally with the help of a solution of potassium chloride in the reaction mixture. Thus the effect of further increase in chloride ion 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 concentrations, the independent nature of chloride ions on the rate would have become obvious. Further the nature shown by the oxidant is somewhat surprising, at higher concentrations instead of showing zero order kinetics the rate starts decreasing. Here it is interesting to note that decrease in the rate starts only when the concentration of oxidant increases a fixed value of about 6.0×10^{-4} M in the reaction mixture in both the cases. Falling off the reaction velocity at higher concentrations of oxidant may be due to the 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 acid, nitric acid [26, 29] and perchloric acid [30], while existence of trimeric cerium has been reported in acetic acid medium [31]. In a number of studies it has been reported that the first order velocity constant k_1 values decrease with increasing Ce(IV) concentrations due to the formation of dimeric species. Conversion of reactive species of cerium(IV) into the unreactive dimer may be the cause of retardation in the reaction rate at higher oxidant concentrations. Retarding trend shown by the oxidant at its higher concentrations may also be due to the formation of complex between the reactive species of oxidant with sulfuric acid according to the following equilibrium

$$Ce(SO_4)_2 + HSO_4^- \underset{}{\overset{K'}{\rightleftharpoons}} HCe(SO_4)_3^- \quad (13)$$

$$HCe(SO_4)_3^- + HSO_4^- \underset{}{\overset{K''}{\rightleftharpoons}} H_2Ce(SO_4)_4^{2-} \quad (14)$$

$$Ce(SO_4)_2 = \frac{[H_2Ce(SO_4)_4]^{2-}}{[HSO_4^-]^2} \quad (15)$$

$[H_2Ce(SO_4)_4]^{2-}$, a well known un-reactive species of cerium(IV) sulfate in sulfuric acid medium [2, 32] retards the rate as given in equation (15). Similar type of behavior of the

oxidant has been reported in the oxidation of hydrocarbons by cerium(IV) [33]

Further verification of the final rate law (9) may be given by rewriting the equation as

$$\frac{1}{-d[Ce^{IV}]/dt} = \frac{[Ce^{III}][H^+]}{2 \, kK_1K_2K_3[S][Ce^{IV}][Cl^-][Rh^{III}]_T} + \frac{1}{2 \, k \, [Rh^{III}]_T} \quad (16)$$
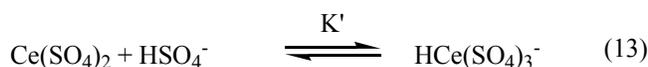
From this equation k values calculated from the intercepts of the graphs (1/rate versus 1/[S] and [H$^+$]) come out to be 47.6 and 59.5, similarly $kK_1K_2K_3$ values from the slopes of the graphs (1/rate versus 1/[S] and [H$^+$]) come out to be 5.6 and 5.7 for propane-1,2-diol and 5.8 and 3.35 for butane-2,3-diol respectively. Fair constancy in the rate constant values obtained from different graphs further supports the validity of the proposed mechanism and the rate law. While calculating the rate constant values, concentrations of cerium(III) and the chloride ions were ignored because these ions were added externally in the reaction mixture. Cerium (III) is produced by the reduction of cerium(IV) in the reaction mixture and since the rates were measured in the beginning of the reaction therefore the concentration of cerium(III) at the point where the rates were measured will be negligible. Similarly in the absence of external addition, concentration of chloride ions will be only due to catalyst present in the reaction mixture and this also may be ignored while calculating the rate constants. The kinetic measurements were extended at four temperatures. The energy of activation for propane-1,2-diol and butane-2,3-diol comes out to be 15.96 and 14.59 (kJ mol^{-1}), respectively. The entropy of activation was found to be – 44.30 and 44.54 (JK^{-1} mol^{-1}), Free energy of activation values were found to be 29.47 and 28.16 (kJ mol^{-1}).

CONCLUSION

Catalytic activity of rhodium(III) chloride in the oxidation of vicinal diols in acidic medium has not been reported properly from the kinetic point of view. In the un-catalyzed oxidation of diols when hydroxyl groups are not at the vicinal position scission of C-H bond instead of C-C bond takes place and corresponding hydroxy aldehyde is found to be the oxidation product. This is not the case in vicinal diols where C-C bond is broaken. 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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CONFLICT OF INTEREST

None declared.

SUPPLEMENTARY MATERIAL

This article is also accompanied with supplementary material and it can be viewed at publisher's website.

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