

Iridium(III) catalyzed oxidation of cyclic ketones by cerium(IV)

Praveen K. Tandon*, Alok K. Singh, Ramesh Baboo and Priy B. Dwivedi
Department of Chemistry, University of Allahabad, Allahabad 211002, India

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Abstract

IrCl_3 which is considered to be a sluggish catalyst in alkaline media, was found to surpass the catalytic efficiency of even osmium and ruthenium in acidic media in the oxidation of cyclopentanone and 2-methylcyclohexanone by cerium(IV) sulphate in aqueous sulphuric acid medium. It was observed that the order of the reaction shows direct proportionality with respect to low concentrations of the oxidant and alcohols, but tends to become independent of concentration at higher concentrations. On increasing the concentrations of externally added Cl^- , H^+ and Ce^{III} ions, the rate of the reaction decreases sharply initially but the decrease in rate becomes less prominent as their concentration is increased. The rate of reaction is directly proportional with respect to IrCl_3 concentrations. Kinetic data suggest that the production of Ce^{III} ion occurs before the rate-determining step. Parameters such as the energy of activation, free energy of activation and entropy data collected at five different temperatures suggest that cyclopentanone forms the activated complex more easily.

Introduction

Among transition metal ions, which have been reported to be very important from the technological point of view [1], osmium and ruthenium have been used extensively as homogeneous catalysts in the oxidation of organic and inorganic compounds. Being injurious in acidic medium, use of osmium is restricted to alkaline media only. Ruthenium compounds have the advantage that they can be used in acidic as well as in the alkaline medium. Moreover, osmium adds to the double bond while ruthenium compounds are reported to break the double bond [2]. It may be mentioned here that the catalytic activities of ruthenium(VIII) in acidic medium [3] and the mechanistic steps involved in iridium(III) chloride catalysis in alkaline medium [4] were reported for the first time by our laboratory. Homogeneous catalysis by ruthenium and osmium compounds has been reported by several workers but the use of iridium(III) chloride as a homogeneous catalyst in acidic medium has not yet been reported. In the present study it was observed that the average concentration of iridium(III) chloride required to catalyze the oxidation of cycloketones lies in the 10^{-6} M range, while at least 10 times higher concentrations of ruthenium(III) chloride with cerium(IV) sulphate in acidic medium [5] and osmium(VIII) oxide with hexacyanoferrate(III) in alkaline medium [6] were required to oxidize various ketones. Herein we report a study of the oxidation of cyclopentanone and 2-methyl cyclohexanone by cerium(IV) sulphate in aqueous sulphuric acid medium catalyzed by iridium(III) chloride at constant ionic strength

of the medium. To ascertain the exact mechanistic path, the effects of externally added chloride, hydrogen and cerium(III) ions were also studied.

Experimental

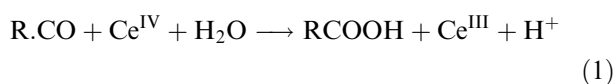
Cerium(IV) sulphate, cerium(III) sulphate (Loba Chemie Indastranal Co.), sulphuric acid, ferrous ammonium sulphate, potassium chloride, ferroin (E. Merck), cyclopentanone (Fluka AG) and 2-methylcyclohexanone (Aldrich) were used as such without further purification and their solutions were prepared by directly dissolving the weighed sample in doubly distilled water. A solution of iridium(III) chloride (Johanson Matthey & Co.) was prepared by dissolving the sample in the minimum amount of hydrochloric acid (A.R.); the final strengths of acid and catalyst were 0.00624 and 3.35×10^{-3} M respectively. The strength of cerium(IV), prepared by dissolving the sample in 1:1 sulphuric acid, was determined by titrating it against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. All other chemicals used were either Analar or chemically pure substances. Progress of the reaction was measured (at constant temperature $\pm 0.1^\circ\text{C}$) at different intervals of time by transferring the aliquots to a fixed amount of ferrous ammonium sulphate solution [in slight excess to cerium(IV) sulphate initially taken] and titrating the ferrous ammonium sulphate remaining, 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. In all kinetic runs the cycloketone was present in excess.

* Author for correspondence

Determination of kinetic orders and stoichiometry

Iridium(III) chloride catalyzed oxidation of cyclopentanone and of 2-methylcyclohexanone by cerium(IV) sulphate in aqueous sulphuric acid was studied under the conditions and range in which the uncatalyzed reaction was negligible. The rate of reaction ($-dc/dt$), was obtained from the initial slopes of individual graphs plotted between the remaining concentration of cerium(IV) sulphate ($a-x$) versus time. The rate values ($-dc/dt$), thus obtained, were finally plotted against the changing concentrations 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 calculating rate values using the integrated first order rate equation (not given), by plotting $-dc/dt$ values versus concentration of the reactant, and by calculating the rate constant for molar concentrations (catalyst variation). Tables and figures contain initial concentrations of the reactants. Effects of cerium(III), chloride and hydrogen ions on the reaction velocity were studied by adding the ions externally. The ionic strength of the medium was kept constant with the help of a standard solution of potassium chloride.

The stoichiometry of the reaction was studied by taking cerium(IV) sulphate in a large excess compared to the organic substrate in different ratios, and thus complete oxidation of the organic substrate was ensured. The total amount of cerium(IV) sulphate consumed by one mole of organic substrate for its complete oxidation was determined. The final products, identified with the help of TLC and the spot test methods [7], were found to be the corresponding acids in both the cases. The stoichiometry of the reaction may be given according to the following equation:



where $R = -(CH_2)_4$ and $-CH_3CH(CH_2)_4$ for cyclopentanone and methylcyclohexanone respectively.

Results and discussion

Rate values increased with increasing concentration of the oxidant in the beginning, but at higher concentrations of the oxidant, the increase was not prominent (Table 1). This trend becomes clear on plotting $-dc/dt$ values versus [oxidant] (Figure 1), where the straight line passing through the origin tends to become parallel to the x -axis at higher concentrations. This shows that the reaction follows first order kinetics at low concentrations which tends to become zeroth order at higher concentrations of oxidant. This nature is further confirmed on plotting $\log(a-x)$ values [where, ($a-x$) is the remaining concentration of cerium(IV) at different time intervals] versus time (Figure 2), where deviations from straight lines are prominent at higher [Cerium(IV)]. Thus, if we

Table 1. Effect of variation of $[Ce(SO_4)_2]$, [Organic substrate], $[H^+]$ and $[IrCl_3]$ on the reaction rate at 30°C

$[Ce(SO_4)_2]^a$ $\times 10^3 M$	$-dc/dt \times 10^5 M \text{ min}^{-1}$		[Organic substrate] ^b $\times 10^2 M$	$-dc/dt \times 10^5 M \text{ min}^{-1}$		$[H^+]^c M$	$-dc/dt \times 10^5 M \text{ min}^{-1}$		$[IrCl_3]^d \times 10^6 M$	$-dc/dt/[IrCl_3] \text{ min}^{-1}$	
	(A)	(B)		(A)	(B)		(A)	(B)		(A)	(B)
0.25	—	0.36	0.20	—	0.92	0.16	—	2.00	0.17	—	16.47
0.35	0.72	0.47	0.30	—	1.10	0.20	2.75	—	0.25	—	14.40
0.45	0.91	—	0.40	1.41	1.25	0.22	—	1.62	0.33	—	11.51
0.50	—	0.50	0.50	—	1.22	0.28	2.60	—	0.35	11.42	—
0.60	1.13	—	0.60	1.53	—	0.30	—	1.50	0.50	10.90	10.60
0.70	—	0.84	0.70	—	1.40	0.40	2.20	1.22	0.80	12.50	—
0.90	1.38	—	0.80	1.70	—	0.60	2.00	1.12	0.84	—	9.80
1.0	—	1.21	1.00	1.88	1.50	0.80	1.77	—	1.17	—	10.43
1.25	1.50	—	1.40	2.00	1.60	0.90	—	0.80	1.20	10.42	—
1.40	—	1.55	2.00	1.83	1.69	1.00	1.70	—	1.68	—	9.52
1.80	1.75	1.84	3.00	2.10	—	1.20	1.50	0.80	1.80	9.42	—
2.50	1.77	2.00	4.00	2.20	—	1.60	—	0.54	2.35	—	10.04
3.50	1.80	—	—	—	—	1.70	1.33	—	2.50	10.28	—
									3.50	11.00	—

A cyclopentanone; B 2 methylcyclohexanone; $\mu = 2.60 M$. (A) $[Ce(SO_4)_2] = 1.25 \times 10^{-3} M$ (for b, c and d); [cyclopentanone] = $8.0 \times 10^{-3} M$ (for a, c and d); $[H_2SO_4] = 1.0 M$ (for a, b and d); $[IrCl_3] = 1.80 \times 10^{-6} M$ (for a, b and c); (B) $[Ce(SO_4)_2] = 1.00 \times 10^{-3} M$ (for b, c and d); [2-methylcyclohexanone] = $5.0 \times 10^{-3} M$ (for a, c and d); $[H_2SO_4] = 0.40 M$ (for a, b and d); $[IrCl_3] = 1.17 \times 10^{-6} M$ (for a, b and c).

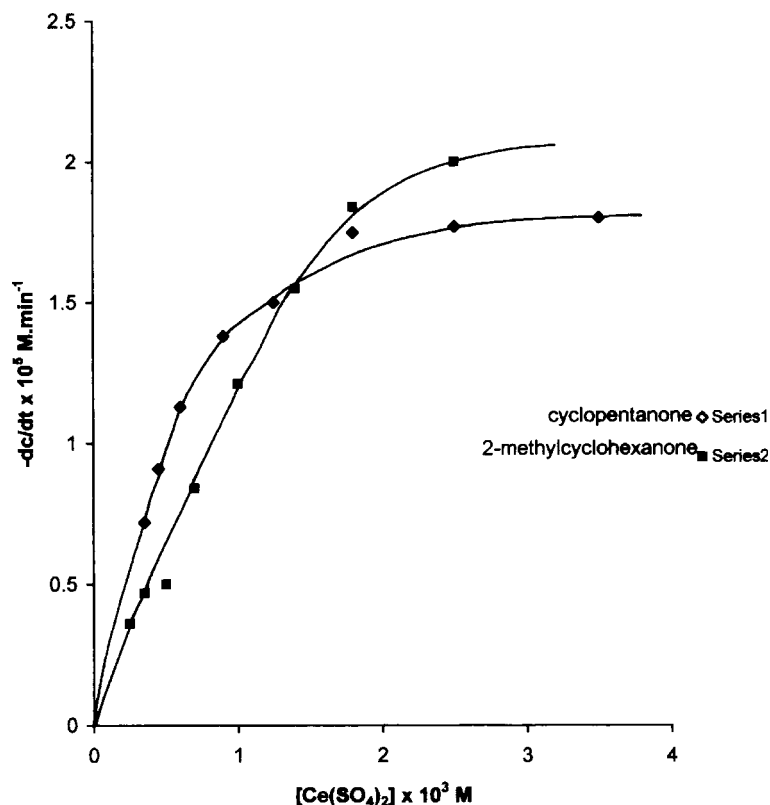


Fig. 1. Effect of variation of $[\text{Ce}(\text{SO}_4)_2]$ on the reaction rate at 30°C . (A) $[\text{Cyclopentanone}] = 8.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $[\text{IrCl}_3] = 1.8 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$. (B) $[\text{2-methylcyclohexanone}] = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$; $[\text{IrCl}_3] = 1.17 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$.

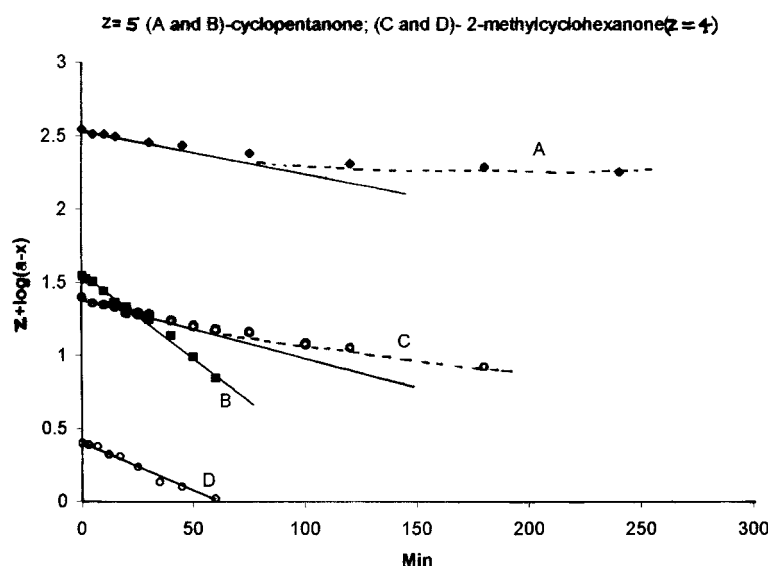


Fig. 2. Sample individual time plots for consumption of Ce^{IV} at 30°C for its highest and lowest concentrations. (A) $[\text{Ce}(\text{SO}_4)_2] = 3.50 \times 10^{-3} \text{ M}$; (B) $[\text{Ce}(\text{SO}_4)_2] = 0.35 \times 10^{-3} \text{ M}$; $[\text{Cyclopentanone}] = 8.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $[\text{IrCl}_3] = 1.8 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$. (C) $[\text{Ce}(\text{SO}_4)_2] = 2.50 \times 10^{-3} \text{ M}$; (D) $[\text{Ce}(\text{SO}_4)_2] = 0.25 \times 10^{-3} \text{ M}$; $[\text{2-methylcyclohexanone}] = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$; $[\text{IrCl}_3] = 1.17 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$.

plot $(a-x)$ values versus time, only in the higher concentration range of the oxidant, we obtain parallel straight lines (not given). The rate of the reaction shows first order kinetics with respect to cycloketones at low concentrations, which tend to become zeroth order at

higher concentrations of organic substrates (Table 1 and Figure 3). Increase in $-\text{dc}/\text{dt}$ values with increasing concentrations of the catalyst (Figure 4) and fair constancy in the rate values obtained for molar concentration of the catalyst (Table 1) indicate that the reaction

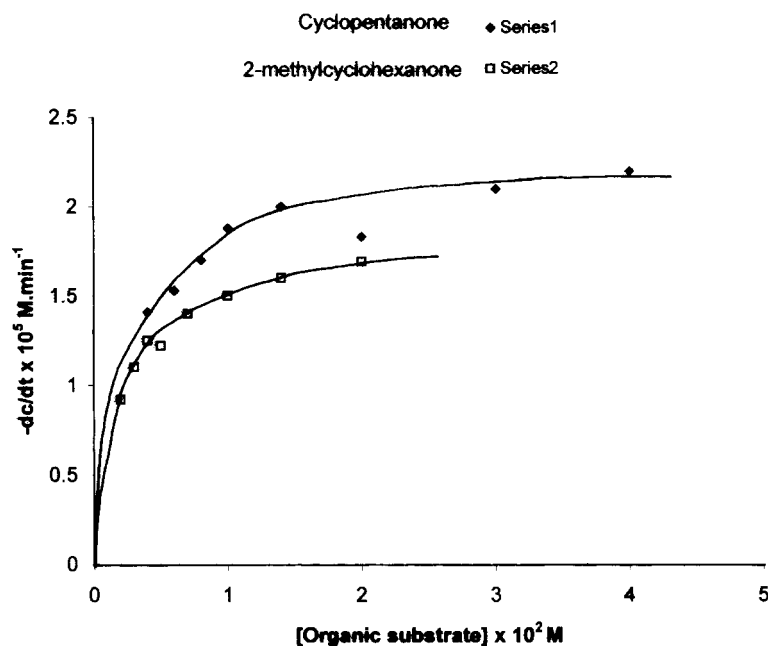


Fig. 3. Effect of variation of [organic substrate] on the reaction rate at 30°C. (A) $[\text{Ce}(\text{SO}_4)_2] = 1.25 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $[\text{IrCl}_3] = 1.8 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$. (B) $[\text{Ce}(\text{SO}_4)_2] = 1.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$; $[\text{IrCl}_3] = 1.17 \times 10^{-6} \text{ M}$; $\mu = 2.6 \text{ M}$.

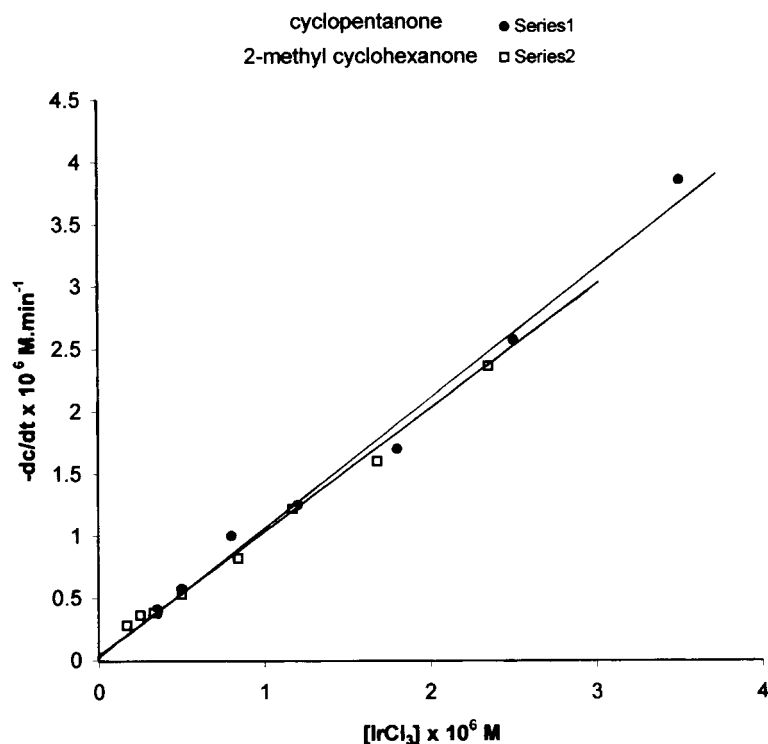


Fig. 4. Effect of variation of [Catalyst] on the reaction rate at 30°C. (A) $[\text{Ce}(\text{SO}_4)_2] = 1.25 \times 10^{-3} \text{ M}$; $[\text{cyclopentanone}] = 8.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $\mu = 2.6 \text{ M}$. (B) $[\text{Ce}(\text{SO}_4)_2] = 1.0 \times 10^{-3} \text{ M}$; $[\text{2-methylcyclohexanone}] = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$; $\mu = 2.6 \text{ M}$.

follows first order kinetics with respect to iridium(III) chloride for its manifold variation in concentration. 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 particularly prominent (Figures 5A and 6A). A similar trend in Table 2 for $[\text{Ce}^{\text{III}}]$ (Figures 5B and 6B) and $[\text{Cl}^-]$ (Figures 5C and 6C) ions is obtained. The rate

of the reaction was found to lie in the order: cyclopentanone > 2-methylcyclohexanone. This sequence is also confirmed from the energy of activation, entropy of activation and free energy of activation values, which were found to be 10.29 and 14.87, -69.56 and -68.41 , 21.09 and 20.79 for cyclopentanone and 2-methylcyclohexanone respectively. It is clear from the energy of activation values that the ease of formation of the

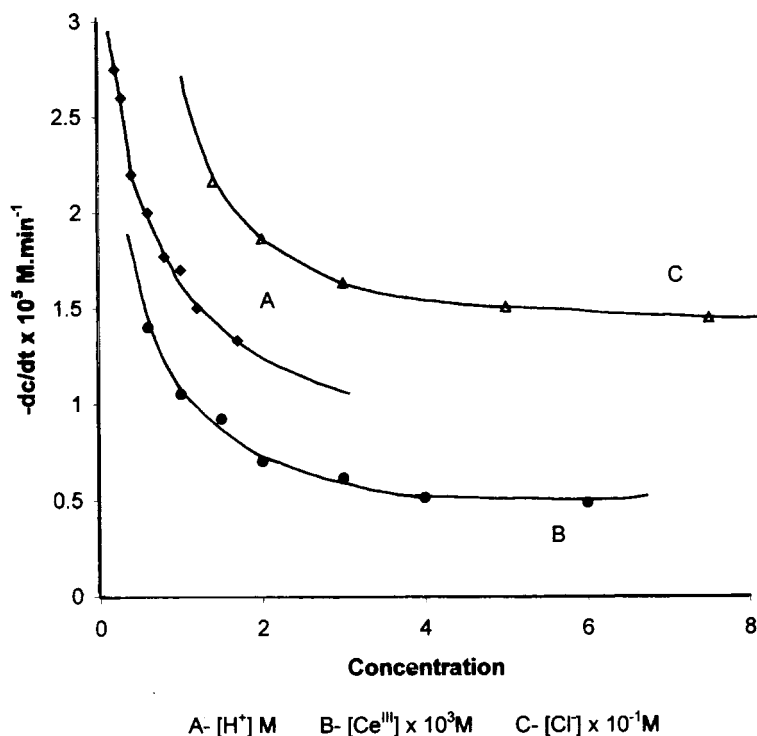


Fig. 5. Effect of variation of $[H^+]$, $[Ce^{III}]$ and $[Cl^-]$ on the reaction rate for cyclopentanone at 30°C (A). $[Ce(SO_4)_2] = 1.25 \times 10^{-3}$ M; $[cyclopentanone] = 8.0 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M (for B and C).

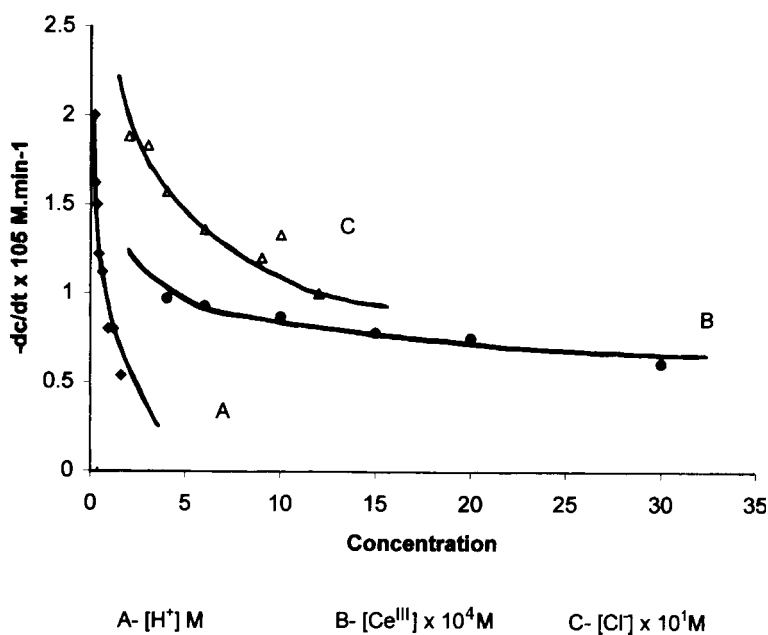
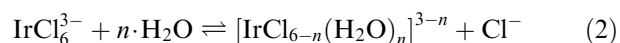


Fig. 6. Effect of variation of $[H^+]$, $[Ce^{III}]$ and $[Cl^-]$ on the reaction rate for 2-methylcyclohexanone at 30°C. (A) $[Ce(SO_4)_2] = 1.0 \times 10^{-3}$ M; $[2\text{-methylcyclohexanone}] = 5.0 \times 10^{-3}$ M, $\mu = 2.6$ M. $[H_2SO_4] = 0.40$ M (for B and C).

activated complex also lies in the above sequence. A similar trend is observed with the entropy values also. Nearly constant values of free energy of activation indicate that a similar mechanism is operative in the oxidation of both the cycloketones.

It is known that $IrCl_3$ in HCl gives $IrCl_6^{3-}$. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [9]. Furthermore, the

aquation of $[IrCl_6]^{3-}$ gives $[IrCl_5H_2O]^{2-}$, $[IrCl_4H_2O]^{2-}$ and $[IrCl_3(H_2O)_3]$ species [10–12] as shown by the following equilibrium (2)



During our study, the observation of a strong retarding effect by Cl^- ions on the reaction rate indicates that the

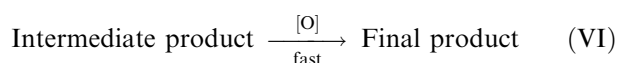
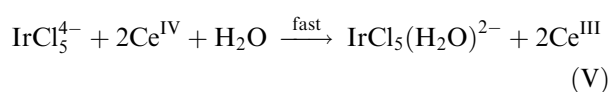
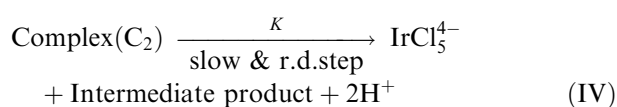
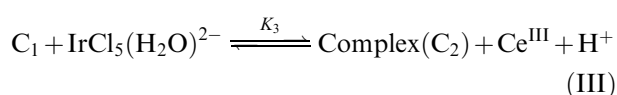
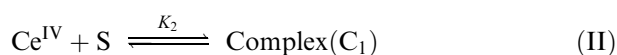
Table 2. Effect of variation of $[\text{Ce}^{\text{III}}]$ and $[\text{Cl}^-]$ ions concentrations on the reaction rate at 30°C

$[\text{Ce}_2(\text{SO}_4)_3] \times 10^3 \text{ M}$		0.40	0.60	1.00	1.50	2.00	3.00	4.00	6.00		
$-\text{dc}/\text{dt} \times 10^5 \text{ M min}^{-1}$	(A)		1.40	1.05	0.92	0.70	0.61	0.51	0.48		
	(B)	0.97	0.93	0.87	0.78	0.75	0.61	—	—		
$[\text{KCl}] \times 10^2 \text{ M}$		14.0	20.0	30.0	40.0	50.0	60.0	75.0	90.0	120.0	160.0
$-\text{dc}/\text{dt} \times 10^5 \text{ M min}^{-1}$	(A)	2.16	1.86	1.63	—	1.50	—	1.44	—	—	—
	(B)	—	1.88	1.83	1.57	—	1.36	—	1.20	1.33	1.00

(A) $[\text{Ce}(\text{SO}_4)_2] = 1.25 \times 10^{-3} \text{ M}$; [cyclopentanone] = $8.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $[\text{IrCl}_3] = 1.80 \times 10^{-6} \text{ M}$; $\mu = 2.60 \text{ M}$.

(B) $[\text{Ce}(\text{SO}_4)_2] = 1.00 \times 10^{-3} \text{ M}$; [2-methylcyclohexanone] = $5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$; $[\text{IrCl}_3] = 1.17 \times 10^{-6} \text{ M}$; $\mu = 2.60 \text{ M}$.

above equilibrium is shifted more towards the right hand side and that IrCl_6^{3-} cannot be considered as the reactive species [4, 13]. Therefore, considering our experimental results, $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ has been considered to be the reactive species of iridium(III) chloride in the present study. Cerium(IV) exists in various forms in sulphuric acid solution. Bugaenko and Huaf [14] have suggested that $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3$ are the prominent species up to 2.0 M and that $\text{H}_3\text{Ce}(\text{SO}_4)_4^{4-}$ exists above 2M H_2SO_4 . If we consider $\text{HCe}(\text{SO}_4)_3$ as the reactive species of cerium(IV) in the present study, then contrary to our experimental findings, direct proportionality of the reaction rate with increase in $[\text{H}^+]$ should be obtained. Hence, considering the range of acid concentration in which the study was performed, $\text{Ce}(\text{SO}_4)_2$ has been considered as the reactive species of cerium(IV). Thus, according to the proposed mechanism given in Scheme 1, cerium(IV) species combines with the organic substrate to give complex C_1 which in turn combines with iridium(III) hydroxy species to give the C_2 complex along with the elimination of cerium(III) and a hydrogen ion. Complex C_2 in the slow and rate determining step which breaks down into the iridium(I) species and the intermediate products. The iridium(I) species in the fast step takes up two cerium(IV) molecules to regenerate the iridium(III) hydroxy species while the intermediate product is further oxidized in the fast step to the final oxidation products.



where $[\text{S}]$ is organic substrate

Scheme 1.

Formation of a 1:1 complex between cerium(IV) and alcohols [15] and ketones [16], with the elimination of cerium(III) and H^+ ions, is well documented. Complex formation between cerium(IV) and alcohols to give complexes of composition $[\text{ROH.Cerium(IV)}]^{4+}$ and Michaelis–Menten type of kinetics has been reported [17]. While similar results have been reported in the case of ketones also [18, 19]. Formation of a complex between cerium(IV) and the organic substrate as obtained from our data, is supported by the change from first order to zero order kinetics and also from the constancy in the calculated rate constant k values only in the beginning when the complex formation is small. Deviations from constancy become more pronounced with increasing cerium(IV) or substrate concentrations. Now total concentration of iridium may be given according to Equation (3)

$$[\text{Ir}^{\text{III}}]_{\text{Total}} = [\text{IrCl}_6]^{3-} + [\text{IrCl}_5(\text{H}_2\text{O})]^{2-} + [\text{Complex C}_2] \quad (3)$$

Considering equilibrium concentration for steps I–III in the above mechanism, $[\text{IrCl}_5(\text{H}_2\text{O})^{2-}]$ can be calculated from step III by putting the value of complex C_1 from step II. Similarly $[\text{IrCl}_6^{3-}]$ can be calculated from step I, after putting the value of $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ obtained from step III. Equation (3) can be written in the terms of the concentration of the complex C_2 as:

$$[\text{Ir}^{\text{III}}]_{\text{T}} = \frac{[\text{C}_2][\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-]}{K_1 K_2 K_3 [\text{Ce}^{\text{IV}}][\text{S}]} + \frac{[\text{C}_2][\text{Ce}^{\text{III}}][\text{H}^+]}{K_2 K_3 [\text{Ce}^{\text{IV}}][\text{S}]} + \text{C}_2 \quad (4)$$

From the Equation (4), concentration of complex C_2 is obtained as

$$[\text{C}_2] = \frac{K_1 K_2 K_3 [\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}}{[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-] + K_1 [\text{Ce}^{\text{III}}][\text{H}^+] + K_1 K_2 K_3 [\text{Ce}^{\text{IV}}][\text{S}]} \quad (5)$$

Now the rate of the reaction in terms of decreasing concentrations of cerium(IV) from step (IV) 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 final rate law is obtained as given by Equation (6)

$$-d[\text{Ce}^{\text{IV}}]/dt = \frac{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}}{[\text{Ce}^{\text{III}}][\text{H}^+]\{[\text{Cl}^-] + K_1\} + K_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]} \quad (6)$$

This equation clearly accounts for first order kinetics with respect to iridium(III) chloride concentrations. The retarding effect of cerium(III), Cl^- and H^+ ions and the nature shown by cerium(IV) and organic substrate concentrations on the reaction velocity is also quite clear. Under the experimental conditions at low concentrations of cerium(IV) and organic substrate when $[\text{Cl}^-] \gg K_1$, the inequality $[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-] \gg K_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]$ may be assumed to be valid and the rate law(6) reduces to:

$$-d[\text{Ce}^{\text{IV}}]/dt = \frac{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}}{[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-]} \quad (7)$$

Equation (7) explains the first order kinetics with respect to cerium(IV) and organic substrate at low concentrations. The retarding nature shown by $[\text{Ce}^{\text{III}}]$, $[\text{H}^+]$ and $[\text{Cl}^-]$ on the reaction velocity is also explained. At higher concentrations the reverse inequality $[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-] \ll K_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]$ may be considered because the rate values were determined at the beginning of the reaction where the $[\text{Ce}^{\text{III}}]$ 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, $[\text{Cl}^-]$ will also be quite low. With the above inequality rate law (6) gives rise to Equation (8) which accounts for the first order kinetics as shown by iridium(III) chloride up to its manifold variations.

$$-d[\text{Ce}^{\text{IV}}]/dt = 2k[\text{Ir}^{\text{III}}]_{\text{T}} \quad (8)$$

The final rate law (6) can also be written in the form as

$$\begin{aligned} \frac{-d[\text{Ce}^{\text{IV}}]/dt}{[\text{Ir}^{\text{III}}]_{\text{T}}} &= k' \\ &= \frac{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]}{[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-] + K_1[\text{Ce}^{\text{III}}][\text{H}^+] + K_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]} \end{aligned} \quad (9)$$

Rate law (6) and (9) can be verified by rewriting these equations as (10) and (11) respectively

$$\begin{aligned} \frac{1}{\text{rate}} &= \frac{[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-]}{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}} \\ &+ \frac{[\text{Ce}^{\text{III}}][\text{H}^+]}{2kK_2K_3[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}} + \frac{1}{2k[\text{Ir}^{\text{III}}]_{\text{T}}} \end{aligned} \quad (10)$$

and

$$\frac{1}{k'} = \frac{[\text{Ce}^{\text{III}}][\text{H}^+][\text{Cl}^-]}{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]} + \frac{[\text{Ce}^{\text{III}}][\text{H}^+]}{2kK_2K_3[\text{Ce}^{\text{IV}}][\text{S}]} + \frac{1}{2k} \quad (11)$$

From Equation (10) it is clear that if $1/\text{rate}$ is plotted against $1/[\text{Ir}^{\text{III}}]$ or from equation (11) if $1/k'$ is plotted against $1/[\text{Ce}^{\text{IV}}]$, $1/[\text{S}]$ or $[\text{H}^+]$, we should obtain straight lines with positive intercepts at the y -axes. From the slopes of these straight lines k and kK_2K_3 values were calculated and are given in Table 3. While calculating the rate values, the concentration of cerium(III) produced in the reaction mixture was neglected, because at the beginning of the reaction where the rate values were calculated the concentration of cerium(III) produced in the reaction mixture will be quite small and can be neglected for the sake of simplicity. Fair agreement in k and kK_2K_3 values calculated from four different graphs further supports the proposed mechanism and the final rate law.

Alternatively $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ ion obtained from step I of Scheme 1 may combine with cycloketone in the second step giving rise to C_1 complex which may be oxidized by cerium(IV) as according to Scheme 2.

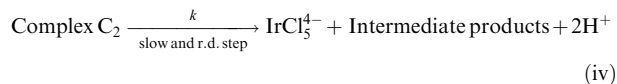
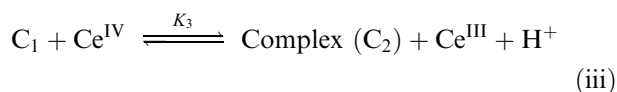
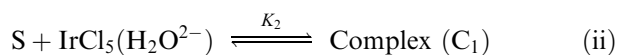
Other steps being same as in Scheme 1. In this case the final rate law in terms of the concentrations of various species comes out to be:

$$\begin{aligned} -d[\text{Ce}^{\text{IV}}]/dt &= \frac{2kK_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_{\text{T}}}{[\text{Ce}^{\text{III}}][\text{H}^+]\{[\text{Cl}^-] + K_1 + K_1K_2[\text{S}]\} + K_1K_2K_3[\text{Ce}^{\text{IV}}][\text{S}]} \end{aligned} \quad (12)$$

This rate law, although similar to the rate law obtained from Scheme 1, has an additional term in the denom-

Table 3. Rates obtained from the slopes and intercepts of various graphs at 30 °C

S. No.	Organic substrate	From the slope of the graph	$K \times 10^4$	$kK_2K_3 \times 10^{-6}$
(1)	Cyclopentanone	$1/k' \text{ versus } [\text{H}^+]$	—	1.77
		$1/k' \text{ versus } 1/[\text{S}]$	—	1.25
		$1/k' \text{ versus } 1/[\text{Ce}^{\text{IV}}]$	—	3.50
		$1/\text{rate versus } 1/[\text{Ir}^{\text{III}}]$	6.37	—
(2)	2-Methyl cyclohexanone	$1/k' \text{ versus } [\text{H}^+]$	—	1.22
		$1/k' \text{ versus } 1/[\text{S}]$	—	1.05
		$1/k' \text{ versus } 1/[\text{Ce}^{\text{IV}}]$	—	0.70
		$1/\text{rate versus } 1/[\text{Ir}^{\text{III}}]$	5.63	—



where [S] is organic substrate

Scheme 2.

inator and is ruled out because it is inconsistent with a linear plot of $1/\text{rate}$ versus $1/[\text{Ir}^{\text{III}}]$ and a linear dependence on cerium(IV) concentrations in the region where there is a linear dependence of the rate on catalyst concentrations. Further, the production of $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ during the oxidation of cyclohexanone by IrCl_6^{2-} , as reported by previous workers [20], also negates the probability of formation of complex directly between cycloketones and $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ species.

Another possibility for the production of $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ species in the system and its reaction with cycloketone to generate $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ along with elimination of hydrogen ion cannot be considered because the production of $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ before the rate determining step can not be accounted by the first order kinetics as shown by the catalyst in the present case.

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