

Kinetics and Mechanism of Ir(III) Catalyzed Oxidation of Acetone by Cerium(IV) in Aqueous Perchloric Acid Media

FIROZ KHAN, USHA KUSHWAHA, AMITA SINGH and A.K. SINGH*
Department of Chemistry, Bipin Bihari P.G. College, Jhansi-284 001, India
E-mail: firoz_khan_12345@yahoo.com

Kinetics and mechanism of iridium(III) (*ca.* 10^{-6} mol dm⁻³) catalyzed oxidation of acetone by cerium(IV) in aqueous perchloric acid medium have been investigated at different temperatures (20-35 °C) under the conditions $[\text{CH}_3\text{COCH}_3]_{\text{T}} \gg [\text{Ce(IV)}]_{\text{T}} \gg [\text{Ir}]_{\text{T}}$. The rate law conforms

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

where *k*, *K*₁ and *K*₂ are constants at a particular temperature at a fixed $[\text{H}^+]$ and $[\text{Ir}]_{\text{T}}$ gives the total concentration of iridium added as catalyst. An intermediate involving the oxidant, catalyst and substrate has been proposed as being formed in pre-equilibrium steps before the electron transfer step through the Ir(III)/Ir(IV) catalytic cycle. The electron transfer (inner sphere mechanism) leads to the partially oxidized product which is rapidly oxidized by cerium(IV) at a fast step. The predominant species of Ce(IV) perchlorate in aqueous perchloric acid medium is monomeric, hence unhydrolyzed species Ce⁴⁺ and hydrolyzed species Ce(OH)³⁺ have been found as the kinetically active species.

Key Words: Acetone, Perchloric acid, Cerium(IV) perchlorate, Hydrolyzed species, Thermodynamic parameters.

INTRODUCTION

Several kinetic investigations on redox reactions involving Ce(IV) and different type of inorganic and organic compounds including different alcohols have been carried out¹⁻³. Singh *et al.*⁴ in the oxidation of aliphatic ketone by N-bromoacetamide (NBA) have reported first order dependence on $[\text{H}^+]$. General scheme for the formation of complex between cerium(IV) species and ketone has been discussed by Bamford and Tipper⁵. Kinetics of oxidation of some ketones and alcohol has been well studied by Tandon *et al.*⁶⁻⁸ by Ce(IV) and various other oxidant using ruthenium or palladium metal ions has homogenous catalysts in acidic or alkaline medium. Thus the present system appears worth exploring from the stand point of comparison with that of Ru(III) catalysis in the title reaction.

Different metal ion catalysts have been used⁹ in oxidation reaction by Ce(IV) in aqueous perchloric acid media. Among the different metal ions, Ru(III)^{10,11} and Ir(III)¹² have been found to be highly efficient. Ir(III) catalysis in oxidation reactions by Ce(IV) in aqueous perchloric acid media has been reported in a very few cases.

In different cases, different reaction mechanism have been proposed. Moreover some previous workers have reported¹³ Ir(III) catalyzed decompositions of Ce(IV) in aqueous sulphuric acid media at elevated temperatures through the oxidation of water. Oxidation of D-arabinose and D-ribose by N-bromoacetamide in perchloric acid medium was studied by Singh *et al.*¹⁴. Oxidation of benzaldehyde was studied by Tandon *et al.*¹⁵ The presence of such catalytic decomposition of Ce(IV) may complicate the interpretation of kinetic data. Infact, more work is needed to understand the mechanistic routes for Ir(III) catalysis in oxidation reactions by Ce(IV) in aqueous perchloric acid medium.

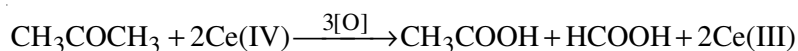
EXPERIMENTAL

The solutions of various substrates were prepared by directly dissolving the weighed sample in double distilled water. The solution of ceric sulphate, which was used as titrant, was prepared by taking approximate amount in 1:1 sulphuric acid. The mixture was heated with constant stirring and addition of small quantities of distilled water several times until major part of the salt was dissolved. The estimation of ceric sulphate was done with a standard solution of ferrous ammonium sulphate using ferroin as a redox indicator. The solution of ceric perchlorate was prepared by precipitating the ceric hydroxide from the prepared solution of ceric ammonium nitrate with dilute solution of NH_4OH . A gelatinous precipitate was obtained which was filtered and washed several times with distilled water till the complete removal of sulphate ion. Precipitate was dried and then it was redissolved in perchloric acid to get a clear solution of ceric perchlorate. The solution of iridium(III) chloride was prepared by dissolving the sample (Johnson Matthey Chemicals Ltd.) in dilute solution of hydrochloric acid. The final strengths of hydrochloric acid and iridium(III) chloride were 6.24 and 3.35×10^{-3} M, respectively.

The calculated quantity of organic compound was transferred into the conical flask containing Ce(IV) perchlorate, perchloric acid and the catalyst. The time was noted when nearly half of the component had passed into the reaction vessel. Progress of the reaction was measured at different intervals of time by estimating the remaining amount of Ce(IV) sulphate in the reaction mixture. The amount of ferrous ammonium sulphate (quenching agent) left was titrated against a standard solution of ceric sulphate to the ferroin end point. The progress of the reaction was noted by withdrawing an aliquot of 5 mL from the reaction mixture at different time intervals and pouring it in a conical flask containing a calculated slight excess of ferrous ammonium sulphate. The titer values of ceric sulphate were directly proportional to the ceric perchlorate consumed in the reaction mixture.

Stoichiometry and the product analysis: A series of experiments were performed by taking a number of reaction mixtures in which the concentration of ceric perchlorate was kept in large excess compared to that of organic substrates in varying ratios. The reaction mixtures were kept at room temperature (25 °C) for 24 h. The solution was concentrated on a water bath. The components in the concentrated

solution were identified with the help of paper chromatography technique using authentic samples of the various components. The results suggest that the main over all iridium(III) catalyzed redox process conforms to the following stoichiometry.



RESULTS AND DISCUSSION

Dependence of rate on cerium(IV) concentration: Under the condition $[\text{CH}_3\text{COCH}_3]_{\text{T}} \gg [\text{Ce(IV)}]_{\text{T}} \gg [\text{Ir}]_{\text{T}}$ in 0.75 mol dm^{-3} perchloric acid media, the rate of disappearance of Ce(IV) shows a first order dependence on $[\text{Ce(IV)}]$. Confirmation of the nature of the reaction can be seen from the individual plots (Figs. 1 and 2) final confirmation of the order of reaction with respect to ceric perchlorate concentration was obtained by plotting $-\text{dc}/\text{dt}$ values against the concentration of ceric perchlorate as shown in Fig. 3, from which it is clear that the reaction follows first order kinetics at low concentrations of the oxidant tending toward zero order at its higher concentration. The dependence is given by:

$$\frac{-\text{d} \ln[\text{Ce(IV)}]}{\text{d}t} = k_0 \quad (1)$$

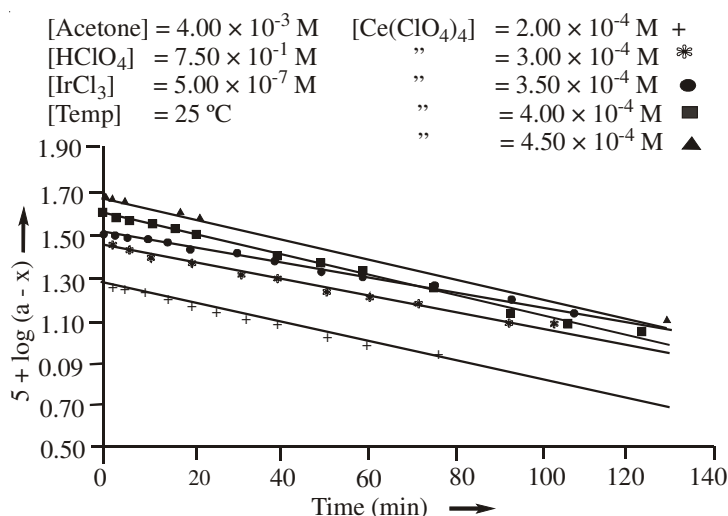


Fig. 1. Individual plots showing change of $[\text{Ce(ClO}_4)_4]$ in case of acetone

Dependence of rate on acetone concentration: At lower concentration of acetone the reaction follows first order kinetics with respect to $[\text{acetone}]$ which tends to become zero order at its higher concentration final confirmation comes from Fig. 4, where on plotting $-\text{dc}/\text{dt}$ values against acetone concentrations a straight line is obtained in the beginning which becomes parallel to the x-axis at higher concentration of acetone. The dependence can be expressed as:

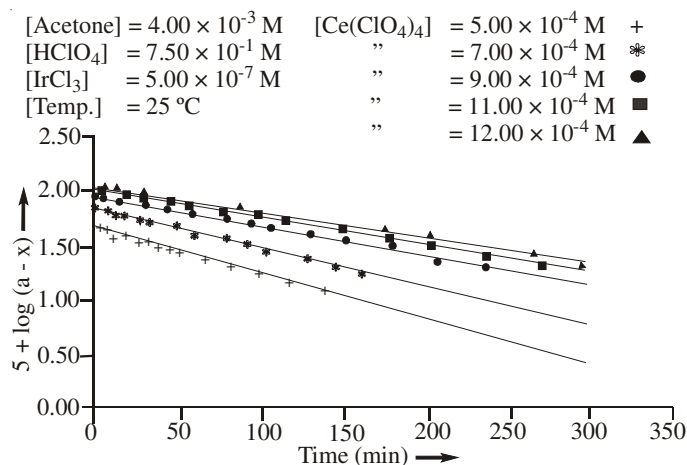
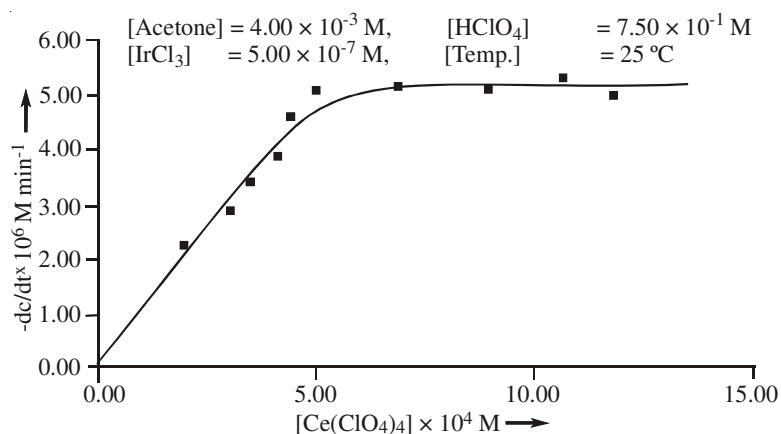
Fig. 2. Individual plots showing change of [Ce(ClO₄)₄] in case of acetone

Fig. 3. Effect of variation of cerium(IV) perchlorate concentration on the reaction velocity in the oxidation of acetone

$$k_0 = \frac{m[\text{CH}_3\text{COCH}_3]_T}{n + p[\text{CH}_3\text{COCH}_3]_T} \quad (2)$$

(where $[\text{CH}_3\text{COCH}_3]_T$ give the total concentration of acetone; m , n and p are constant). At high values of $[\text{CH}_3\text{COCH}_3]_T$, $p[\text{CH}_3\text{COCH}_3] \gg n$ and it explains the zero order dependence on substrate concentration.

Dependence of rate on catalyst concentration: Under the experimental conditions, the catalysis is so efficient that the uncatalyzed path remains kinetically non-existent. There is direct proportionality of the reaction velocity with the concentration of iridium(III) chloride. The final confirmation of direct proportionality of the reaction velocity with the concentrations of iridium(III) chloride comes (Fig. 5), where a straight line is obtained with a slope value of 0.926.

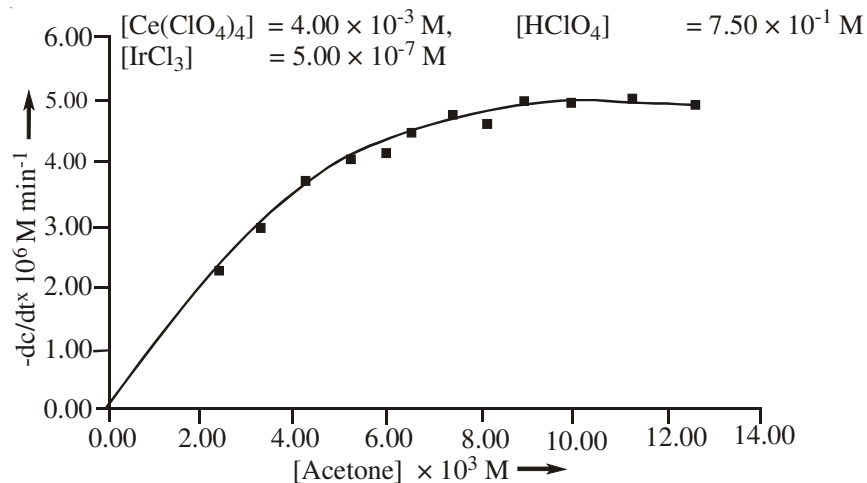
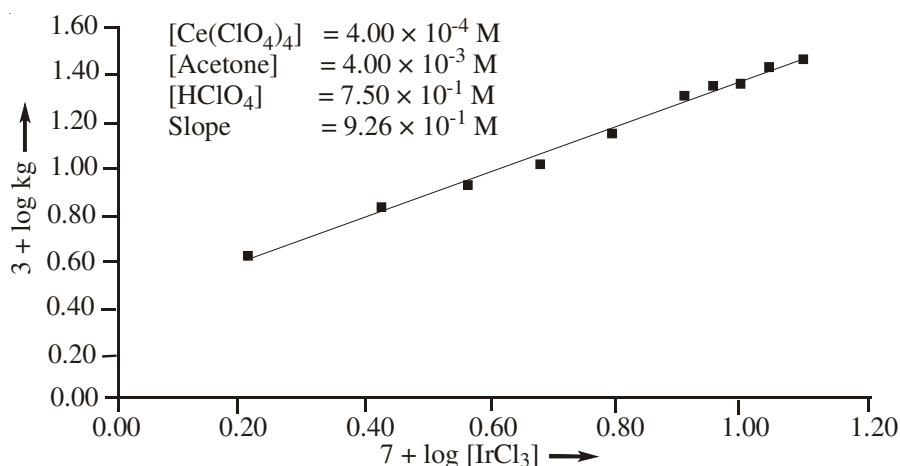


Fig. 4. Effect of variation of [acetone] on the reaction velocity at 25 °C

Fig. 5. Effect of variation of $[\text{IrCl}_3]$ on the reaction velocity in the oxidation of acetone at 25 °C

Dependence of rate on perchloric acid concentration: It is observed that the rate constant value *i.e.* k graphical as well as k calculated value decrease in the beginning with increasing $[\text{H}^+]$. After a short period the rate values start increasing proportionately with increasing $[\text{H}^+]$. After a short period the rate values start increasing proportionately with increasing acid concentrations. This trend becomes more clear from Fig. 6, where $-\text{dc}/\text{dt}$ values are plotted against acid concentrations. The trends of $-\text{dc}/\text{dt}$ values in Fig. 6 and k graphical and k calculated values in Table-1 clearly indicate that the rate of reaction follows first order kinetics in major part of the reaction.

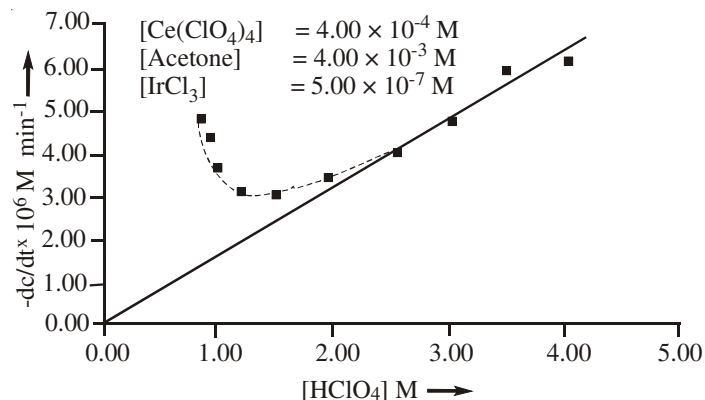


Fig. 6. Effect of variation of $[H^+]$ on the reaction velocity in the oxidation of acetone at 25 °C

TABLE-1
Temp. 25 °C, $[Ce(ClO_4)_4] = 4.00 \times 10^{-4} M$, $[Acetone] = 4.00 \times 10^{-3} M$,
 $[IrCl_3] = 5.00 \times 10^{-7} M$ (a-x) = $3.50 \times 10^{-4} M$

$[HClO_4] M$	$-dc/dt \times 10^6 M. min^{-1}$	$k g \times 10^2 min^{-1}$	$k_{calc.} (average) \times 10^2 min^{-1}$
0.50	5.45	1.56	1.53
0.60	5.00	1.43	1.49
0.75	3.85	1.10	1.09
1.00	3.42	0.98	0.92
1.50	3.20	0.91	0.96
2.00	3.66	1.05	0.93
2.50	4.06	1.16	1.18
3.00	5.00	1.42	1.08
3.50	6.00	1.71	1.28
4.00	6.43	1.84	1.88

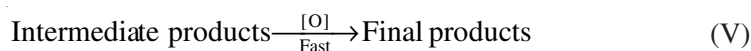
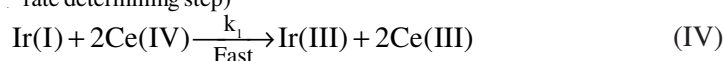
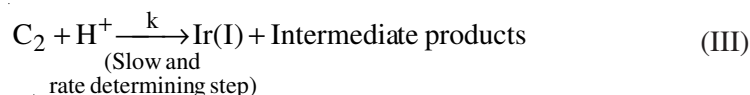
Mechanism of the reaction: The rate of oxidation follows first order kinetics at low concentrations tending toward zero order at higher concentrations with respect to acetone shown in Fig. 2. At this higher concentration range of the substrate the reaction shows first order with respect to iridium(III) chloride concentration as shown in Fig. 5. All these indicate a probable way of association of oxidant, substrate and catalyst in some pre-equilibrium steps. Such associations are well documented in many metal ion catalyzed redox reaction. Silver(I) catalyzed oxidation of hydrogen peroxide and hypo phosphorous acid by [ethylene-*bis*-(biguanide)] silver(I) cation in acid media and osmium(VIII) catalyzed oxidation of arsenic(III) by cerium(IV) and vanadium(V), iridium(III) catalyzed oxidation of different organic substrates. It was observed that in all cases that on increasing concentration of H^+ ions $-dc/dt$ values decrease slightly in the beginning at low acid concentrations. After a certain concentration the trend was reversed and in the major part of the variation $-dc/dt$ values go on increasing with increasing concentration of H^+ ions showing that reaction follows direct proportionality with respect to $[H^+]$. This nature of the reaction becomes

more clear (Fig. 6). Effect of variation of ionic strength of the medium on the reaction velocity was studied and observed that change in ionic strength of medium does not effect the reaction velocity.

On the basis of experimental findings given above the following rate expression may be proposed at moderate concentration of ceric perchlorate and the organic substrate acetone.

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

Reaction **Scheme-I** (in which the substrate acetone is denoted by S) is reasonable to explain the experimental findings



Formation of 1:1 complexes between ceric perchlorate and ketones is well documented¹³.

Present experimental data also support the formation of complex C₁ during the course of the reaction. It was observed that in the individual plots, between log of remaining concentrations of cerium(IV) perchlorate *versus* time, deviation from the straight line in the later part of the reactions is not prominent at low concentrations, both the ceric variation as well as in the substrate variation. while deviations from the straight line become more prominent at higher concentrations of ceric perchlorate as well as of organic substrate.

From the above mechanistic steps considering the equilibrium concentration of complexes C₁ and C₂ their concentrations may be given as

$$[\text{C}_1] = K_1[\text{S}][\text{Ce(IV)}] \quad (2)$$

$$[\text{C}_2] = K_2[\text{C}_1][\text{Ir(III)}] \quad (3)$$

The concentrations of iridium(III) from step II of the mechanism can be given as

$$[\text{Ir(III)}] = \frac{[\text{C}_2]}{K_2[\text{C}_1]} \quad (4)$$

on putting the concentration of complex C₁ from the eqn. 2 we get.

$$[\text{Ir(III)}] = \frac{[\text{C}_2]}{K_1 K_2 [\text{S}][\text{Ce(IV)}]} \quad (5)$$

Now the total concentration of [Ir(III)] may be given as

$$[\text{Ir(III)}]_{\text{T}} = [\text{Ir(III)}] + [\text{C}_2] \quad (6)$$

Putting the concentration of Ir(III) from eqns. 5 into 6 we get.

$$[\text{Ir(III)}]_{\text{T}} = \frac{[\text{C}_2]}{K_1 K_2 [\text{S}] [\text{Ce(IV)}]} + [\text{C}_2] \quad (7)$$

From eqn. 7 concentration of complex C_2 may be given as

$$[\text{C}_2] = \frac{K_1 K_2 [\text{S}] [\text{Ce(IV)}] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 K_2 [\text{S}] [\text{Ce(IV)}]} \quad (8)$$

Now the rate in terms of decreasing concentrations of cerium(IV) from step (III) of the mechanism may be given as

$$\frac{-d[\text{Ce(IV)}]}{dt} = K[\text{C}_2][\text{H}^+] \quad (9)$$

or

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{k K_1 K_2 [\text{S}] [\text{Ce(IV)}] [\text{Ir(III)}]_{\text{T}} [\text{H}^+]}{1 + K_1 K_2 [\text{S}] [\text{Ce(IV)}]} \quad (10)$$

Since two moles of Ce(IV) are required to get back the original Ir(III) species therefore eqn. 10 has to be multiplied by 2 and we get the final rate law in terms of decreasing concentration of cerium(IV) perchlorate as:

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2k K_1 K_2 [\text{S}] [\text{Ce(IV)}] [\text{Ir(III)}]_{\text{T}} [\text{H}^+]}{1 + K_1 K_2 [\text{S}] [\text{Ce(IV)}]} \quad (11)$$

At low concentrations of cerium(IV) and acetone the inequality $1 \gg K_1 K_2 [\text{S}] [\text{Ce(IV)}]$ may hold good and under such conditions the final rate eqn. 10 reduces to

$$\frac{-d[\text{Ce(IV)}]}{dt} = k K_1 K_2 [\text{S}] [\text{Ce(IV)}] [\text{Ir(III)}]_{\text{T}} [\text{H}^+] \quad (12)$$

This equation clearly explains first order kinetics with respect to [Ce(IV)] and [acetone]. At their low concentrations the nature shown by Ir(III) and H^+ ion is also quite clear.

At comparatively high concentrations of [Ce(IV)] and acetone the reverse inequality $1 \ll K_1 K_2 [\text{S}] [\text{Ce(IV)}]$ may hold good and the final rate law (eqn. 11) takes the form.

$$\frac{-d[\text{Ce(IV)}]}{dt} = K[\text{Ir(III)}]_{\text{T}} [\text{H}^+] \quad (13)$$

Eqn. 13 is found to be in good agreement with the experimental results.

The final rate eqn. 11 may also be written as

$$\frac{-d[\text{Ce(IV)}]}{dt} = k' = \frac{2kK_1K_2[\text{S}][\text{Ce(IV)}]}{1 + K_1K_2[\text{S}][\text{Ce(IV)}]} \quad (14)$$

where k' is first order rate constant. Further verification of the final rate eqn. 11 may be done by rewriting the eqn. 14 in the form as:

$$\frac{1}{V_i} = \frac{1}{k'} = \frac{1}{2kK_1K_2[\text{S}][\text{Ce(IV)}]} + \frac{1}{2k} \quad (15)$$

It is clear from this equation that if we plot a graph between $1/k'$ vs. $1/[\text{substrate}]$ or $1/k'$ vs. $1/[\text{cerium(IV)}]$, we should get a straight line with a positive intercept at Y-axis this graph is shown in Fig. 7.

From the slopes and intercept of the straight line, K and kK_1K_2 values were calculated and are given in Table-2, fair constancy of K and kK_1K_2 values obtained from two different graphs (Figs. 7 and 8) finally confirms the proposed mechanism and the final rate law 11.

TABLE-2

Substrate	kK_1K_2 from the slope of $1/k'$ versus $1/[\text{sub}] \times 10^6$	kK_1K_2 the slope of $1/k'$ versus $1/[\text{Ce(IV)}] \times 10^6$	k from the intercept of $1/k'$ versus $1/[\text{sub}]$	k from the intercept of $1/k'$ versus $1/[\text{Ce(IV)}]$
Acetone	5.00	4.17	16.00	21.05

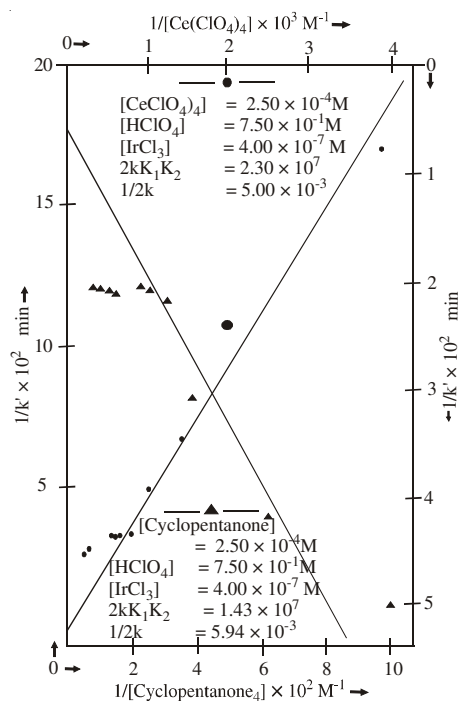


Fig. 7

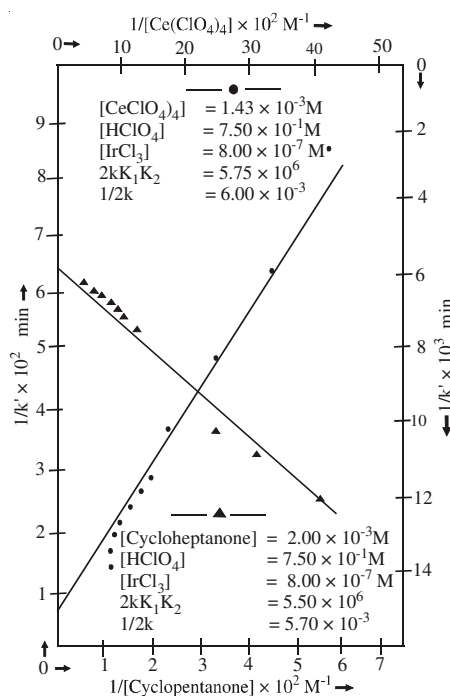


Fig. 8

The values of various thermodynamic parameters obtained in the oxidation of acetone under investigation, are given in Table-3.

TABLE-3
THE VALUES OF ΔE_a , ΔS^\ddagger and ΔF^\ddagger CALCULATED AT 298 K

Organic Substrate	ΔE_a Kcal mol ⁻¹	ΔS^\ddagger e.u.	ΔF^\ddagger Kcal mol ⁻¹	Kr $\times 10^3$ min ⁻¹
Acetone	12.76	-26.66	20.71	11.00

Reactive species of Ce(IV): In perchloric acid medium, Ce(IV) exist in hydrolyzed and unhydrolyzed species it has been reported that predominant species of cerium(IV) perchlorate in aqueous perchloric acid medium is monomeric. The various species of Ce(IV) which may exist in perchloric acid medium are governed by the following equilibrium.

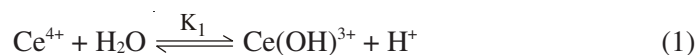


Table-4 gives the values of both species at different concentrations of hydrogen ions. Ce^{4+} refers to the unhydrolysed Ce^{4+} species and $\text{Ce}(\text{OH})^{3+}$ refers to the hydrolyzed species of Ce(IV).

TABLE-4

H ⁺	Ce ⁴⁺	Ce(OH) ³⁺
0.1	0.007	0.451
0.2	0.079	0.610
0.4	0.045	0.731
1.0	0.112	0.782
2.0	0.287	0.720
3.0	0.310	0.661
4.0	0.377	0.600

It has been reported that high perchloric acid concentration decreases the amount of hydrolyzed species of Ce(IV) which do not react with water, while on the other hand high concentration of ceric favours the formation of unreactive polynuclear complexes. This probability can be seen from Table-4. The present results, in the range of acid concentrations where the studies were performed, indicate that both hydrolyzed as well as unhydrolyzed species are present in low acid concentrations, while at higher concentrations of perchloric acid more and more hydrolyzed species gets converted into the unhydrolyzed species. The concentration range in which present studies were performed, only unhydrolyzed species acts as the reactive species.

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(Received: 21 March 2009;

Accepted: 14 December 2009)

AJC-8187

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