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Oxidation of cyclic alcohols by cerium(IV) in acidic medium in the presence of iridium(III) chloride

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Abstract

Kinetic data suggest reduction of Ce^{IV} into Ce^{III} and elimination of Cl^- and H^+ ions before the rate-determining step in iridium(III) chloride catalyzed oxidation of cyclohexanol and cyclooctanol by cerium(IV) sulphate in aqueous sulphuric acid medium. $IrCl_3$ was found to be equal or even a better catalyst compared to ruthenium for oxidations involving ceric ions. Effects of change of concentrations of Ce^{IV}, cycloalcohols, Ir^{III}, H^+, Cl^- and Ce^{III} on the reaction rate were determined. The order of the reaction changes from one to zero on increasing the concentration of the oxidant. Rate of the reaction was found to follow direct proportionality with respect to catalyst concentrations. Change in the order of reaction from first to zero was observed on increasing the concentration of organic substrate. External addition of H^+, Cl^- and Ce^{III} ions retards the reaction velocity. Spectrophotometric evidence was provided that it is the cerium and not catalyst, which forms complex with substrate. Parameters such as energy of activation, free energy of activation and entropy data were collected at five different temperatures, which suggest that cyclooctanol is more easily oxidizable compared to cyclohexanol.

Keywords: Oxidation; Cyclic alcohols; Iridium(III); Cerium(IV) and Catalysis

1. Introduction

Compounds of ruthenium and osmium have been extensively used as homogeneous catalysts. In many cases osmium compounds show better catalytic activity compared to ruthenium compounds but the tendency of osmium compounds to form hazardous osmates in acidic medium restricts their use as homogeneous catalysts in alkaline medium only. In this respect ruthenium compounds are advantageous as they can be used both in acidic as well as in alkaline medium. Kinetics of oxidation of a number of organic compounds in acidic [1] and alkaline [2] medium has been reported from our laboratory in which compounds of ruthenium and osmium, respectively, were found to be effective catalysts. We were the first to report mechanistic steps involved in iridium(III) chloride catalysis in alkaline medium [3] and the catalytic activity of ruthenium(VIII) oxide in acidic medium [4]. Initially, the use of iridium(III) chloride as a homogeneous catalyst attracted little attention because it was not an effective catalyst in alkaline medium [3]. Potential of iridium(III) chloride to act as a homogeneous catalyst in oxidation processes was recognized when it was used in acidic medium. Oxidation of propan-1-ol and propan-2-ol [5], ethanol [6], methanol [7] and formic acid [8] by cerium(IV) sulphate in sulphuric acid medium catalyzed by iridium(III) chloride was reported. It was suggested that the complex formed between catalyst, oxidant and organic substrate decomposes in the rate-determining step and $Ce(SO4)_2{}^{2-}$ was considered to be the active species of cerium(IV). On the other hand, in the oxidation of butan-2-ol [9] and aliphatic alcohols (methanol, ethanol, propanol, butanol and iso-butanol) [10] with same catalyst, oxidant and acid, $Ce(SO_4)_2$ was considered as the active species, which does not participate in the complex formation. In some recent studies with *t*-butyl alcohol [11] and isobutyl alcohol [12], a complex involving cerium(IV), catalyst and organic substrate has been reported which decomposes in the slow step but $Ce(SO_4)_2$ species was considered to be the active species. Reported diversity in the results and complex formation in these studies may be due to the fact that the effects of Ce^{III} and Cl^-

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ions on the rate were not studied. From the mechanistic point of view it becomes necessary to ascertain, firstly, whether Ce^{III} is released before the slow step or not and secondly in which form iridium(III) chloride is catalyzing the reaction. Here, we report the oxidation of cyclohexanol and cyclooctanol by cerium(IV) sulphate in aqueous sulphuric acid medium catalyzed by iridium(III) chloride. Interestingly the average concentration of catalyst (10^{-6} M) required to catalyze the oxidation was similar to that of ruthenium(III) chloride [13] and ruthenium(VIII) oxide [14], when these cyclic alcohols were oxidized by alkaline hexacyanoferrate(III) (with [cyclic alcohols] = 1.0–3.0 × 10^{-2} M and [$K_3Fe(CN)_6$] = 2.0 × 10^{-3} M). While same or even higher concentrations of ruthenium(III) chloride were required to catalyze the oxidation of these cyclic alcohols by cerium(IV) sulphate in acidic medium under similar conditions (with [cyclic alcohols] = 0.8–5.0 × 10^{-2} M and [$Ce(SO_4)_2$] = 2.0 × 10^{-3} M) [15]. To ascertain the mechanistic path, we have studied the effects of externally added chloride, hydrogen and cerium(III) ions on the rate and extent of oxidation. Study was performed at constant ionic strength of the medium.

2. Experimental

Cerium(IV) sulphate, cerium(III) sulphate (Loba), sulphuric acid, ferrous ammonium suphate, potassium chloride, ferroin (E. Merck), cyclohexanol and cyclooctanol (KOCH-LIGHT) were used as such without further purification and their solutions were prepared by directly dissolving the weighed samples in double distilled water. Solution of iridium(III) chloride was prepared by dissolving the sample (sodium hexachloroiridate(III) (Johnson Matthey & Co.)) in minimum amount of HCl (A.R.) and the final strengths of acid and catalyst were 0.00624 and 3.35 × 10^{-3} M, respectively. Cerium(IV) sulphate, prepared by dissolving the sample in 1:1 sulphuric acid, was standardized with a standard solution of ferrous ammonium sulpahate using ferroin (CDH) as an external indicator. All other chemical used were either Analar or chemically pure substances. IR spectra were recorded in KBr (ABB Bomen, FTLA 2000 104) spectrophotometer while UV–vis spectra were recorded on Systronics double beam spectrophotometer (2203 SMART).

2.1. Determination of kinetic orders

Study was made at constant temperature (±0.1 °C). At different time intervals progress of the reaction was measured by mixing 5.0 ml aliquot of the reaction mixture to the same volume of ferrous ammonium sulphate solution of slightly higher concentration compared to the concentration of cerium(IV) sulphate initially taken in that particular set. Remaining ferrous ions in the mixture were titrated with a standard cerium(IV) sulphate solution using ferroin as an internal indicator. In this way the titre values directly correspond to the amount of cerium(IV) sulphate consumed in the reaction mixture. Reactions were studied under the conditions and range where the un-catalyzed reaction was negligible. Rate of the reaction ($-dc/dt$ values) were calculated from the initial slopes of the individual graphs plotted between residual cerium(IV) sulphate (a–x) versus time. Rate of the reaction ($-dc/dt$) values were finally plotted against the changing concentration of the particular reactant for which order of the reaction was to be obtained. Orders, with respect to various reactants were further confirmed by different methods, i.e. by plotting log (a–x) versus time (in oxidant variation), by calculating rate constant of the reaction using the integrated first order rate equation and by calculating the rate constant for molar concentrations (in catalyst variation) by dividing rate of the reaction ($-dc/dt$ values) by the catalyst concentration. Fair constancy in the values of the rate of the reaction with average deviation 2.18 ± 0.16 (M min^{-1}), in a sample set repeated four times in oxidant, organic substrate, catalyst and acid variations (entries in bold letters in Table 1) confirms reproducibility of the results. Studies were made at constant ionic strength of the medium with the help of a standard solution of KCl. Effects of cerium(III), chloride and hydrogen ions on the reaction velocity were studied by adding these ions externally.

2.2. Stoichiometry and product study

Stoichiometry of the reaction was studied by taking cerium(IV) sulphate in large excess compared to organic substrate in 11:1; 9:1 and 8:1 ratios, respectively. For this purpose reaction mixtures were kept at 30 °C for a long duration. Total amount of cerium(IV) sulphate consumed by 1 mol of organic substrate was estimated as given in 2.1. It was found that 8.88, 8.51 and 8.16 mol of cerium(IV) sulphate were required by 1 mol of organic substrate for its complete oxidation. After completion of the reaction, reaction mixture was repeatedly extracted with ether. Ether extract on evaporation gave white crystalline solids (18.0 and 10.97 mg, respectively, when 0.963 and 0.152 mmol of cyclohexanol and cyclooctanol were initially taken). Adipic acid and suberic acid were identified as the oxidation products of cyclohexanol and cyclooctanol, respectively, by running the tlc plates with authentic samples, mmp. (151–164 and 140–141 °C, respectively) and spot test methods [16]. IR spectra of the products showed peaks at 928 and 1026 (O–H bending out of plane), 1298 and 1251 (C–O stretch), 1418 and 1410 (O–H bending in plane), 1698 and 1700 (C=O stretch) and 2833 to 3259 and 3250 to 3420 with a peak at 3381 (broad O–H stretch) in case of cyclohexanol and cyclooctanol, respectively. However, α-diketones and 2-hydroxycycloketones, which were detected in the oxidation of cyclohexanol by manganese(III) pyrophosphate [17] and chromic acid [18] and the presence of cycloketones as intermediates could not be detected in both the cases due to the overlapping of peaks. Stoichiometry of the reaction may be given by Eq. (1)

$$\begin{aligned} &CH_2(CH_2)_nCHOH + 8Ce^{IV} + 3H_2O \\ &\quad \rightarrow (CH_2)_n(COOH)_2 + 8Ce^{III} + 8H^+ \end{aligned} \tag{1}$$

$n = 4$ for cyclohexanol and 6 for cyclooctanol.

3. Results and discussion

On plotting log (a–x) values (where 'a–x' is the remaining concentration of cerium(IV) at different time intervals) versus time (Fig. 1), deviations from straight lines were prominent only

Table 1
Effect of change of concentration of various reactants on the reaction rate at 30 °C

$[\mathrm{Ce^{IV}}]$ $\times 10^3$ M	$-\mathrm{d}c/\mathrm{d}t \times 10^5$ M min^{-1}		[Organic substrate] $\times 10^2$ M	$-\mathrm{d}c/\mathrm{d}t \times 10^5$ M min^{-1}		$[\mathrm{H^+}]$ M	$-\mathrm{d}c/\mathrm{d}t \times 10^5$ M min^{-1}		$[\mathrm{IrCl_3}]$ $\times 10^6$ M	$k = (-\mathrm{d}c/\mathrm{d}t/[\mathrm{IrCl_3}])$ min^{-1}	
	(A)	(B)		(A)	(B)		(A)	(B)		(A)	(B)
0.30	1.07	–	0.20	1.35	1.33	0.16	–	4.40	0.70	–	9.28
0.35	–	0.83	0.30	2.66	1.50	0.20	8.57	4.00	1.00	–	7.20
0.45	1.82	0.98	0.45	–	1.83	0.28	–	3.25	1.17	11.60	7.20
0.60	2.11	1.18	0.50	3.27	–	0.30	7.50	–	1.50	–	10.53
0.80	2.33	–	**0.66**	–	**2.00**	0.40	6.50	2.36	1.68	10.45	–
0.90	–	1.82	0.80	5.00	–	0.60	5.10	2.18	**2.20**	–	**9.03**
1.25	–	**2.40**	0.90	–	2.16	0.80	4.75	2.20	2.68	9.33	–
1.60	3.33	–	1.00	5.25	–	1.00	4.85	2.00	3.00	–	9.53
1.80	–	2.80	1.25	6.00	–	**1.10**	–	**2.20**	3.68	9.93	–
2.00	3.50	–	1.40	–	2.18	1.30	–	2.00	4.00	–	9.00
2.50	–	3.27	1.75	7.20	–	1.60	–	2.14	5.00	–	8.60
3.00	3.71	–	2.00	7.90	2.18	–	–	–	5.36	9.05	–
3.50	–	3.43	3.00	8.40	–	–	–	–	7.00	–	
									8.38	8.60	–
									11.72	8.87	–

Entries in bold show reproducibility of the results 2.18 ± 0.16 (Section 2.1). Concentrations in (A) are for cyclohexanol and in (B) are for cycooctanol. For variation of $[\mathrm{Ce(SO_4)_2}]$: (A) [cyclohexanol] = 8.0×10^{-3} M, $[\mathrm{IrCl_3}] = 5.36 \times 10^{-6}$ M, $[\mathrm{H_2SO_4}] = 1.0$ M, $\mu = 1.65$ M. (B) [cyclooctanol] = 6.66×10^{-3} M, $[\mathrm{IrCl_3}] = 2.20 \times 10^{-6}$ M, $[\mathrm{H_2SO_4}] = 1.00$ M, $\mu = 2.60$ M. For variation of [Organic substrates]: (A) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, $[\mathrm{IrCl_3}] = 5.36 \times 10^{-6}$ M, $[\mathrm{H_2SO_4}] = 1.0$ M, $\mu = 1.65$ M. (B) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, $[\mathrm{IrCl_3}] = 2.20 \times 10^{-6}$ M, $[\mathrm{H_2SO_4}] = 1.0$ M, $\mu = 2.60$ M. For variation of $[\mathrm{H^+}]$: (A) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, [cyclohexanol] = 8.00×10^{-3} M, $[\mathrm{IrCl_3}] = 5.36 \times 10^{-6}$ M, $\mu = 1.65$ M. (B) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, [cyclooctanol] = 6.66×10^{-3} M, $[\mathrm{IrCl_3}] = 2.20 \times 10^{-6}$ M, $\mu = 2.60$ M. For variation of $[\mathrm{IrCl_3}]$: first order rate constant, $k = -\mathrm{d}c/\mathrm{d}t/[\mathrm{IrCl_3}]$. (A) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, [cyclohexanol] = 8.00×10^{-3} M, $[\mathrm{H_2SO_4}] = 1.0$ M, $\mu = 1.65$ M. (B) $[\mathrm{Ce(SO_4)_2}] = 1.25 \times 10^{-3}$ M, [cyclooctanol] = 6.66×10^{-3} M, $[\mathrm{H_2SO_4}] = 1.0$ M, $\mu = 2.60$ M.

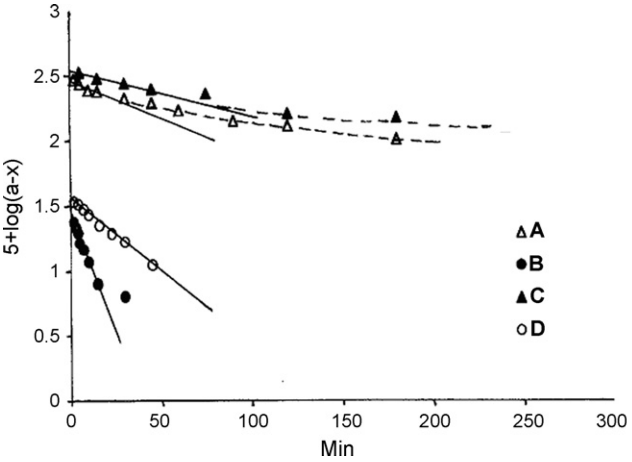


Fig. 1. Sample individual time plots for cerium(IV) for its highest and lowest concentrations at 30 °C. (A)$[Ce(SO_4)_2] = 3.0 \times 10^{-3}$ M. (B) $[Ce(SO_4)_2]=0.30 \times 10^{-3}$ M, [Cyclohexanol]$=8.0 \times 10^{-3}$ M, $[H_2SO_4]=1.0$ M, $[IrCl_3]=5.36 \times 10^{-6}$ M, $\mu=1.65$ M. (C) $[Ce(SO_4)_2]=3.50 \times 10^{-3}$ M. (D) $[Ce(SO_4)_2]=0.35 \times 10^{-3}$ M, [Cyclooctanol]$=6.66 \times 10^{-3}$ M, $[H_2SO_4]=1.0$ M, $[IrCl_3]=2.20 \times 10^{-6}$ M, $\mu=2.6$ M.

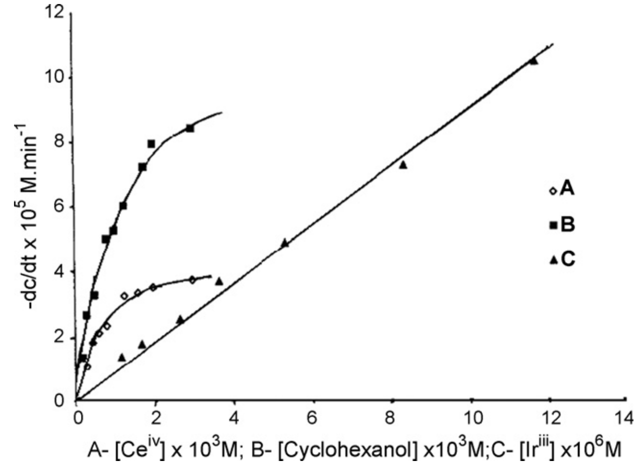
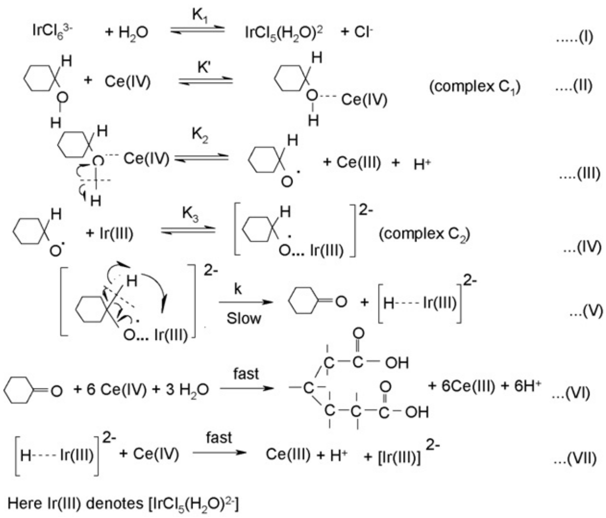


Fig. 2. Effect of variation of $[Ce^{IV}]$, [Cyclohexanol] and $[Ir^{III}]$ on the reaction rate at 30 °C. (A) [Cyclohexanol]$=8.0 \times 10^{-3}$ M, $[H_2SO_4]=1.0$ M, $[IrCl_3]=5.36 \times 10^{-6}$ M, $\mu=1.65$ M. (B)$[Ce(SO_4)_2]=1.25 \times 10^{-3}$ M, $[H_2SO_4]$ $=1.0$ M, $[IrCl_3]=5.36 \times 10^{-6}$ M, $\mu=1.65$ M. (C) $[Ce(SO_4)_2]=1.25 \times 10^{-3}$ M, [Cyclohexanol]$=8.0 \times 10^{-3}$ M, $[H_2SO_4]=1.0$ M, $\mu=1.65$ M.

at higher cerium(IV) concentrations. Rate constant values in a particular set, calculated with the help of integrated first order rate equation $\{k=2.303/t \log a/(a–x)$, showed constancy only at low concentrations of cerium(IV) when the amount of complex formed between the oxidant and substrate (complex C_1 in step II of Scheme 1) and interference from products was negligible. $-dc/dt$ values increase with increasing concentration of oxidant in the beginning but at higher concentrations of the oxidant increase in $-dc/dt$ values was not prominent (Table 1). On plotting $-dc/dt$ values versus cerium(IV) concentrations, straight line passing through the origin is obtained in the beginning but at higher concentrations the line tends to become parallel to the *x*-axis (Figs. 2A and 3E for cyclohexanol and cyclooctanol, respectively). This type of trend in the rate values is further supported because straight lines are obtained on plotting log (*a–x*) versus time (first order plots) at low oxidant concentrations and (*a–x*) versus time (zero order plots) at higher concentrations of the oxidant. Calculations of the order with respect to time and with respect to concentration in case of cerium^{IV} indicate that one of the products is acting as an inhibitor [19], which is clear from Fig. 1 and the effect of change of $[Ce^{III}]$ on the reaction velocity (Table 1). All these factors collectively confirm that the reaction shows direct proportionality at low concentrations of cerium(IV), while order of the reaction tends to become zero at higher concentrations of the oxidant. In Table 1, $-dc/dt$ values increase proportionally with the increasing concentrations of organic substrate in the beginning but the increase is not prominent at higher concentrations of the organic substrate. This trend in the rate values again indicates changing nature of the reaction order from unity at low concentrations to zero at higher concentrations of cyclic alcohols. Graphically this can be verified by plotting $-dc/dt$ values versus organic substrate concentrations in which straight line, passing through the origin, tends to



Scheme 1. .

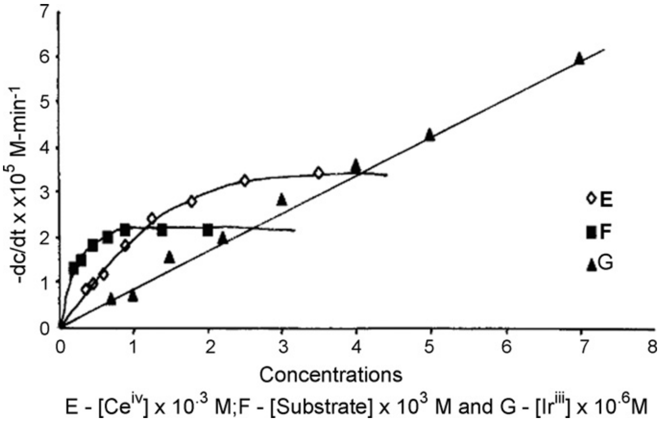


Fig. 3. Effect of variation of $[Ce^{IV}]$, [Cyclooctanol] and $[Ir^{III}]$ on the reaction rate at 30 °C. (E) [Cyclooctanol] $= 6.66 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M, $[IrCl_3] = 2.20 \times 10^{-6}$ M, $\mu = 2.60$ M. (F) $[Ce(SO_4)_2]$ $= 1.25 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M, $[IrCl_3] = 2.20 \times 10^{-6}$ M, $\mu = 2.60$ M. (G) $[Ce(SO_4)_2] = 1.25 \times 10^{-3}$ M, [Cyclooctanol] $= 6.66 \times 10^{-3}$ M, $[H_2SO_4]$ $= 1.0$ M, $\mu = 2.60$ M.

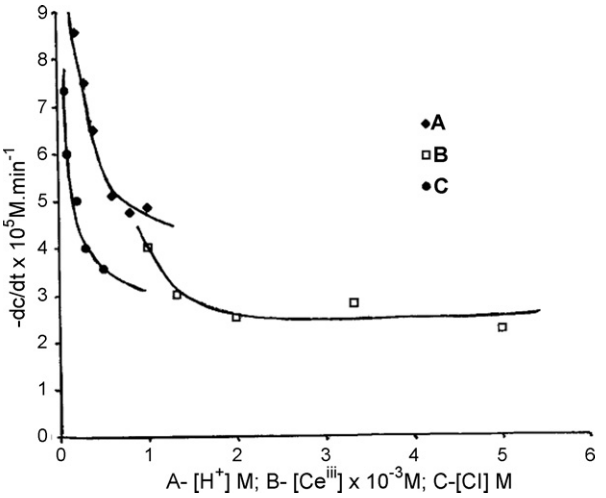


Fig. 4. Variation of [H$^+$], [Ce^{III}] and [Cl$^-$] on the reaction rate for cyclohexanol at 30 °C. For (A–C) [Ce(SO$_4$)$_2$] = 1.25 × 10^{-3} M, [Cyclohexanol] = 8.0 × 10^{-3} M, [IrCl$_3$] = 5.36 × 10^{-6} M, μ = 1.65 M. For (B and C) [H$_2$SO$_4$] = 1.0 M.

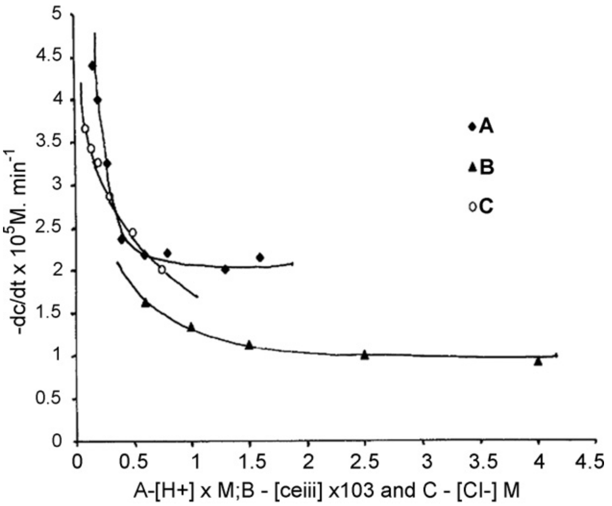


Fig. 5. Variation of [H$^+$], [Ce^{III}] and [Cl$^-$] on the reaction rate for cyclooctanol at 30 °C. For (A–C) [Ce(SO$_4$)$_2$] = 1.25 × 10^{-3} M, [Cyclooctanol] = 6.66 × 10^{-3} M, [IrCl$_3$] = 2.20 × 10^{-6} M, μ = 2.60 M. For (B and C) [H$_2$SO$_4$] = 1.0 M.

become parallel to the x-axis at higher concentrations of organic substrate. This type of nature is shown by the both organic substrates (Figs. 2B and 3F for cyclohexanol and cyclooctanol, respectively).

Proportionate increase in the rate values with 10-folds increase in the concentration of catalyst indicates direct proportionality of the rate with respect to catalyst concentrations. Fair constancy in first order rate constant 'k' values for molar concentration of catalyst and the straight line passing through origin on plotting −dc/dt values versus catalyst concentrations (Figs. 2C and 3G for cyclohexanol and cyclooctanol, respectively) further confirm that in both the cases order of the reaction with respect to catalyst concentration is one.

From Table 1, it is clear that the rate values decrease sharply with increasing concentrations of H$^+$ ions in the beginning but at higher concentrations the decrease is not much prominent. In Table 2 also similar trends are obtained for [Ce^{III}] and [Cl$^-$] ions (Figs. 4 and 5 for cyclohexanol and cyclooctanol, respectively).

Rate of oxidation was found to be in the order cyclooctanol > cyclohexanol and was confirmed from the energy of activation, entropy of activation and free energy of activation values (accuracy 2.18 ± 0.16). These values (with average deviation ±0.16) were found to be 20.18 and 13.98 (kJ mol^{-1}), −66.78 and −68.56 (kJ^{-1} mol^{-1}), 20.26 and 20.79 (kJ mol^{-1}) for cyclohexanol and cyclooctanol, respectively. It is clear from the values of energy of activation that the ease of formation of activated complex is also in the above sequence. Similar trend is observed with the entropy values also. Nearly constant values of free energy of activation confirm that a similar mechanism is operative in the oxidation of both cycloalcohols.

3.1. Reactive species of iridium(III) chloride

It is known that IrCl$_3$ in HCl medium gives IrCl$_6{}^{3-}$ species [20]. It has also been reported that Ir ^{III} and Ir ^{I} ions are the stable species of iridium [21]. Further, the aquation of [IrCl$_6$]$^{3-}$ gives [IrCl$_5$H$_2$O]$^{2-}$, [IrCl$_4$(H$_2$O)$_2$]$^{1-}$ and [IrCl$_3$(H$_2$O)$_3$] species [22–24]. This transformation may be shown by the general equilibrium

$$\mathrm{IrCl_6}^{3-} + n\mathrm{H_2O} \rightleftharpoons [\mathrm{IrCl}_{6-n}(\mathrm{H_2O})_n]^{3-n} + \mathrm{Cl}^- \qquad (2)$$

During our study, observation of strong retarding effect of Cl$^-$ ions on the reaction rate indicates that the above equilibrium is shifted more towards the right hand side and IrCl$_6{}^{3-}$ cannot be considered as the reactive species [3,25]. Therefore, considering our experimental results, IrCl$_5$(H$_2$O)$^{2-}$ has been considered as the reactive species of iridium(III) chloride in the present study.

Table 2
Effect of variation of [Ce^{III}] and [Cl$^-$] ion concentrations on the reaction rate at 30 °C

[Ce$_2$(SO$_4$)$_3$] × 10^3 M	0.60	1.00	1.33	1.50	2.00	2.50	3.33	4.00	5.00
−dc/dt × 10^5 (A)	–	4.00	3.00	–	2.50	–	2.80	–	2.25
M min^{-1} (B)	1.62	1.33	–	1.12	–	1.00	–	0.92	–
[KCl] × 10^2 M	7.50	9.00	10.0	14.0	20.0	30.0	50.0	75.0	
−dc/dt × 10^5 (A)	7.33	–	6.00	–	5.00	4.00	3.55	–	
M min^{-1} (B)	–	3.66	–	3.43	3.26	2.86	2.44	2.00	

(A) [Ce(SO$_4$)$_2$] = 1.25 × 10^{-3} M, [cyclohexanol] = 8.0 × 10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [IrCl$_3$] = 5.36 × 10^{-6} M, μ = 1.65 M. (B) [Ce(SO$_4$)$_2$] = 1.25 × 10^{-3} M, [cyclooctanol] = 6.66 × 10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [IrCl$_3$] = 2.20 × 10^{-6} M, μ = 2.60 M.

3.2. Reactive species of cerium(IV) sulphate

Cerium(IV) forms a number of complexes in sulphuric acid solution. Hardwick and Robertson [26] have reported the following equilibrium between various complexes in sulphuric acid solutions of 2 M ionic strength.

$$Ce^{4+} + HSO_4{}^- \overset{K_1}{\rightleftharpoons} CeSO_4{}^{2+} + H^+ \quad K_1 = 3500 \tag{3}$$

$$CeSO_4{}^{2+} + HSO_4{}^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \quad K_2 = 200 \tag{4}$$

$$Ce(SO_4)_2 + HSO_4{}^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3{}^- + H^+ \quad K_3 = 20 \tag{5}$$

Equilibrium constants for the above steps are 3500, 200 and 20, respectively, at 25 °C. Under our experimental conditions, we are of the opinion that total cerium(IV) is mainly present as $Ce(SO_4)_2$. Concentration of Ce^{4+} species in a solution having [cerium(IV)] = 0.00125 M, and $[H_2SO_4] = 1.0$ M may be calculated from (6), which has been derived from Eq. (3) and (4). The value is found to be 1.0×10^{-9} M.

$$[\text{Cerium(IV)}]_{\text{Total}} = [Ce^{4+}]\left(1 + \frac{K_1[HSO_4{}^-]}{[H^+]} + \frac{K_1K_2[HSO_4{}^-]^2}{[H^+]^2}\right) \tag{6}$$

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 sulphuric acid indicates that the other species would be present in insignificantly small concentrations and may be considered negligible. Thus, $Ce(SO_4)_2$ has been taken as the reactive species of Ce^{IV} in aqueous sulphuric acid medium, which has been considered by other workers also [27,28].

3.3. Mechanism

According to Scheme 1, which is also consistent with the stoichiometry, $IrCl_6{}^{3-}$ gives $IrCl_5(H_2O)^{2-}$ species in aqueous medium. Organic substrate (e.g. cyclohexanol) firstly combines with Ce^{IV} and gives the complex C_1. In the subsequent step complex C_1 disproportionates into a radical, Ce^{III} and H^+ ion. The radical then combines with $IrCl_5(H_2O)^{2-}$ species of catalyst to give complex C_2, which in the rate-determining step gives rise to ketone. In the subsequent fast step $H^\bullet$ ion, complexed with catalyst, transfers its electron to cerium(IV) to give the original $IrCl_5(H_2O)^{2-}$ species. Generally, in the oxidation of alcohols by cerium(IV) to give carbonyl compounds, both $H^\bullet$ formed by the homolysis of O–H and C–H bonds are taken up by two cerium molecules but it may be possible that attachment of a bulky group with substrate hinders the transfer of second $H^\bullet$ to cerium due to steric hinderance and thus the electron of the hydrogen is transferred to iridium instead of cerium. Now in the subsequent steps cyclohexanone, by taking six cerium(IV) ions and three H_2O molecules, ultimately gives rise to adipic acid. Oxidation of cyclohexanone to adipic acid by cerium(IV) in aqueous sulphuric acid medium has been reported earlier also [29]. 1:1 Complexes between cerium(IV) and alcohols [30] and ketones [31] with the elimination of Ce^{III} and H^+ ions are very well documented. Complex of the composition $[ROH.Ce(IV)]^{4+}$ between Ce^{IV} and alcohols and Michaelis–Menten type of kinetics has also been reported [32]. Similar results have been reported in case of ketones [33–38] and cyclic alcohols [39] also. Strong retarding effect of Ce(III), H^+ and Cl^- ions on the rate in the present study, clearly suggests their elimination before the rate-determining step. In the present case formation of complex between Ce^{IV} and the organic substrate is supported by the change of kinetic orders from one to zero and also from the constancy in the calculated rate constant *k* values in the beginning only when the complex formation is small. Deviations from constancy become pronounced with increasing Ce^{IV} or organic substrate concentrations. To see whether the organic substrate forms the complex with cerium(IV) or with iridium(III), UV–vis spectra of aqueous solution of cerium(IV) (1.25×10^{-3} M) in 1.0 M sulphuric acid (Fig. 6A) and after mixing cyclohexanol (0.8×10^{-2} M) (Fig. 6B) were recorded under similar conditions. Shifting of peak from 361 to 316 nm and absorbance from 2.26 to 1.38 (in 15 min after mixing cyclohexanol) indicates the formation of complex between cerium(IV) and cyclohexanol. On the other hand, spectra of aqueous solution of iridium(III) (1.67×10^{-3} M) shows peak at 233.6 nm and absorbance 2.052, which remains almost constant at 233.6 nm 1.999, even after 30 min after mixing cyclohexanol ([Ir(III)] = 1.67×10^{-3} M, [cyclohexanol] = 0.8×10^{-2} M) showing no complex formation. Formation of complex between iridium(III) (step I, Scheme 1) and cycloalcohol (step II, Scheme 1) which then combines with cerium(IV) to give the complex C_2, can also be ruled out on the basis of experimental results because in that condition the final rate law will be inconsistent with a linear plot of 1/rate versus $1/[Ir^{III}]$ and a linear dependence on cerium(IV) concentrations in the region where there is a linear dependence of the rate on catalyst concentrations.

3.4. Derivation of the rate law

Total concentration of Ir^{III} (in all equations total concentration of Iridium(III) is represented as $[Ir^{III}]_T$, and concentration of organic substrate is represented as [S]) according to Scheme 1 may be given by Eq. (7).

$$[Ir^{III}]_T = [IrCl_6]^{3-} + [IrCl_5(H_2O)]^{2-} + [\text{Complex } C_2] \tag{7}$$

Considering equilibrium concentration for steps I to IV and calculating $[IrCl_6{}^{3-}]$ and $[IrCl_5(H_2O)^{2-}]$ from steps I and IV, respectively of the Scheme 1, Eq. (7) after rearrangement can be written as Eq. (8)

$$[Ir^{III}]_T = \frac{[C_2][Ce^{III}][H^+][Cl^-]}{K_1K_2K_3[Ce^{IV}][S]} + \frac{[C_2][Ce^{III}][H^+]}{K_2K_3[Ce^{IV}][S]} + C_2 \tag{8}$$

Here K_2 includes K'_2 term also.

Now rate of the reaction in terms of decreasing concentrations of Ce^{IV} from step (V) may be given as the product of the rate constant and concentration of the complex C_2, which is multiplied by a factor of 2 because two molecules of cerium(IV) are required to regenerate the catalyst in its original form. Thus, the

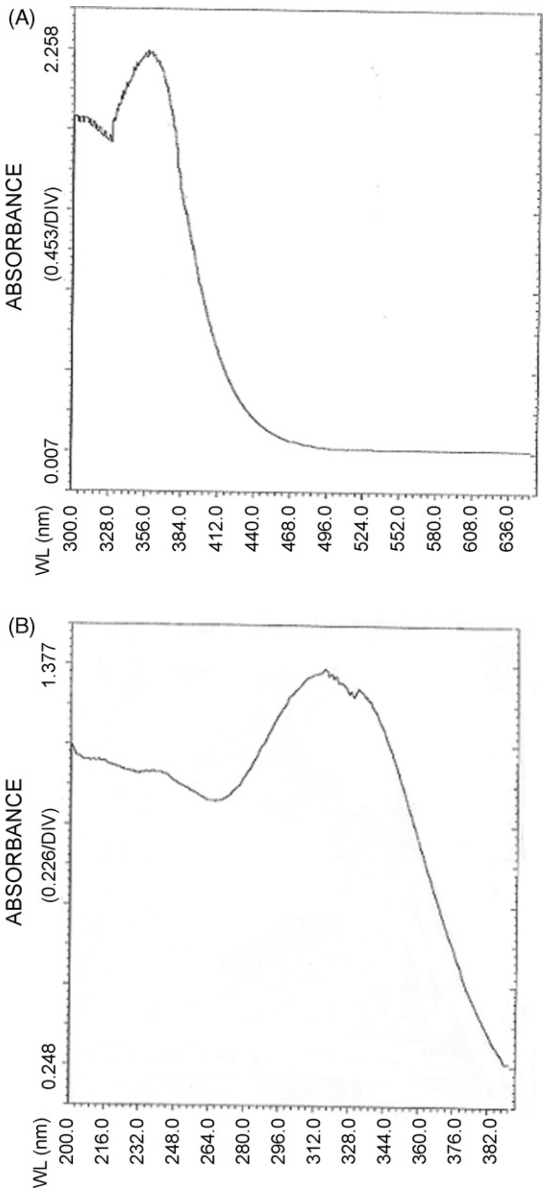


Fig. 6. (A) Spectrum of cerium(IV) in H_2SO_4 at 30 °C. $[Ce(SO_4)_2] = 1.25 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M. (B) Spectrum of Cerium(IV) after mixing cyclohexanol at 30 °C. $[Ce(SO_4)_2] = 1.25 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M, [cyclohexanol] $= 0.8 \times 10^{-2}$ M.

final rate law is obtained as given by Eq. (9)

$$\frac{-\mathrm{d}[\mathrm{Ce^{IV}}]}{\mathrm{d}t} = \frac{2kK_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}][\mathrm{Ir^{III}}]_\mathrm{T}}{[\mathrm{Ce^{III}}][\mathrm{H^+}]\{[\mathrm{Cl^-}] + K_1\} + K_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}]} \tag{9}$$

Here also K'_2 is included in K_2.

This equation clearly accounts for first order kinetics with respect to iridium(III) chloride concentrations. Retarding effect of cerium(III), Cl^- and H^+ ions and the nature shown by cerium(IV) and organic substrate concentrations on the reaction velocity are also quite clear. Under the experimental conditions at low concentrations of cerium(IV) and the organic substrate when $[\mathrm{Cl^-}] \gg K_1$, the inequality $[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}] \gg K_1K_2K_3$ $[\mathrm{Ce^{IV}}][\mathrm{S}]$ may be assumed to be valid and the rate law (9) reduces to

$$\frac{-\mathrm{d}[\mathrm{Ce^{IV}}]}{\mathrm{d}t} = \frac{2kK_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}][\mathrm{Ir^{III}}]_\mathrm{T}}{[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}]} \tag{10}$$

Eq. (10) explains the first order kinetics with respect to cerium(IV) and organic substrate at low concentrations. The retarding nature shown by $[\mathrm{Ce^{III}}]$ $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$ on the reaction velocity is also explained. At higher concentrations the reverse inequality $[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}] \ll K_1K_2K_3$ $[\mathrm{Ce^{IV}}][\mathrm{S}]$ may be considered because the rate values were determined in the beginning of the reaction where the $[\mathrm{Ce^{III}}]$ concentration will be quite low and at higher oxidant concentrations a small amount of KCl will be required to keep the ionic strength of the medium constant and therefore, $[\mathrm{Cl^-}]$ will also be quite low. With the above inequality rate law (9) gives rise to Eq. (11) that accounts for the first order kinetics as shown by iridium(III) chloride up to its manifold variations.

$$\frac{-\mathrm{d}[\mathrm{Ce^{IV}}]}{\mathrm{d}t} = 2k[\mathrm{Ir^{III}}]_\mathrm{T} \tag{11}$$

The final rate law (9) can also be written in the form as

$$\frac{-\mathrm{d}[\mathrm{Ce^{IV}}]/\mathrm{d}t}{[\mathrm{Ir^{III}}]_\mathrm{T}} = k' = \frac{2kK_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}]}{[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}] + K_1[\mathrm{Ce^{III}}][\mathrm{H^+}] + K_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}]} \tag{12}$$

Rate law (9) and (12) can be verified by rewriting these Eqs. (13) and (14), respectively

$$\frac{1}{\mathrm{rate}} = \frac{[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}]}{2kK_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}][\mathrm{Ir^{III}}]_\mathrm{T}} + \frac{[\mathrm{Ce^{III}}][\mathrm{H^+}]}{2kK_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}][\mathrm{Ir^{III}}]_\mathrm{T}} + \frac{1}{2k[\mathrm{Ir^{III}}]_\mathrm{T}} \tag{13}$$

and

$$\frac{1}{k'} = \frac{[\mathrm{Ce^{III}}][\mathrm{H^+}][\mathrm{Cl^-}]}{2kK_1K_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}]} + \frac{[\mathrm{Ce^{III}}][\mathrm{H^+}]}{2kK_2K_3[\mathrm{Ce^{IV}}][\mathrm{S}]} + \frac{1}{2k} \tag{14}$$

From these equations, graphs can be plotted between 1/rate versus $1/[\mathrm{Ir^{III}}]$ or $1/k'$ versus $1/[\mathrm{Ce^{IV}}]$, 1/[S] or $[\mathrm{H^+}]$, which should give a straight line with positive intercept on y-axis from where kK_2K_3 values can be calculated. From the slope of the straight line thus obtained on plotting $1/k'$ (where $k' = \mathrm{rate}/[\mathrm{Ir^{III}}]_\mathrm{T}$) against $1/[\mathrm{Ce^{IV}}]$, 1/[S] or $[\mathrm{H^+}]$ (Fig. 7), kK_2K_3 values were found to be 7.50, 5.50 and 5.83 (cyclohexanol) and 20.0, 11.2 and 5.15 (cyclooctanol), respectively. [Ce(III)] will be produced in the reaction mixture only with the progress of the reaction. The rate values were calculated in the beginning of the reaction when a negligibly small fraction of cerium(IV) would have been converted, therefore, for the sake of simplicity, its concentration may logically be ignored while calculating the kK_2K_3 values, which were calculated by the slope of the graph. Thus, while calculating the kK_2K_3 values, concentration of cerium(III) produced in the reaction mixture was neglected. Fair agreement in kK_2K_3 values calculated from three different

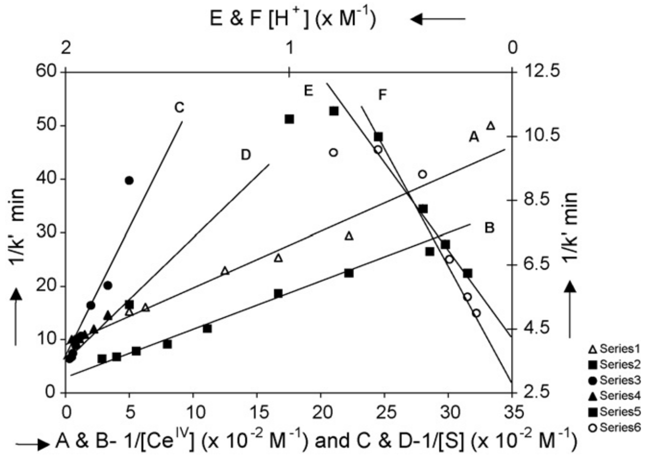


Fig. 7. Plots between 1/*k*′ vs. 1/[Ce(IV)], 1/[S] and [H$^+$]. For (A) [Cyclohexanol]=8.0 × 10^{-3} M, [H_2SO_4]=1.0 M, [$IrCl_3$]=5.36 × 10^{-6} M, μ=1.65 M. For (B) [Cyclooctanol]=6.66 × 10^{-3} M, [H_2SO_4]=1.0 M, [$IrCl_3$]=2.20 × 10^{-6} M, μ=2.60 M. For (C) [$Ce(SO_4)_2$]=1.25 × 10^{-3} M, [H_2SO_4]=1.0 M, [$IrCl_3$]=5.36 × 10^{-6} M, μ=1.65 M. For (D) [$Ce(SO_4)_2$] =1.25 × 10^{-3} M, [H_2SO_4]=1.0 M, [$IrCl_3$]=2.20 × 10^{-6} M, μ=2.60 M. For (E) [$Ce(SO_4)_2$]=1.25 × 10^{-3} M, [Cyclohexanol]=8.0 × 10^{-3} M, [$IrCl_3$]=5.36 × 10^{-6} M, μ=1.65 M. For (F) [$Ce(SO_4)_2$]=1.25 × 10^{-3} M, [Cyclooctanol]=6.66 × 10^{-3} M, [$IrCl_3$]=2.20 × 10^{-6} M, μ = 2.60 M.

graphs further supports the proposed mechanism and the final rate law.

4. Conclusion

The present work clearly shows that it is cerium(IV) that initially forms the complex with organic substrate and not iridium(III) chloride. Retarding effects of chloride, hydrogen and cerium(III) ions on the reaction velocity confirm the removal of these ions before the rate-determining slow step. The present work shows that iridium(III) chloride acts as a highly efficient catalyst when used in acidic medium and indicates great potential of cerium(IV) sulpahte–iridium(III) chloride system for synthetic applications.

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