

Oxidation of cyclic ketones by cerium(IV) in presence of iridium(III) chloride

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Received 13 April 2006; received in revised form 23 May 2006; accepted 25 May 2006

Available online 11 July 2006

Abstract

Interestingly 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. Kinetic data, in iridium(III) chloride catalyzed oxidation of cyclopentanone and cycloheptanone by cerium(IV) perchlorate in aqueous perchloric acid medium, suggest the formation of complex C_1 between cerium(IV) and organic substrate in the first equilibrium step, which in turn gives rise to another complex C_2 with the catalyst. This second complex in the rate-determining step gives rise to the intermediate products. Rate decreases in the beginning at low acid concentrations, but after reaching to a minimum it becomes directly proportional to acid concentrations. Probably on increasing the acid concentration hydrolyzed species of ceric perchlorate gradually converts into the un-hydrolyzed species, which then accelerates the rate at higher $[\text{H}^+]$ resulting in the observed peculiar effect of hydrogen ions on the rate. Initial concentrations of cerium(IV) and acid determine the extent of reduction of cerium(IV) by water. Order of the reaction shows direct proportionality with respect to the low concentrations of oxidant and ketone, but tends to become zeroth order at their higher concentrations. Rate of the reaction shows direct proportionality with respect to $[\text{IrCl}_3]$ while change in ionic strength of the medium does not affect the reaction velocity. 2-Hydroxy cycloheptanone was confirmed spectrophotometrically as a reaction intermediate in the case of cycloheptanone. Energy of activation, free energy of activation and entropy parameters suggest that cyclopentanone forms the activated complex more easily compared to cycloheptanone. © 2006 Elsevier B.V. All rights reserved.

Keywords: Oxidation; Cyclic ketones; Cerium(IV) perchlorate; Iridium(III) chloride; Catalysis

1. Introduction

Several workers have reported homogeneous catalysis by ruthenium and osmium compounds. 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. 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 [1]. Homogeneous catalysis by iridium(III) chloride, which also belongs to the same group of periodic table, has been given little attention due to its sluggish catalytic activity in alkaline medium [2,3]. We have reported catalytic activity of ruthenium(VIII) in acidic medium [4] and mechanistic steps involved in iridium(III)

chloride catalysis in alkaline medium [2]. Interestingly it was observed by us [5] that the average concentration of iridium(III) chloride ($10^{-7} \text{ mol dm}^{-3}$), required to catalyze the oxidation of n-ketones, is at least hundred times less compared to the concentration of ruthenium(III) chloride with cerium(IV) sulphate [6] and osmium tetroxide with alkaline hexacyanoferrate(III) [7]. To see the efficiency of iridium(III) chloride to catalyze the oxidation of cyclic ketones, we have studied the oxidation of cyclopentanone and cycloheptanone by cerium(IV) perchlorate in aqueous perchloric acid medium catalyzed by iridium(III) chloride.

2. Experimental

Sodium perchlorate, cerium(IV) sulphate (Loba Chemie Industral Co.), sulphuric acid, ferrous ammonium sulphate, ferroin (E. Merck), cyclopentanone and cycloheptanone (Fluka A.G.) were used as supplied without further purification by preparing their solutions in doubly distilled water. Strength

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of sodium hexachloroiridate(III) (Johanson Matthey & Co.), prepared by dissolving the sample in minimum amount of A.R. HCl ($0.62 \times 10^{-2} \text{ mol dm}^{-3}$), was $3.35 \times 10^{-3} \text{ mol dm}^{-3}$. Cerium(IV) sulphate, prepared by dissolving the sample in 1:1 sulphuric acid, was titrated against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. Solution of ceric perchlorate was prepared by precipitating ceric hydroxide [8] from the prepared solution of ceric ammonium nitrate with dilute solution of ammonium hydroxide. The gelatinous precipitate thus obtained, after several washings with distilled water, was dried and re-dissolved in perchloric acid. All other chemicals used were either Analar or chemically pure substances. Progress of the reaction was measured (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 estimating the remaining ferrous ammonium sulphate, with a standard cerium(IV) sulphate solution using ferroin as an internal indicator. Thus, titre values directly correspond to the amount of $[\text{Ce}(\text{ClO}_4)_4]$ consumed in the reaction mixture. In all kinetic runs [ketone] was in excess.

2.1. Determination of kinetic orders and stoichiometry

Study was made after checking the un-catalyzed reaction. In the case of oxidant variation $-dc/dt$ values were calculated at a fixed initial time, while in all other cases values were calculated at a fixed initial concentration. Rate values ($-dc/dt$), obtained from the initial slopes of individual graphs between the residual concentrations of cerium(IV) at various time intervals, were finally plotted against the changing concentrations of the particular reactant for which order of the reaction was to be obtained. Close resemblance in the rate values obtained by two methods, i.e. $k_{\text{calculated}}$ (by using integrated first order rate equation 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. The study could not be made at constant ionic strength of the medium due to large quantities of sodium perchlorate required to keep the ionic strength constant. However, effect of μ on the rate was studied separately with the help of a standard solution of sodium perchlorate.

2.1.1. Stoichiometry

Stoichiometry of the reaction was studied by taking cerium(IV) perchlorate in large excess compared to the organic substrate in different ratios, to ensure complete oxidation of the organic substrate. Total amount of cerium(IV) perchlorate consumed by one mole of organic substrate for its complete oxidation was determined. Formation of dicarboxylic acids in both cases was confirmed by spot test methods [9] and chro-

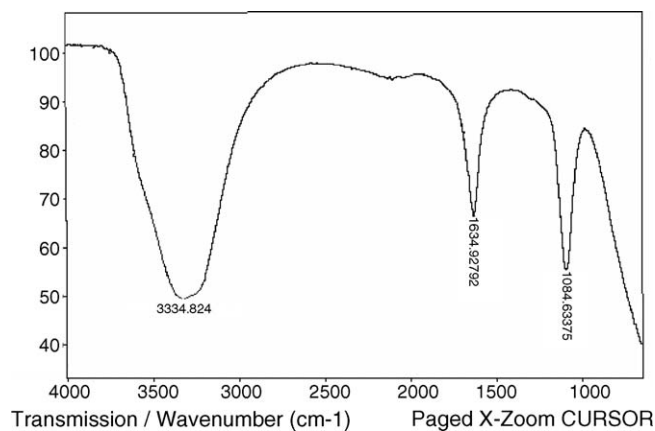
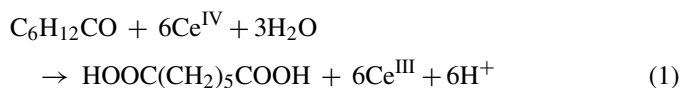


Fig. 1. IR spectra of hydroxyketone. $[\text{Ce}(\text{ClO}_4)_4] = 3.8 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{cycloheptanone}] = 1.7 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 5.5 \text{ mol dm}^{-3}$, $[\text{IrCl}_3] = 2.2 \times 10^{-5} \text{ mol dm}^{-3}$.

matographic techniques [10]. However, to follow the exact path by which the oxidation takes place, reaction mixture containing substrate: oxidant ratio (1:2.5 mol), was kept at desired temperature and then was repeatedly extracted with ether ($5 \times 25 \text{ ml}$). IR spectra of the ether extract of the reaction mixture in case of cycloheptanone (Fig. 1) (ABB Bomen, FTLA 2000 104), showed the peaks at 1094 (C–O stretch), 1635 (C=O stretch of ketone), 3335 (shifting of O–H stretch due to hydrogen bonding) indicating the formation of α -hydroxy ketone. This confirmed that the oxidation proceeds by the formation of α -hydroxy ketone, which converts into α -diketone and finally into the dicarboxylic acid. However, α -diketone could not be detected in the reaction mixture. Stoichiometry of the reaction, e.g. for cycloheptanone may be given by the following equation:



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. 2). Rate constant values obtained by two methods ($k_{\text{graphical}}$ and $k_{\text{calculated}}$) show fair constancy amongst themselves. These values start decreasing gradually with increasing [oxidant], while $-dc/dt$ values increase with increasing [oxidant] in the beginning but increase is not prominent at higher concentrations (Table 1). Thus, indicating that the reaction follows first order kinetics at low concentrations, which tends to become zeroth order at higher [oxidant]. This trend becomes clear on plotting $-dc/dt$ values versus $[\text{Ce}(\text{ClO}_4)_4]$ where straight line passing through the origin tends to become parallel to the x -axis at higher concentrations (Fig. 3). 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. 4). In

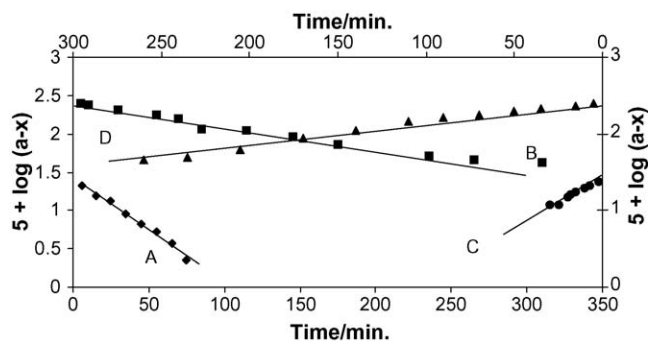


Fig. 2. Sample individual time plots for consumption of Ce^{IV} at 30°C . Cyclopentanone A and B; cycloheptanone C and D. $[\text{HClO}_4] = 0.75 \text{ mol dm}^{-3}$, $[\text{cyclopentanone}] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{IrCl}_3] = 4.0 \times 10^{-7} \text{ mol dm}^{-3}$, $[\text{Ce}(\text{ClO}_4)_4] = 0.25 \times 10^{-3} \text{ mol dm}^{-3}$ (A), $2.50 \times 10^{-3} \text{ mol dm}^{-3}$ (B). $[\text{HClO}_4] = 0.75 \text{ mol dm}^{-3}$, $[\text{cycloheptanone}] = 1.33 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{IrCl}_3] = 8.0 \times 10^{-7} \text{ mol dm}^{-3}$, $[\text{Ce}(\text{ClO}_4)_4] = 0.25 \times 10^{-3} \text{ mol dm}^{-3}$ (C), $2.50 \times 10^{-3} \text{ mol dm}^{-3}$ (D).

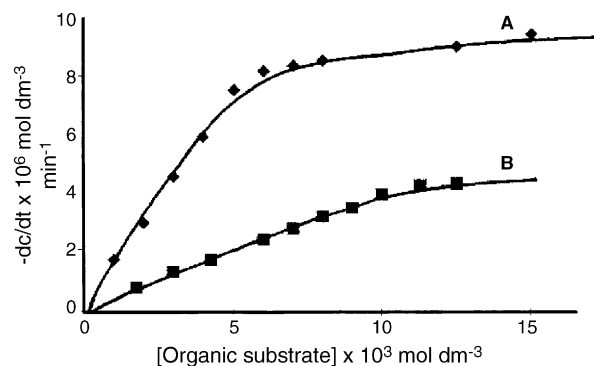


Fig. 4. Effect of variation of [organic substrate] on the rate at 25°C : cyclopentanone A; cycloheptanone B. (A) Cyclopentanone: $[\text{Ce}(\text{ClO}_4)_4] = 0.25 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.75 \text{ mol dm}^{-3}$, $[\text{IrCl}_3] = 4.0 \times 10^{-7} \text{ mol dm}^{-3}$. (B) Cycloheptanone: $[\text{Ce}(\text{ClO}_4)_4] = 1.43 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.75 \text{ mol dm}^{-3}$, $[\text{IrCl}_3] = 8.0 \times 10^{-7} \text{ mol dm}^{-3}$.

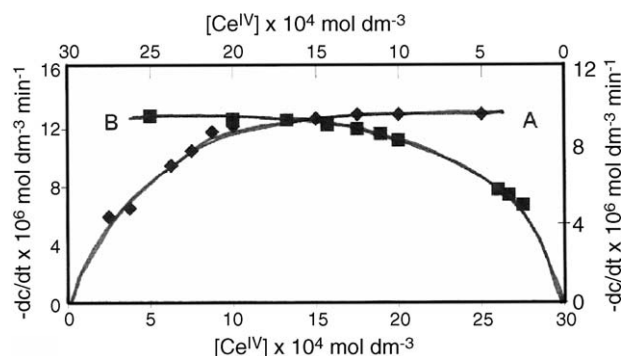


Fig. 3. Effect of variation of $[\text{Ce}^{\text{IV}}]$ on the rate at 25°C : cyclopentanone A; cycloheptanone B. A and B captions are same as in Fig. 1 except for $[\text{Ce}(\text{ClO}_4)_4]$.

Table 1 also $-\text{dc}/\text{dt}$, k_{gr} and k_{calc} values increase proportionately with increasing concentrations of organic substrates in the beginning but at higher concentrations the increase is not so prominent. Proportionate increase in $-\text{dc}/\text{dt}$, k_{gr} and k_{calc} values for more than 10-folds variation in catalyst concentration and fair constancy in k_{molar} values obtained for molar concentration of the catalyst $\{(k_{\text{molar}} = k_{\text{gr}}/[\text{IrCl}_3]) = 7.50 \pm 0.36$ and $4.88 \pm 0.93 (\times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1})$ for cyclopentanone and cycloheptanone, respectively} indicate that the reaction follows first order kinetics with respect to iridium(III) chloride concentrations (Table 2). On plotting double logarithmic graphs between $\log k_{\text{gr}}$ and $\log[\text{IrCl}_3]$ straight lines with slope values 0.97 and 1.01 were obtained (Fig. 5), which further supports direct proportionality of the reaction velocity w.r.t. $[\text{IrCl}_3]$. Trend in $-\text{dc}/\text{dt}$, k_{gr} and k_{calc} values given in Table 2 for perchloric acid variation indicates a specific nature. It is seen that these val-

Table 1
Effect of variation of [cerium(IV)] and [cyclic ketones] on the rate at 25°C

| $[\text{Ce}^{\text{IV}}]^b \times 10^4$ mol dm^{-3} | $-\text{dc}/\text{dt} \times 10^6 \text{ mol dm}^{-3} \text{ min}^{-1}$ | | $k_{\text{gr}} \times 10^2 \text{ min}^{-1}$ | | $k_{\text{calc}} \times 10^2 \text{ min}^{-1}$ | | [ketone] ^a $\times 10^3 \text{ mol dm}^{-3}$ | $k_{\text{gr}} \times 10^2 \text{ min}^{-1}$ | | $k_{\text{calc}} \times 10^2 \text{ min}^{-1}$ | |
|---|---|------|--|------|--|------|--|--|------|--|------|
| | A | B | A | B | A | B | | A | B | A | B |
| 2.5 | 5.90 | 5.0 | 3.03 | 2.50 | 2.99 | 2.47 | 1.00 | 0.80 | – | 0.84 | – |
| 3.33 | – | 5.50 | – | 2.40 | – | 2.23 | 1.75 | – | 0.60 | – | 0.84 |
| 3.75 | 6.50 | – | 2.46 | – | 2.07 | – | 2.00 | 1.31 | – | 1.20 | – |
| 4.0 | – | 5.78 | – | 1.70 | – | 1.78 | 3.00 | 2.07 | 1.04 | 2.17 | 1.11 |
| 6.25 | 9.47 | – | 1.75 | – | 1.50 | – | 4.00 | 2.68 | – | 2.85 | – |
| 7.50 | 10.50 | – | 1.64 | – | 1.50 | – | 4.25 | – | 1.39 | – | 1.79 |
| 8.75 | 11.80 | – | 1.69 | – | 1.57 | – | 5.00 | 3.41 | – | 3.41 | – |
| 10.0 | 12.20 | 8.40 | 1.37 | 0.91 | 1.20 | 0.94 | 6.00 | 3.71 | 2.00 | 3.75 | 2.05 |
| 11.11 | – | 8.75 | – | 0.87 | – | 0.93 | 7.00 | 3.79 | 2.28 | 3.69 | 2.33 |
| 12.50 | – | 9.00 | – | 0.82 | – | 0.85 | 8.00 | 3.89 | 2.61 | 4.03 | 2.58 |
| 14.30 | – | 9.20 | – | 0.67 | – | 0.78 | 9.00 | – | 2.86 | – | 2.58 |
| 15.0 | 12.73 | – | 0.92 | – | 0.94 | – | 10.00 | – | 3.25 | – | 3.00 |
| 16.75 | – | 9.47 | – | 0.59 | – | 0.69 | 11.25 | – | 3.50 | – | 3.34 |
| 17.50 | 13.0 | – | 0.81 | – | 0.86 | – | 12.50 | 4.10 | 3.58 | 4.25 | 3.94 |
| 20.0 | 13.0 | 9.50 | 0.74 | 0.50 | 0.74 | 0.56 | 15.00 | 4.26 | – | 4.40 | – |
| 25.0 | 13.0 | 9.70 | 0.59 | 0.40 | 0.63 | 0.49 | – | – | – | – | – |

^a $[\text{IrCl}_3] = \text{A: } 4.0, \text{ B: } 8.0 (\times 10^{-7} \text{ mol dm}^{-3})$; $(a-x) = \text{A: } 0.22, \text{ B: } 1.20 (\times 10^{-3} \text{ mol dm}^{-3})$; A: $[\text{cyclopentanone}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$; B: $[\text{cycloheptanone}] = 1.33 \times 10^{-3} \text{ mol dm}^{-3}$.

^b $[\text{HClO}_4] = 0.75 \text{ mol dm}^{-3}$; $[\text{Ce}(\text{ClO}_4)_4] = \text{A: } 0.25, \text{ B: } 1.43 (\times 10^{-3} \text{ mol dm}^{-3})$.

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

| $[Ir^{III}] \times 10^7$ mol dm^{-3} | $k_{gr} \times 10^2 \text{ min}^{-1}$ | | $k_{cal} \times 10^2 \text{ min}^{-1}$ | | $k_{molar} \times 10^4 \text{ min}^{-1}$ | | $[H^+] \times M$ | $-dc/dt \times 10^6$ $\text{mol dm}^{-3} \text{ min}^{-1}$ | | $k_{gr} \times 10^2 \text{ min}^{-1}$ | | $k_{cal} \times 10^2 \text{ min}^{-1}$ | |
|--|---------------------------------------|------|--|------|--|------|------------------|---|------|---------------------------------------|------|--|------|
| | A | B | A | B | A | B | | A | B | A | B | A | B |
| 0.25 | – | 0.16 | – | 0.16 | – | 6.40 | 0.60 | – | 4.68 | – | 4.93 | – | 4.88 |
| 0.45 | 0.36 | – | 0.36 | – | 7.89 | – | 0.75 | – | 4.20 | – | 4.42 | – | 4.42 |
| 0.50 | 0.40 | 0.31 | 0.41 | 0.31 | 7.90 | 6.20 | 1.00 | 3.30 | – | 3.67 | – | 3.30 | – |
| 0.75 | 0.59 | – | 0.60 | – | 7.87 | – | 1.25 | 2.96 | – | 3.29 | – | 3.28 | – |
| 1.00 | 0.75 | 0.52 | 0.88 | 0.53 | 7.50 | 5.20 | 1.50 | – | 3.60 | – | 3.79 | – | 3.86 |
| 3.00 | 2.22 | 1.29 | 2.20 | 1.12 | 7.40 | 4.30 | 2.00 | 2.27 | – | 2.52 | – | 2.63 | – |
| 4.00 | 2.95 | 1.79 | 2.93 | 1.59 | 7.38 | 4.50 | 2.20 | – | 3.80 | – | 4.00 | – | 4.17 |
| 5.00 | 3.57 | – | 3.07 | – | 7.14 | – | 2.70 | – | 4.47 | – | 4.71 | – | 4.78 |
| 6.00 | 4.17 | – | 3.76 | – | 6.94 | – | 3.00 | 2.06 | – | 2.29 | – | 2.68 | – |
| 6.50 | – | 2.67 | – | 2.77 | – | 4.10 | 3.20 | – | 5.00 | – | 5.26 | – | 5.30 |
| 8.00 | – | 3.33 | – | 3.20 | – | 4.20 | 3.50 | 2.18 | – | 2.42 | – | 2.29 | – |
| 10.0 | – | 4.17 | – | 4.12 | – | 4.20 | 4.00 | – | 6.15 | – | 6.47 | – | 5.53 |
| | | | | | | | 4.50 | 2.50 | – | 2.78 | – | 2.76 | – |
| | | | | | | | 5.00 | 2.90 | 6.90 | 3.20 | 7.26 | 3.44 | 7.30 |
| | | | | | | | 5.50 | 3.13 | – | 3.48 | – | 3.15 | – |
| | | | | | | | 6.00 | 3.57 | 9.44 | 3.97 | 9.94 | 3.94 | 9.89 |
| | | | | | | | 7.00 | 4.30 | 11.0 | 4.78 | 11.6 | 4.69 | 11.1 |

A: cyclopentanone, B: cycloheptanone. For catalyst variation— $[Ce(ClO_4)_4]$ =A: 0.25, B: 0.40 ($\times 10^{-3} \text{ mol dm}^{-3}$); [cyclic ketone]=A: 4.0, B: 1.33 ($\times 10^{-3} \text{ mol dm}^{-3}$); $[HClO_4]$ =0.75 mol dm^{-3} ; $(a-x)$ =A: 0.20, B: 0.30 ($\times 10^{-3} \text{ mol dm}^{-3}$). For acid variation— $[Ce(ClO_4)_4]$ =A: 1.0, B: 1.11 ($\times 10^{-3} \text{ mol dm}^{-3}$); A: [cyclic ketone] (A and B)= $2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $(a-x)$ =A: 0.90, B: 0.95 ($\times 10^{-3} \text{ mol dm}^{-3}$).

ues decrease in the beginning but after coming to a minimum, start increasing with increasing $[H^+]$. This nature becomes clear from Fig. 6 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 ' μ ' 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 9.42 ± 0.35 and 2.57 ± 0.07 ($\times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$) when oxidant, organic substrate, acid and catalyst concentrations were $0.40 \times 10^{-3} \text{ mol dm}^{-3}$, $4.0 \times 10^{-3} \text{ mol dm}^{-3}$, 0.75 mol dm^{-3} and $6.0 \times 10^{-7} \text{ mol dm}^{-3}$ respectively for cyclopentanone and $0.40 \times 10^{-3} \text{ mol dm}^{-3}$, $1.33 \times 10^{-3} \text{ mol dm}^{-3}$, 0.75 mol dm^{-3} and $6.0 \times 10^{-7} \text{ mol dm}^{-3}$ respectively for cycloheptanone.

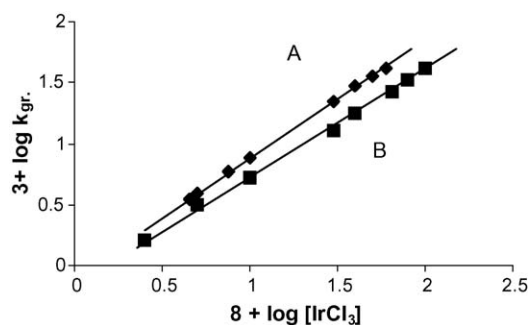
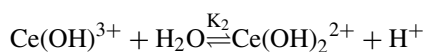


Fig. 5. Effect of variation of [catalyst] on the rate at 25 °C: cyclopentanone A; cycloheptanone B. (A) $[Ce(ClO_4)_4]$ = $0.25 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4]$ = 0.75 mol dm^{-3} , [cyclopentanone]= $1.25 \times 10^{-3} \text{ mol dm}^{-3}$, $(a-x)$ = $0.20 \times 10^{-3} \text{ mol dm}^{-3}$. (B) $[Ce(ClO_4)_4]$ = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4]$ = 0.75 mol dm^{-3} , [cycloheptanone]= $1.33 \times 10^{-3} \text{ mol dm}^{-3}$, $(a-x)$ = $0.30 \times 10^{-3} \text{ mol dm}^{-3}$.

4. Discussion

Below 50% concentration and temperatures up to 50–60 °C, there is no release of oxygen from perchloric acid, although it is a strong oxidant. Thus, it will not act as oxidant under the conditions in which the study was performed. Cerium(IV) in perchloric acid exists [11] in hydrolyzed and un-hydrolyzed forms as according to the following equilibrium:



Predominant species of ceric perchlorate in aqueous perchloric acid medium is monomeric [12]. Increasing the concentration of H^+ ions from 0.10 to 4.0 mol dm^{-3} , concentration of

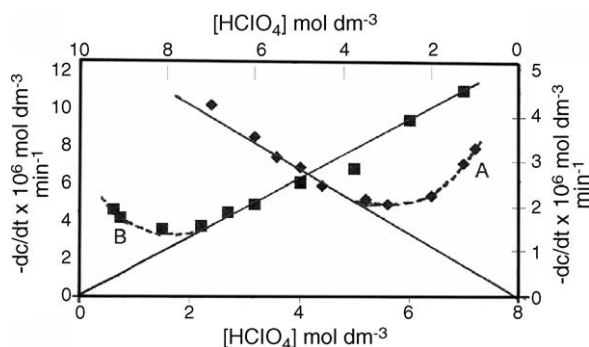
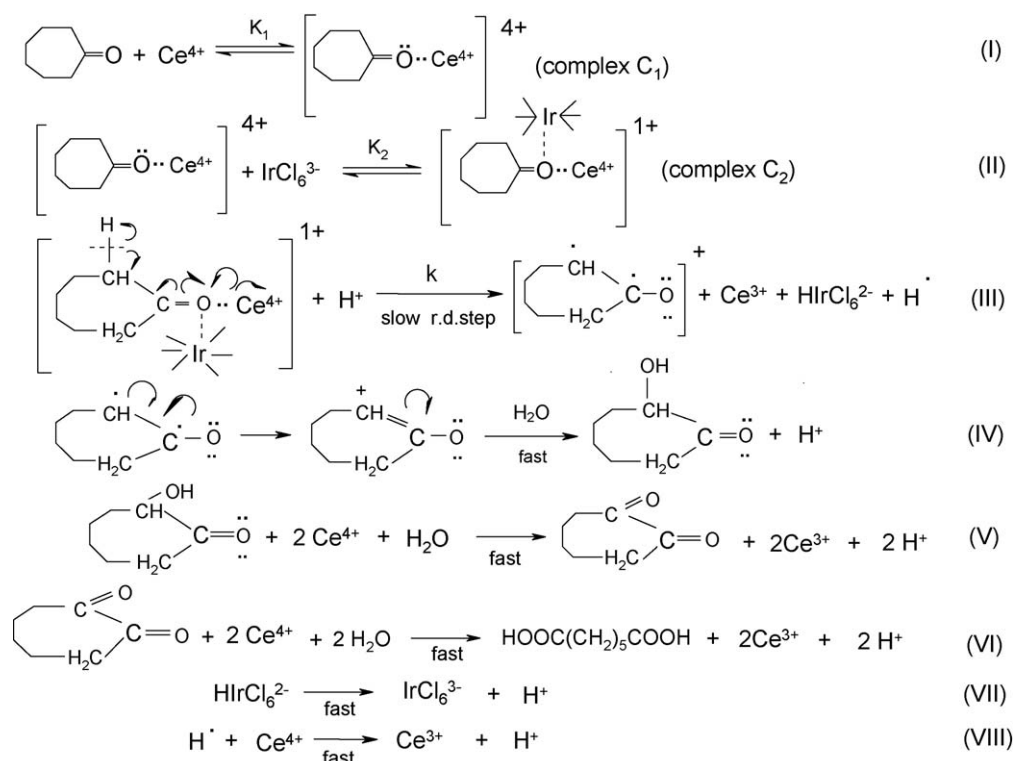


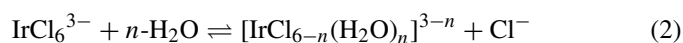
Fig. 6. Effect of variation of $[HClO_4]$ on the rate at 25 °C: cyclopentanone A; cycloheptanone B. (A) $[Ce(ClO_4)_4]$ = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, [cyclopentanone]= $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[IrCl_3]$ = $5.0 \times 10^{-7} \text{ mol dm}^{-3}$. (B) $[Ce(ClO_4)_4]$ = $1.11 \times 10^{-3} \text{ mol dm}^{-3}$, [cycloheptanone]= $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[IrCl_3]$ = $2.0 \times 10^{-7} \text{ mol dm}^{-3}$.



Scheme 1.

un-hydrolyzed species increases continuously while the concentration of hydrolyzed species first increases and then from the vicinity of 1.0 mol dm^{-3} starts decreasing [13]. Our results, in the range of acid concentration where the studies were performed, indicate the presence of both hydrolyzed as well as un-hydrolyzed species at low acid concentrations, while at higher concentrations of perchloric acid more and more hydrolyzed species gets converted into the un-hydrolyzed species. From Fig. 6 it is clear that dip in the graphs corresponds closely to the concentration from where concentration of hydrolyzed species starts decreasing. This is probably due to the reason that hydrolyzed species of cerium(IV) present at low acid concentrations, being more reactive reacts with H^+ ions giving rise to un-hydrolyzed species, which ultimately takes part in the reaction as given in Scheme 1. Rate decreases due to the conversion of hydrolyzed species into the un-hydrolyzed species, which takes up hydrogen ions at low acid concentrations. With increasing $[\text{H}^+]$ this conversion slows down and removal of H^+ ions from the reaction mixture stops and normal accelerating effect of the 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. deviations in the initial titre values from those of the calculated ones, in case of cyclopentanone and cycloheptanone, were found to be 34.66–2.86% and 54.8–1.56% respectively from the lowest to the highest cerium(IV) concentrations. All most same increase (± 2 –3%) in zero readings was obtained even on performing the blank sets at similar concentrations without adding the organic substrate and catalyst. This indicates 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 cerium(IV) concentration is high but high cerium(IV) concentrations favour the formation of un-reactive polynuclear complexes. Possibly high acidity decreases the amount of hydrolyzed species, which do not react with water. Thus, the study was performed at 0.75 M acid (except in acid variation) and maximum possible cerium(IV) concentration, to minimize the reduction of cerium(IV) to cerium(III) by water. The rate of reaction was found to be in the order: cyclopentanone > cycloheptanone. Arrhenius equation was found to be applicable and from the slopes of the Arrhenius plots and by using Eyring equation, different thermodynamic parameters were calculated. The sequence in the rate of oxidation is also confirmed from the energy of activation, entropy of activation and free energy of activation values, which were found to be 11.02 and 15.60 (kJ mol^{-1}), -33.24 and -15.12 ($\text{J K}^{-1} \text{ mol}^{-1}$), 20.10 and 20.93 (kJ mol^{-1}) for cyclopentanone and cycloheptanone, respectively. It is clear from the energy of activation values that the ease of formation of the activated complex also is in the above sequence. A similar trend is observed with the entropy values also. Nearly constant values of free energy of activation indicate that similar mechanism is operative in the oxidation of both the ketones. It is known that IrCl_3 in hydrochloric acid gives IrCl_6^{3-} species [14]. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [15]. Further, the equation 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 [16–18]. This equilibrium may be shown by the general Eq. (2):



No effect of chloride ions on the reaction rate in the present study 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 [2,3]. Therefore, considering our experimental results, IrCl_6^{3-} has been considered to be the reactive species of iridium(III) chloride in the present study. Further, change in the oxidation state of iridium during the course of the reaction may also result in the removal of chloride ion(s), leading to their negative effect on the reaction velocity, which was not observed in the present case indicating that change in the oxidation state of iridium may not be possible. Thus, according to Scheme 1, cerium(IV) species combines with organic substrate to give complex C_1 , which in turn combines with iridium(III) species to give the complex C_2 . Complex C_2 in the slow and rate-determining step takes up a hydrogen ion giving rise to protonated iridium species and the intermediate product, which on quick rearrangement gives rise to 2-hydroxycycloheptanone. Protonated iridium species quickly breaks up giving rise to the original iridium(III) species and a hydrogen ion. 2-Hydroxycycloheptanone by taking more of cerium(IV) ions ultimately gives rise to dicarboxylic acid.

Formation of 1:1 complexes between cerium(IV) and alcohols [19] and ketones [20] is well documented. Complex formation between cerium(IV) and alcohols to give complexes of composition $[\text{ROH}\cdot\text{cerium(IV)}]^{4+}$ and Michaelis–Menten type of kinetics has been reported [21]. While similar results have been reported in the case of ketones also [22–24]. Formation of complex between cerium(IV) and organic substrate in our data, gets support by the change from first order to zero order kinetics and also from the constancy in $-dc/dt$, k_{gr} and k_{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 [substrate]. Considering the equilibrium concentrations of complexes C_1 and C_2 in steps (I) and (II) of the mechanism and putting concentration of 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 the following equation:

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

From Eq. (3) concentration of complex 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

$$\frac{-d[\text{Ce}^{\text{IV}}]}{dt} = \frac{2kK_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}][\text{H}^+]}{1 + K_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}]} \quad (5)$$

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 $1 \gg kK_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}]$ may hold and Eq. (5) reduces to (6)

which, explains the nature shown by various reactants:

$$\frac{-d[\text{Ce}^{\text{IV}}]}{dt} = 2kK_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}][\text{H}^+] \quad (6)$$

At higher concentrations of oxidant and substrate, Eq. (5) may be written as

$$\frac{-d[\text{Ce}^{\text{IV}}]/dt}{[\text{Ir}^{\text{III}}]_{\text{T}}[\text{H}^+]} = k' = \frac{2kK_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}]}{1 + K_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}]} \quad (7)$$

where k' is another constant. Further verification of the rate law (5) may be given by rewriting Eq. (7) as

$$\frac{1}{V_i} = \frac{1}{k'} = \frac{1}{2kK_1 K_2 [\text{Ce}^{\text{IV}}][\text{S}]} + \frac{1}{2k} \quad (8)$$

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 100.0; 84.20 and 83.33; 87.72, while the value of $kK_1 K_2$ from the slopes comes out to be 11.50; 7.15 ($\times 10^6$) and 2.88; 2.75 ($\times 10^6$) for cyclopentanone and cycloheptanone, 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 rise to 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, we can safely assume the validity of the final rate law (5) and formation of complexes before the rate-determining step.

Acknowledgements

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.

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