

# Oxidation of ketones by ceric perchlorate catalysed by iridium(III)

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Received 12 November 2004; accepted 20 January 2005

## Abstract

In search of economical and effective catalysts it was found that  $\text{IrCl}_3$ , a sluggish catalyst in alkaline media, surpasses catalytic efficiency of osmium and ruthenium in aqueous perchloric acid medium in the oxidation of aliphatic ketones by ceric perchlorate. Rate decreases in the beginning at low acid concentrations, reaches to a minimum and then becomes proportional to  $[\text{HClO}_4]$ , probably due to conversion of hydrolysed to unhydrolysed species of ceric perchlorate, which then accelerates the rate. Reduction of oxidant by water depends on the concentrations of acid and [cerium(IV)] initially used. Orders are one with catalyst, one initially with respect to oxidant and ketones tending to become zeroth order at higher concentrations. No effect of change of  $\mu$  on the rate was observed. Thermodynamic data suggest that diethyl ketone (DET) forms the activated complex more easily compared to dimethyl ketone (DMT).

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*Keywords:* Iridium(III) chloride; Catalysis; Cerium(IV) perchlorate; Oxidation; Ketones

## 1. Introduction

Homogeneous catalysis by iridium(III) chloride in the oxidation of organic compounds has not been given attention due to sluggish catalytic behaviour of iridium compounds in alkaline medium. Interestingly it was observed by us that the average concentration of iridium(III) chloride ( $10^{-7}$  M), required to catalyse the oxidation of similar ketones, is at least hundred times less compared to the concentration of ruthenium(III) chloride with cerium(IV) sulphate [1] and osmium tetroxide with alkaline hexacyanoferrate(III) [2]. Formation of hazardous osmates restricts the use of osmium as homogeneous catalyst to the alkaline medium only while, ruthenium compounds get advantage as they can be used in acidic as well as in alkaline medium both. Main difference between the two lies in the fact that osmium adds to the double bond while ruthenium compounds are reported to break the double bond [3]. Homogeneous catalysis by iridium(III) chloride, belonging to the same group of periodic table, has been given little attention due to its sluggish catalytic activity in

alkaline medium [4]. It may be mentioned here that catalytic activities of ruthenium(VIII) in acidic medium [5] and the mechanistic steps involved in iridium(III) chloride catalysis in alkaline medium [4] were reported for the first time from our laboratory. Here we report the oxidation of dimethyl ketone and diethyl ketone by cerium(IV) perchlorate in aqueous perchloric acid medium catalysed by iridium(III) chloride.

## 2. Experimental

Sodium perchlorate, cerium(IV) sulphate (Loba Chemie Industralanal Co.), sulphuric acid, ferrous ammonium sulphate, ferroin, dimethyl ketone(DMT) (E. Merck) and diethyl ketone (DET) (Baker Analysed) were used as such without further purification and their solutions were prepared by directly dissolving the weighed sample in doubly distilled water. Solution of sodium hexachloroiridate(III) (Johnson Matthey and 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  $3.35 \times 10^{-3}$  M, respectively. The strength of cerium(IV) sulphate, prepared by dissolving the sample in 1:1 sulphuric

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acid, was determined by titrating it against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. Solution of ceric perchlorate was prepared by precipitating the ceric hydroxide [6] from the prepared solution of ceric ammonium nitrate with dilute solution of ammonium hydroxide. The gelatinous precipitate thus, obtained was washed several times with distilled water till the complete removal of sulphate ions and after drying the precipitate, it was re-dissolved in perchloric acid. 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 aliquot to a fixed amount of ferrous ammonium sulphate solution (in slight excess to cerium(IV) perchlorate initially taken) and titrating the remaining ferrous ammonium sulphate, 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) perchlorate consumed in the reaction mixture. In all kinetic runs ketone was present in excess.

### 2.1. Determination of kinetic orders and stoichiometry

Iridium(III) chloride catalysed oxidation of dimethyl ketone and diethyl ketone by cerium(IV) perchlorate in aqueous perchloric acid was studied under the conditions and range in which the uncatalysed reaction was negligible. Rate of reaction ( $-dc/dt$ ) was obtained from the initial slopes of individual graphs plotted between the residual concentration of cerium(IV) at various time intervals. In case of oxidant variation rate values were calculated at a fixed initial time while in all other cases they were calculated at a fixed initial concentration. The rate values ( $-dc/dt$ ) thus obtained were finally plotted against the changing concentrations of the particular reactant for which order of the reaction was to be obtained. Close resemblance in the rate values obtained by two methods, i.e.  $k_{\text{calculated}}$  (by using integrated first order rate equation and taking average of values in a particular set) and  $k_{\text{graphical}}$  (by dividing  $-dc/dt$  values with  $(a-x)$ , i.e. the residual concentration of cerium(IV) at the point at which rates were calculated), confirms authenticity of the results. 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). Tables and figures contain initial concentrations of the reactants. Ionic strength of the medium could not be kept constant in all the variations due to large volumes of sodium perchlorate required to keep the ionic strength constant. However, effect of  $\mu$  on the rate was studied separately with the help of a standard solution of sodium perchlorate.

*Stoichiometry* of the reaction was studied by taking cerium(IV) perchlorate in large excess compared to the organic substrate in different ratios, and thus complete

oxidation of the organic substrate was ensured. Total amount of cerium(IV) perchlorate consumed by 1 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  $\text{R} = -(\text{CH}_3)_2$  and  $-(\text{C}_2\text{H}_5)_2$  for DMT and DET, respectively.

### 3. Results

Sample individual time plots between  $\log(a-x)$  versus time for the lowest and highest concentrations of  $[\text{Ce}(\text{ClO}_4)_4]$  for two ketones show parallel straight lines (Fig. 1). In Table 1 the rate constant values obtained by two methods ( $k_{\text{graphical}}$  and  $k_{\text{calculated}}$ ) show constancy in the beginning, but the rate values in both cases start decreasing gradually with increasing [oxidant]. Trend in  $-dc/dt$  values shows that the values increase proportionately with increasing [oxidant] in the beginning but the increase is not prominent at higher concentrations. All these factors indicate that the reaction follows first order kinetics at low concentrations, which tends to become zeroth order at higher [oxidant]. This trend becomes clearer on plotting  $-dc/dt$  values versus  $[\text{Ce}(\text{ClO}_4)_4]$  where

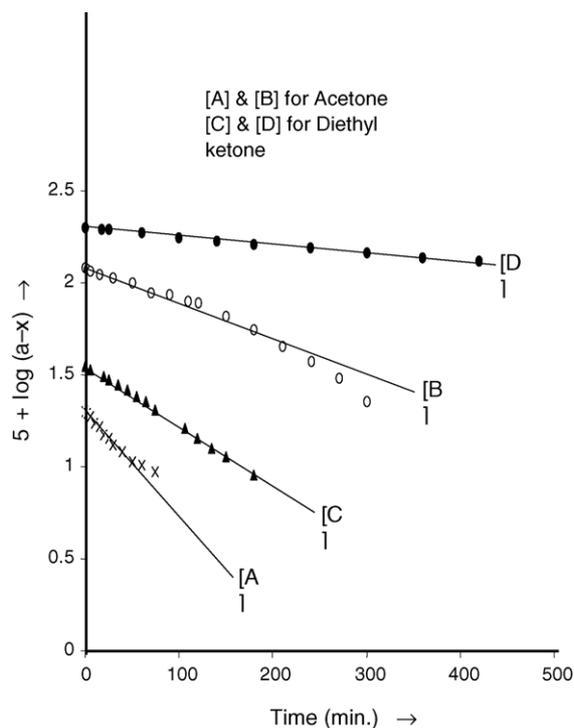


Fig. 1. Sample individual time plots for consumption of  $\text{Ce}^{\text{IV}}$  at  $25^\circ\text{C}$ :  $[\text{HClO}_4] = 0.75\text{ M}$ , (A)  $[\text{DMT}] = 4.0 \times 10^{-3}\text{ M}$ ,  $[\text{IrCl}_3] = 5.0 \times 10^{-7}\text{ M}$ ,  $[\text{Ce}(\text{ClO}_4)_4] = \text{A} - 2.0$ ; B -  $12.0 (\times 10^{-4}\text{ M})$ . (B)  $[\text{DET}] = 1.0 \times 10^{-3}\text{ M}$ ,  $[\text{IrCl}_3] = 2.0 \times 10^{-7}\text{ M}$ ,  $[\text{Ce}(\text{ClO}_4)_4] = \text{C} - 3.50$ ; D -  $20.0 (\times 10^{-4}\text{ M})$ .

Table 1  
Variation of [cerium(IV)] and [ketones] on the reaction rate at 25 °C

[Ce <sup>IV</sup> ] <sup>#</sup> × 10 <sup>4</sup> M min <sup>-1</sup>	-dc/dt × 10 <sup>6</sup> M min <sup>-1</sup>		k <sub>gr.</sub> × 10 <sup>2</sup> M min <sup>-1</sup>		k <sub>cal.</sub> × 10 <sup>2</sup> M min <sup>-1</sup>		[Ketone] <sup>*</sup> × 10 <sup>3</sup>	-dc/dt × 10 <sup>6</sup> M min <sup>-1</sup>		k <sub>gr.</sub> × 10 <sup>2</sup> min <sup>-1</sup>		k <sub>cal.</sub> × 10 <sup>2</sup> min <sup>-1</sup>	
	A	B	A	B <sup>Φ</sup>	A	B		A	B	A	B	A	B
2.0	2.22	–	1.27	–	1.22	–	0.50	–	0.90	–	0.26	–	0.29
3.0	2.92	–	1.08	–	1.00	–	0.75	–	1.20	–	0.34	–	0.39
3.5	3.46	1.72	1.08	5.0	1.03	6.60	2.00	2.19	3.00	0.62	0.86	0.72	0.86
4.0	3.85	1.90	1.07	5.0	1.10	6.00	3.00	3.13	4.16	0.89	1.19	0.98	1.27
4.5	4.50	2.08	1.10	5.1	1.15	5.49	4.00	3.85	5.83	1.10	1.67	1.11	1.70
5.0	5.00	2.16	1.10	4.5	1.15	4.39	5.00	4.23	7.14	1.20	2.04	1.12	2.09
5.5	–	2.27	–	4.3	–	4.40	5.50	4.33	–	1.24	–	1.19	–
7.0	5.00	–	0.81	–	0.88	–	6.00	4.64	8.33	1.33	2.38	1.22	2.40
7.5	–	2.64	–	3.9	–	3.33	7.00	5.00	10.00	1.43	2.86	1.43	2.60
9.0	5.00	2.70	0.59	3.0	0.60	2.49	8.00	5.00	–	1.43	–	1.31	–
10.0	–	2.70	–	2.7	–	2.20	9.00	5.36	12.50	1.53	3.57	1.40	3.58
11.0	5.25	2.67	0.50	2.5	0.53	2.27	10.00	5.36	12.80	1.53	3.66	1.54	3.84
12.0	5.00	2.67	0.45	2.3	0.43	2.00	11.00	5.45	–	1.56	–	1.56	–
12.5	–	2.75	–	2.2	–	1.67	12.00	5.45	–	1.56	–	1.64	–
15.0	–	2.69	–	2.0	–	1.50	–	–	–	–	–	–	–
20.0	–	2.67	–	1.3	–	1.10	–	–	–	–	–	–	–

[Ce(ClO<sub>4</sub>)<sub>4</sub>] = 4.0 × 10<sup>-4</sup> M (for \*), [HClO<sub>4</sub>] = 0.75 M, (A) [DMT] = 4.0 × 10<sup>-3</sup> M (for #), [IrCl<sub>3</sub>] = 5.0 × 10<sup>-7</sup> M (for \* and #). (B) [DET] = 1.0 × 10<sup>-3</sup> M, [IrCl<sub>3</sub>] = 2.0 × 10<sup>-7</sup> M, (for \* and #), for B<sup>Φ</sup>: k<sub>gr</sub> = 10<sup>-3</sup> min<sup>-1</sup>.

straight line passing through the origin tends to become parallel to the *x*-axis at higher concentrations (Fig. 2). Order of the reaction shows first order kinetics at low concentrations of organic substrates, which tends to become zeroth order at their higher concentrations. This trend becomes clear on plotting  $-dc/dt$  values versus [ketone] where straight line passing through the origin tends to become parallel to the *x*-axis at higher concentrations of organic substrates (Fig. 3). In Table 1, it is seen that  $-dc/dt$  values increase proportionately with increasing concentrations of organic substrates in the beginning but at higher concentrations

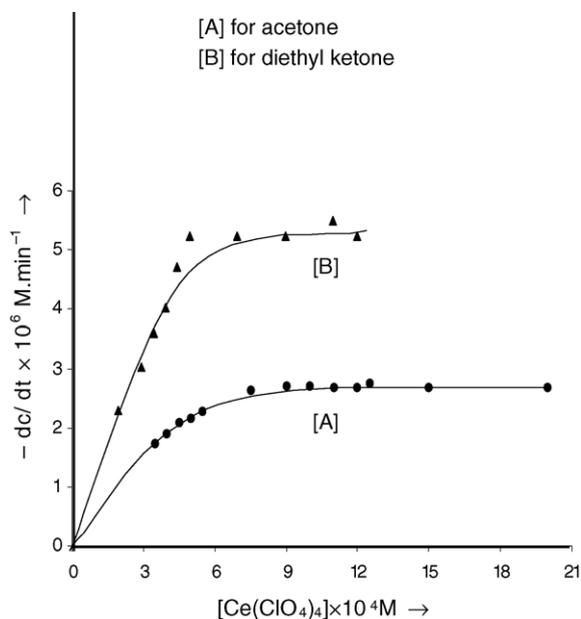


Fig. 2. Effect of variation of cerium(IV) concentrations on the rate at 30 °C. A and B indicate same things as in Fig. 1 except for [Ce(ClO<sub>4</sub>)<sub>4</sub>].

the increase is not so prominent.  $k_{gr}$  and  $k_{calc}$  values in Table 1 for organic substrate variation are constant only at low concentrations of organic substrates, while at higher concentrations a increasing trend is obtained in both these values. Proportionate increase in  $-dc/dt$ ,  $k_{gr}$  and  $k_{calc}$  values for more than ten-fold variation in catalyst concentration and fair constancy in  $k_{molar}$  values obtained for molar concentration of the catalyst  $\{k_{molar} = k_{gr}/[IrCl_3] = 2.43 \pm 0.14$  and  $2.83 \pm 0.16$  for dimethyl ketone and diethyl ketone, respectively} indicate that the reaction follows first order kinetics with respect to iridium(III) chloride concentrations (Table 2). On plotting double logarithmic graphs between  $\log k_{gr}$  and  $\log[IrCl_3]$  straight lines with slope values 0.926 and 1.06 were obtained (Fig. 4), which further confirm

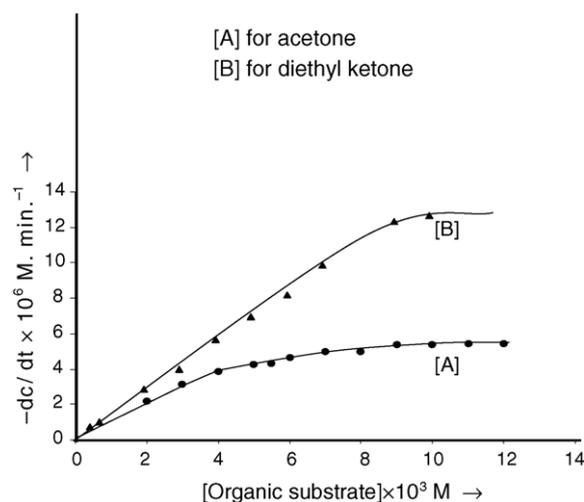


Fig. 3. Effect of variation of [organic substrate] on the reaction rate at 30 °C. (A and B) [Ce(ClO<sub>4</sub>)<sub>4</sub>] = 4.0 × 10<sup>-4</sup> M, [HClO<sub>4</sub>] = 0.75 M, [IrCl<sub>3</sub>] = A – 5.0, B – 2.0 (× 10<sup>-7</sup> M).

Table 2  
Variation of [iridium(III)] and  $[H^+]$  on the reaction rate at 25 °C

$[IrCl_3] \times 10^7$ M	$k_{gr} \times 10^2 \text{ min}^{-1}$		$k_{cal} \times 10^2 \text{ min}^{-1}$		$[HClO_4]$ M	$k_{gr} \times 10^2 \text{ min}^{-1}$		$k_{cal} \times 10^2 \text{ min}^{-1}$	
	A	B	A	B		A	B	A	B
1.0	–	0.32	–	0.34	0.50	1.56	0.71	1.53	0.69
2.0	–	0.59	0.40	0.58	0.60	1.43	0.58	1.49	0.59
3.0	0.71	0.82	0.58	0.86	0.75	1.10	0.55	1.09	0.57
4.0	0.91	1.13	0.72	1.07	1.00	0.98	0.59	0.92	0.69
5.0	1.10	1.43	1.11	1.42	1.50	0.91	0.66	0.96	0.64
6.0	1.43	1.62	1.49	1.59	2.00	1.05	0.82	0.93	0.73
7.0	–	1.96	–	1.99	2.50	1.16	–	1.18	1.18
8.0	2.04	–	2.02	–	3.00	1.42	–	1.08	–
9.0	2.32	2.37	2.31	2.45	3.50	1.71	1.43	1.28	0.99
10.0	2.50	2.77	2.50	2.84	4.00	1.84	1.59	1.88	1.11
11.0	2.86	3.08	2.88	3.05	4.50	–	1.79	–	1.14
12.0	3.07	–	3.18	–	5.00	–	2.00	–	1.14

(A)  $[Ce(ClO_4)_4] = 4.0 \times 10^{-4}$  M,  $[DMT] = 4.0 \times 10^{-3}$  M,  $[IrCl_3] = 5.0 \times 10^{-7}$  M,  $[HClO_4] = 0.75$  M. (B)  $[Ce(ClO_4)_4] = 4.0 \times 10^{-4}$  M,  $[DET] = 1.0 \times 10^{-3}$  M,  $[IrCl_3] = 2.0 \times 10^{-7}$  M,  $[HClO_4] = 0.75$  M.

direct proportionality of the reaction velocity with respect to  $[IrCl_3]$ . Table 2 indicates a peculiar nature in case of perchloric acid variation where it is seen that  $-dc/dt$ ,  $k_{gr}$  and  $k_{cal}$  values decrease in the beginning but after coming to a minimum the rate values start increasing with increasing  $[H^+]$ . This nature becomes clear from Fig. 5 where a dip in the graph is obtained in the beginning. Large volumes of sodium perchlorate required to maintain ionic strength of the medium constant restricted the study to be conducted at constant ionic strength of the medium. However, effect of change of ' $\mu$ ' on the reaction rate was studied separately. Change in ionic strength of the medium with the help of a standard solution of sodium perchlorate does not affect the reaction velocity and the rate values ( $-dc/dt$ ) remain constant at  $6.06 \pm 0.11$  and  $7.62 \pm 0.17$  for dimethyl ketone and diethyl ketone, respectively.

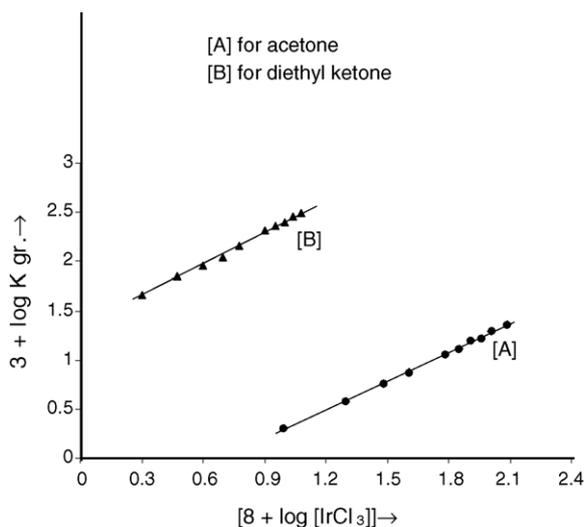


Fig. 4. Effect of variation of [catalyst] on the rate at 30 °C.  $[Ce(ClO_4)_4] = 4.0 \times 10^{-4}$  M,  $[HClO_4] = 0.75$  M, A –  $[DMT] = 4.0$ , B –  $[DET] = 1.0 (\times 10^{-3})$  M.

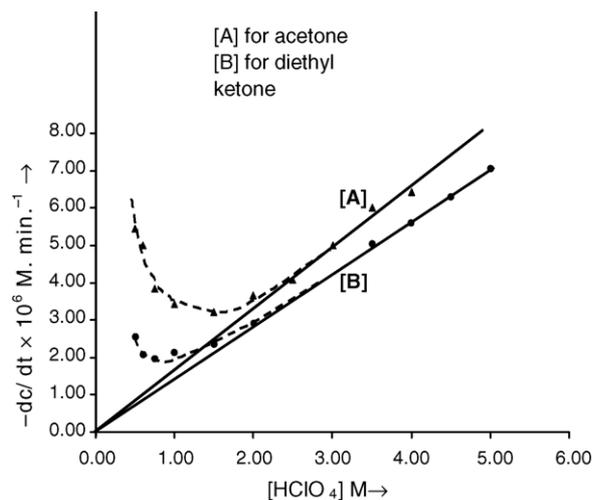
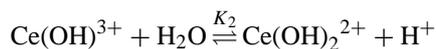


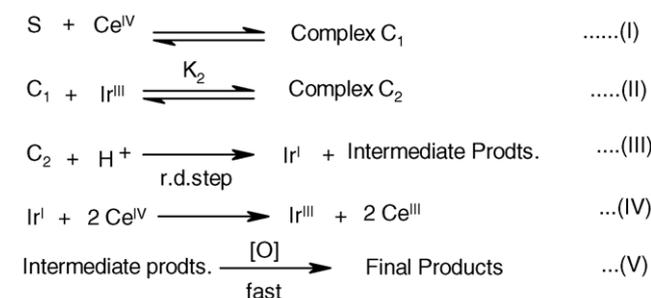
Fig. 5. Effect of variation of  $[H^+]$  on the rate at 25 °C. (A)  $[Ce(ClO_4)_4] = 4.0 \times 10^{-4}$  M,  $[IrCl_3] = 5.0 \times 10^{-7}$  M,  $[DMT] = 4.0 \times 10^{-3}$  M; (B)  $[Ce(ClO_4)_4] = 4.0 \times 10^{-4}$  M,  $[IrCl_3] = 2.0 \times 10^{-7}$  M,  $[DET] = 1.0 \times 10^{-3}$  M.

#### 4. Discussion

Perchloric acid is a strong oxidant but below 50% concentration and temperatures up to 50–60 °C, there is no release of oxygen, thus, it will not act as oxidant under the conditions in which the study was performed. Cerium(IV) in perchloric acid exists [8] in hydrolysed and unhydrolysed forms as according to the following equilibrium:



Predominant species of cerium perchlorate in aqueous perchloric acid medium is monomeric [9]. Increasing the concentration of  $H^+$  ions from 0.1 to 4.0 M, concentration of unhydrolysed species increases continuously while the concentration of hydrolysed species first increases and then



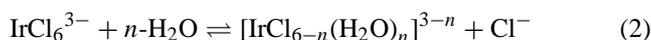
where S is org.substrate

Scheme 1.

from the vicinity of 1.0 M starts decreasing [10]. Our results, in the range of acid concentration where the studies were performed, indicate the presence of both hydrolysed as well as unhydrolysed species at low acid concentrations, while at higher concentrations of perchloric acid more and more hydrolysed species gets converted into the unhydrolysed species. From Fig. 5 it is clear that dip in graphs corresponds closely to the concentration from where concentration of hydrolysed species starts decreasing. This is probably due to the reason that hydrolysed species of cerium(IV) present at low acid concentrations, being more reactive, reacts with  $\text{H}^+$  ions giving rise to unhydrolysed species, which ultimately takes part in the reaction as given in Scheme 1. Rate decreases due to the conversion of hydrolysed species into the unhydrolysed species, which takes up hydrogen ions at low acid concentrations. With increasing  $[\text{H}^+]$  this conversion slows down and removal of  $\text{H}^+$  ions from the reaction mixture stops and normal accelerating effect of the  $\text{H}^+$  ions starts taking place. It was also observed, in ceric perchlorate and perchloric acid variations, that initial titre values were exceptionally high at low cerium(IV) and high acid concentrations, e.g. deviation in the initial titre values from those of the calculated ones, in case of dimethyl ketone and diethyl ketone, was found to be 43.08–14.79% and 22.2–9.79%, respectively, from the lowest to the highest cerium(IV) concentrations. All most same increase ( $\pm 2$ –3%) in zero readings was obtained even on performing the blank sets at similar concentrations without adding the organic substrate and catalyst. Indicating the probability of reduction of cerium(IV) to cerium(III) by water, which is rapid at higher acid concentrations. Reduction of cerium(IV) to cerium(III) may be checked if initial ceric concentration is high but high ceric concentrations favour the formation of unreactive polynuclear complexes. Possibly high acidity decreases the amount of hydrolysed species, which do not react with water. Thus, the study was performed at 0.75 M acid (except in acid variation) and maximum possible ceric concentration, to minimize the reduction of cerium(IV) to cerium(III) by water. The rate of reaction was found to be in the order: diethyl ketone > dimethyl ketone. This sequence is also confirmed from the energy of activation, entropy of activation and free energy of activation values, which were found to be 12.76 and 9.15,  $-26.66$  and  $-3993$ , 20.71 and 21.05 for dimethyl and diethyl ketones, respectively. It is clear from

the energy of activation values that the ease of formation of the 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  $\text{IrCl}_3$  in  $\text{HCl}$  gives  $\text{IrCl}_6^{3-}$  species [11]. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [12]. Furthermore, the aquation of  $[\text{IrCl}_6]^{3-}$  gives  $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ ,  $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$  and  $[\text{IrCl}_3(\text{H}_2\text{O})_3]$  species [13–15] as shown by the following equilibrium (2)



In our study no effect of chloride ions on the reaction rate was observed, which indicates that the above equilibrium is shifted more towards the left side and  $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$  cannot be considered as the reactive species [4,16]. Therefore, considering our experimental results,  $\text{IrCl}_6^{3-}$  has been considered to be the reactive species of iridium(III) chloride in the present study. Thus, according to the proposed mechanism (Scheme 1), cerium(IV) species combines with organic substrate to give complex  $\text{C}_1$ , which in turn combines with iridium(III) species to give the complex  $\text{C}_2$ . Complex  $\text{C}_2$  in the slow and rate determining step takes up a hydrogen ion giving rise to iridium(I) species and the intermediate product. Iridium(I) species in the fast step takes up two cerium(IV) molecules to regenerate the original iridium(III) species while the intermediate product is further oxidized in the fast step to the final oxidation products.

Formation of a 1:1 complex between cerium(IV) and alcohols [17] and ketones [18] 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 [19]. While similar results have been reported in the case of ketones also [20,21]. 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  $-dc/dt$ ,  $k_{\text{gr}}$  and  $k_{\text{calc}}$  values only in the beginning when the complex formation is small. Deviations from constancy become more pronounced at higher  $[\text{Ce}^{\text{IV}}]$  or  $[\text{substrate}]$ . Considering equilibrium concentrations in steps (I) and (II) of the mechanism and putting concentration of  $\text{C}_1$  from step (I) into the concentration of  $[\text{Ir}^{\text{III}}]$  obtained from step (II), total concentration of catalyst may be given as according to Eq. (3)

$$[\text{Ir}^{\text{III}}]_{\text{total}} = \frac{[\text{C}_2]}{K_1 K_2 [\text{S}] [\text{Ce}^{\text{IV}}]} + [\text{C}_2] \quad (3)$$

From Eq. (3) concentration of complex  $\text{C}_2$  is given as

$$[\text{C}_2] = \frac{K_1 K_2 [\text{Ce}^{\text{IV}}] [\text{S}] [\text{Ir}^{\text{III}}]_{\text{T}}}{1 + K_1 K_2 [\text{Ce}^{\text{IV}}]} \quad (4)$$

Rate in terms of decreasing concentration of cerium(IV) from step (III) of the mechanism may be given as

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = \frac{2kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}][\text{H}^+]}{1 + K_1K_2[\text{Ce}^{\text{IV}}][\text{S}]} \quad (5)$$

Equation is multiplied by 2 because two moles of cerium(IV) are required to regenerate the catalyst in its original form. This equation explains all experimental findings except the nature shown by the  $[\text{H}^+]$  ions at their low concentrations. Probable reason for the initial decrease in rate values at low acid concentrations has already been discussed in the beginning. At low concentrations of oxidant and organic substrate the inequality  $1 \gg kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}]$  may hold and Eq. (5) reduces to Eq. (6) which, explains the nature shown by various reactants.

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = 2kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}][\text{H}^+] \quad (6)$$

At higher concentrations of oxidant and substrate the reverse inequality  $1 \ll kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}]$  holds good and the equation becomes

$$\frac{-d[\text{Ce}^{\text{IV}}]/dt}{[\text{Ir}^{\text{III}}]_{\text{T}}[\text{H}^+]} = k' = \frac{2kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}]}{1 + K_1K_2[\text{Ce}^{\text{IV}}][\text{S}]} \quad (7)$$

where  $k'$  is another constant. Further verification of the rate law (5) may be given by rewriting Eq. (8) as

$$\frac{1}{V_i} = \frac{1}{k'} = \frac{1}{2kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}]} + \frac{1}{2k} \quad (8)$$

From this equation value of  $k$  from the intercepts between  $1/k'$  versus  $1/[\text{substrate}]$  and  $1/k'$  versus  $1/[\text{cerium(IV)}]$ , comes out to be 16.0; 21.05 and 62.50; 62.50, while the value of  $kK_1K_2$  from the slopes comes out to be 5.0;  $4.17 (\times 10^6)$  and 1.80;  $1.60 (\times 10^6)$  for dimethyl ketone and diethyl ketone, respectively. Fair constancy in the rate values calculated from two graphs further indicates the validity of Scheme 1 and the rate law (5).

Possibility of interaction between the organic substrate and iridium giving up the complex  $C_1$  in first step of Scheme 1, can be ruled out as no reaction between these two in the absence of oxidant was observed. No effect of chloride ions on the rate negates the possibility of their release before the rate determining step. Thus, the only alternative may be that cerium(IV) reacts with iridium(III) in the first step to form a complex, which in turn reacts with organic substrate to give the complex  $C_2$ . Exceptionally high values of initial

readings at low oxidant or high acid concentrations and reduction of cerium(IV) even in the absence of organic substrate indicate for this possibility, but instability of aqueous Ceric perchlorate solution in aqueous perchloric acid solution as reported by many workers may also result in the high initial readings. However, even the existence of this possibility will not affect the final rate law. Thus we can safely assume the validity of the final rate law and at least formation of the complexes before the rate determining step.

## Acknowledgement

S.S. and A.K.S. (C.S.T., U.P. D-3205) and M.P. (U.G.C. F.12-97/2001,SR-I) are grateful for the financial assistance.

## References

- [1] M.P. Singh, H.S. Singh, M.K. Verma, J. Phys. Chem. 84 (1980) 256.
- [2] V.N. Singh, H.S. Singh, B.B.L. Saxena, J. Am. Chem. Soc. 91 (1969) 2643.
- [3] L.M. Barkowitz, P.N. Rylander, J. Am. Chem. Soc. 80 (1950) 6682.
- [4] Manibala, H.S. Singh, B. Krishna, P.K. Tandon, J. Indian Chem. Soc. LXII (1985) 434.
- [5] P.K. Tandon, B. Krishna, Kinetika i Kataliz (USSR) 26 (1985) 607.
- [6] T.J. Hardwick, E.A. Robertson, J. Chem. Soc. 29 (1951) 828.
- [7] F. Feigl, Spot Tests in Organic Chemistry, Elsevier, New York, 1960, p. 369.
- [8] A.Y. Drummond, W.A. Waters, J. Chem. Soc. (1953) 440, 3119; A.Y. Drummond, W.A. Waters, J. Chem. Soc. (1955) 497.
- [9] K.B. Wiberg, Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965, p. 406.
- [10] K.B. Wiberg, Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965, p. 278.
- [11] J.C. Chang, C.S. Garner, Inorg. Chem. 4 (1965) 209.
- [12] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley-Interscience, 1999, p. 1039.
- [13] V.I. Kravtsov, G.M. Petrova, Russ. J. Inorg. Chem. (Engl. Transl.) 9 (1964) 552.
- [14] I.A. Poulsen, C.S. Garner, J. Am. Chem. Soc. 84 (1962) 2032.
- [15] A.P.J. Domingos, A.M.T.S. Domingos, J.M.P. Gabral, J. Inorg. Nucl. Chem. 31 (1969) 2568.
- [16] M.P. Singh, P.K. Tandon, R.M. Singh, A. Mehrotra, J. Indian Chem. Soc. 67 (1990) 458.
- [17] L.B. Young, W.S. Trahanovsky, J. Am. Chem. Soc. 91 (1969) 5060.
- [18] J.S. Littler, J. Chem. Soc. (1962) 832.
- [19] S.S. Muhammad, K.V. Rao, Bull. Chem. Soc. Jpn. 36 (1963) 943.
- [20] J. Shorter, J. Chem. Soc. (1950) 3425.
- [21] J. Shorter, C.N. Hinshelwood, J. Chem. Soc. (1950) 3276.