



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

A mechanistic study based on kinetics of the oxidation of diethyl ketone by Ir (III) chloride in aqueous perchloric acid medium when cerium (IV) perchlorate is used as a catalyst

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ABSTRACT

This mechanistic study on the oxidation of diethyl ketone by Ir (III) chloride in aqueous perchloric acid medium when cerium (IV) perchlorate is used as a catalyst has been done at temperature range of 293 to 308 K under conditions such that, $[Ir]_T \ll [Ce(IV)]_T \ll [CH_3-CH_2-CO-CH_2-CH_3]$ so that the reaction constants of different steps involved have been evaluated with great ease and accuracy the rate of reaction tends towards zero-order at higher concentration and first order at lower concentration with respect to ceric perchlorate and diethyl ketone. Order of reaction is unity with respect to $[Ir(III)]$ in the concentration range studied. On increasing the concentrations of $[H^+]$ the rate decreases slightly. The effect of ionic strength and the dielectric constant on reaction rate has also been studied. The active species of oxidant is indicated to be Ce^{4+} and $Ce(OH)^{3+}$. An intermediate involving the oxidant, catalyst and substrate has been proposed as being formed in pre-equilibrium steps. The calculation of activation parameters is done with tremendous analysis with respect to slow step of mechanism.

Key Words : Diethyl ketone, Ir (III) Chloride, Ionic Strength, Dielectric constant, Activation parameter.

INTRODUCTION

Different metal ion catalysts like palladium (II)[1,2] chromium[3] ruthenium (III)[4-9] iridium (III)[10-12] etc. have been used in the oxidation by cerium (IV). Among the different metal ions, ruthenium (III) and iridium (III) are highly efficient. Ir(III) catalysis in oxidation reactions by Ce (IV) in aqueous perchloric acid media has been reported in a very few cases. So we were convinced to show our adept and adroit studies on the oxidation of diethyl ketone by Ce (IV) perchlorates. Kinetic behaviour of title reaction abstainment of redundant calculations are done with high clarity.

Transition metals in the higher oxidation state generally can be stabilized by chelation with suitable complex[13-16] agent. Metal complexes are good oxidants in acid or alkaline media under appropriate reaction conditions. Kinetics of oxidation of some ketones and alcohols has been studied well[17-19] by Ce(IV) and various other oxidant using ruthenium or palladium metal ions as homogeneous catalysts in acidic or alkaline medium. A kinetic and mechanistic study of oxidation of tartaric acid by potassium bromate in perchloric acid medium catalysed by Ru (III) reported [20].

Transition metal ions from complexes [21,22] and act as catalyst in oxidation and reduction reactions due to its multiple oxidation states. Osmium, ruthenium, palladium, manganese, chromium, iridium act as catalyst and has drawn considerable interest[23]. By using few transition metal ions as homogenous catalyst, kinetics of oxidation of some molecules have been studied [24-26]. Ru (III) catalysed kinetics of miglitol by Bromamine-T in HCl medium is studied by R. Ramchandrapa and co-workers [27].

Reaction mechanism of various elementary reactions must be investigated to analyze the factors affecting the selectivity. Therefore the basic study of catalytic reaction will provide the basis for improving catalyst selectivity and making high – efficiency catalyst, 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. Recently the oxidation of gabapentin by chloramine –T in perchloric acid medium was studied[28].

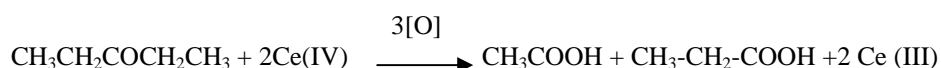
EXPERIMENTAL SECTION

Illimitable solution of ceric sulphate was used as a titrant. It 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 measure part of the salt was dissolved. The emblem and 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 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 Matthay Chemicals Ltd.) in dilute solution of hydrochloric acid. The final strengths of hydrochloric acid and iridium (III) chloride were 6.24×10^{-3} M and 3.35×10^{-3} M respectively.

The calculated and vehement quantity of organic compound was transferred into the conical flask containing Ce(IV) perchlorate, per chloric 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) supphate in the reaction mixture. The amount of F.A.S. (quenching agent) left was titrated against a standard solution of ceric sulphate to the ferroin end point. The exalt progress of 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:-

During experiments the reaction mixtures were kept at room temperature (25°C) for 24 hours such that the concentration of ceric perchlorate was kept interminable as compared to that of organic substrates in varying ratios. 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 overall iridium (III) catalysed redox process conforms to the following stoichiometry.



RESULTS AND DISCUSSION

Dependence of rate on cerium (IV) concentration :-

Endowment and vouch safe of the nature of reaction can be seen from the individual plots (in Table- 1 and Fig. 1) final confirmation of the order of reaction with respect to ceric perchlorate concentration was obtained by plotting – dc/dt values against the concentration of ceric perchlorate as shown in Fig. 2, 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 condition prevails here that $[\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3]_{\text{T}} \gg [\text{Ce (IV)}]_{\text{T}} \gg [\text{Ir}]_{\text{T}}$ in $0.75 \text{ mole dm}^{-3}$ perchloric acid media. The dependence is given by

$$-d \ln[\text{Ce(IV)}] / dt = k_0 \quad \dots\dots\dots (1)$$

Dependence of rate on Diethyl Ketone concentration:-

The dependence can be expressed as :

$$k_0 = \frac{m [\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3]_{\text{T}}}{n + p [\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3]_{\text{T}}} \quad \dots\dots\dots(2)$$

[Diethyl ketone] = 1.00×10^{-3} M
 [HClO₄] = 7.50×10^{-1} M
 [IrCl₃] = 2.00×10^{-7} M
 Temp. = 25°C

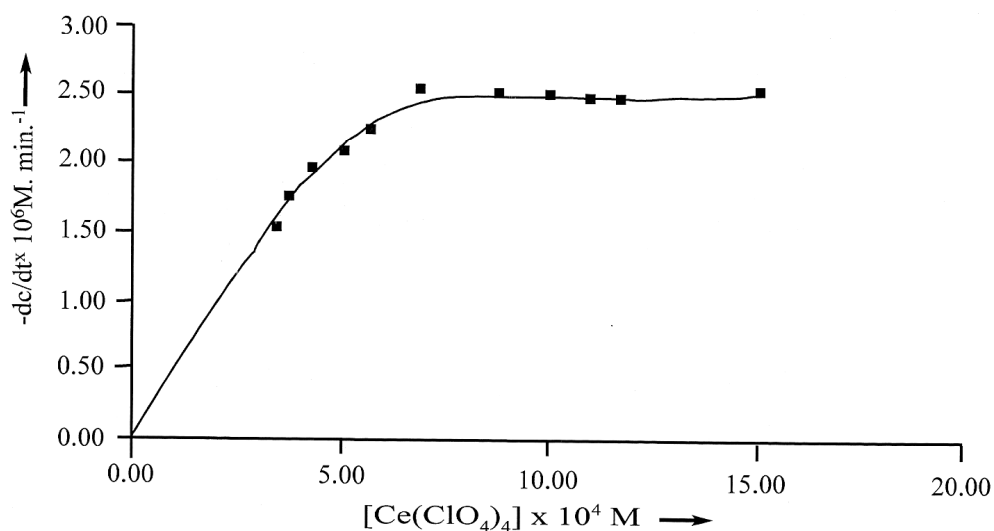


Fig. 2 : Effect of variation of cerium (IV) perchlorate concentration on the reaction velocity in the oxidation of diethyl ketone

[Ce(ClO₄)₄] = 4.00×10^{-4} M
 [HClO₄] = 7.50×10^{-1} M
 [IrCl₃] = 2.00×10^{-7} M

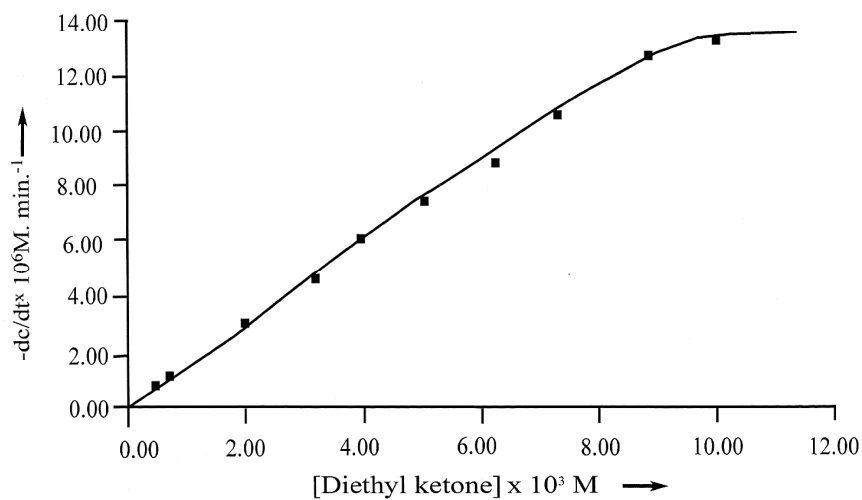


Fig. 3 : Effect of variation of [Diethyl ketone] on the reaction velocity at 25°C.

Table- 2
Temp. 25°C

[Ce(ClO ₄) ₄]	=	4.00 x 10 ⁻⁴ M
[HClO ₄]	=	7.50 x 10 ⁻¹ M
[IrCl ₃]	=	2.00 x 10 ⁻⁷ M

$$(a - x) = 3.50 \times 10^{-4} \text{ M}$$

[Diethyl ketone] x 10 ³ M	-dc/dt x 10 ⁶ M. min ⁻¹	K _{gr.} x 10 ² min ⁻¹	K _{calc.} (average) x 10 ² min ⁻¹
0.50	0.90	0.26	0.29
0.75	1.20	0.34	0.39
2.00	3.00	0.86	0.86
3.00	4.16	1.19	1.27
4.00	5.83	1.67	1.70
5.00	7.14	2.04	2.09
6.00	8.33	2.38	2.40
7.00	10.00	2.86	2.60
9.00	12.50	3.57	3.58
10.00	12.80	3.66	3.84

Dependence of rate on catalyst concentration:-

The catalyst concentration has high acclaim and aglow that under the experimental conditions uncatalysed 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 (Table- 3 and Fig. 4), where we get a straight line with a slope value of 0.926.

Table- 3
Temp. 25°C

[Ce(ClO ₄) ₄]	=	4.00 x 10 ⁻⁴ M
[Diethyl ketone]	=	1.00 x 10 ⁻³ M
[HClO ₄]	=	7.50 x 10 ⁻¹ M

$$(a - x) = 3.25 \times 10^{-4} \text{ M}$$

[Diethyl ketone] x 10 ⁷ M	K _{gr.} x 10 ² min ⁻¹	K _{calc.} (average) x 10 ² min ⁻¹	$k = \frac{k_{gr.}}{[IrCl_3]} \times 10^4$ M ⁻¹ min ⁻¹
1.0	0.32	0.34	3.20
2.0	0.59	0.58	2.95
3.0	0.82	0.86	2.73
4.0	1.13	1.07	2.83
5.0	1.43	1.42	2.86
6.0	1.62	1.59	2.70
7.0	1.96	1.99	2.80
9.0	2.37	2.45	2.63
10.0	2.77	2.84	2.77
11.0	3.08	3.05	2.80

Dependence of rate on perchloric acid concentration:-

When perchloric acid concentration is depicted then it is seen with fortress and gaitly that the rate of reaction follows first order kinetics in major part of the reaction.

It is seen that the rate constant value *i.e.* k graphical as well as k calculated value decrease in the beginning with increasing [H⁺]. After a short period the rate values start increasing proportionately with increasing [H⁺]. After a short period the rate values start increasing proportionately with increasing acid concentrations. This trend becomes more clear from Table- 4 and Fig. 5 where -dc/dt values are plotted against acid concentrations. The trends of -dc/dt values in Fig. 5 and k graphical and k calculated values in Table- 1.

[Ce(ClO ₄) ₄]	= 4.00 × 10 ⁻⁴ M
[Diethyl ketone]	= 1.00 × 10 ⁻³ M
[HClO ₄]	= 7.50 × 10 ⁻¹ M
[Slope]	= 1.06 × 10 ⁰

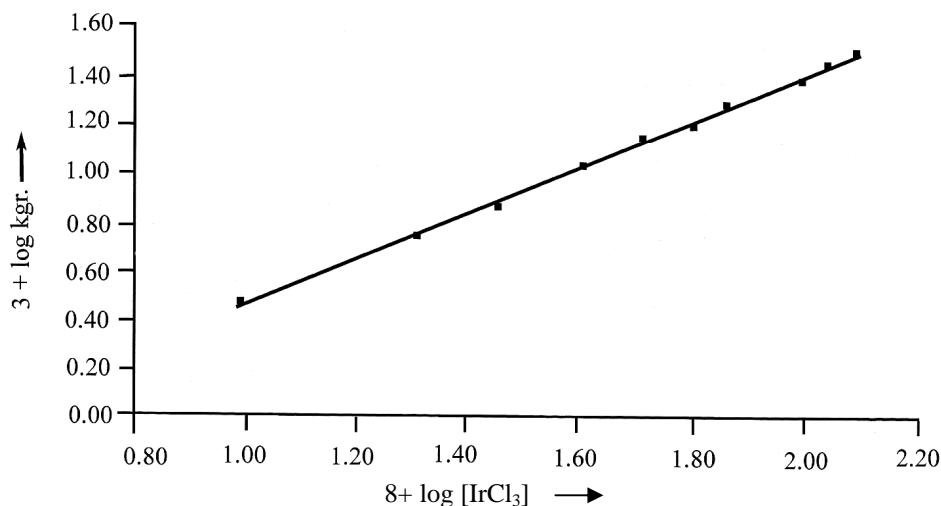


Fig. 4 : Effect of variation of [IrCl₃] on the reaction velocity in the oxidation of diethyl ketone at 25^oC.

Table- 4

Temp. 25°C

[Ce(ClO ₄) ₄]	=	4.00 × 10 ⁻⁴ M
[Diethyl ketone]	=	1.00 × 10 ⁻³ M
[IrCl ₃]	=	2.00 × 10 ⁻⁷ M

$$(a - x) = 3.50 \times 10^{-4} \text{ M}$$

[HClO ₄] M	-dc/dt × 10 ⁶ M. min ⁻¹	K _{gr.} × 10 ² min ⁻¹	K _{calc.} (average) × 10 ² min ⁻¹
0.50	2.50	0.71	0.69
0.60	2.03	0.58	0.59
0.75	1.91	0.55	0.57
1.00	2.08	0.59	0.69
1.50	2.31	0.66	.64
2.00	2.88	0.82	0.73
3.50	5.00	1.43	0.99
4.00	5.55	1.59	1.11
4.50	6.25	1.79	1.14
5.00	7.00	2.00	1.14

Mechanism of the reaction :-

Under this heading the effect of variation of ionic strength of the medium on the basis of reaction velocity was studied in highly mechanised way. The rate of oxidation follows first order kinetics at low concentrations tending toward zero order at higher concentrations with respect to Diethyl Ketone as shown in Fig. 1. At this higher concentration range of the substrate the reaction shows first order with respect to iridium (III) chloride concentration as shown in Fig. 4. All these indicate and points a probable way of association of oxidant, substrate and catalyst in some pre-equilibrium steps. Such associations are well documented in many metal ion catalysed redox reaction, that is silver (I) catalysed oxidation of hydrogen peroxide and hypo phosphorous acid by [ethylene bis (biguanide)] Silver (III) cation in acid media and osmium (VIII) catalysed oxidation of arsenic (III) by cerium (IV) and vanadium (V), iridium (III) catalysed oxidation of different organic substrates. When various cases are mechanised then it was found in all considerations that increase in concentration of H⁺ ions -dc/dt values decreased 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 went on increasing with increasing concentration of H⁺ ions showing that reaction follow direct proportionality with respect to [H⁺]. This nature of the reaction became more clear from Fig. 6. It was observed that change in ionic strength of medium does not effect the reaction velocity.

$$\begin{aligned}
 [\text{Ce}(\text{ClO}_4)_4] &= 4.00 \times 10^{-4} \text{ M} \\
 [\text{Diethyl ketone}] &= 1.00 \times 10^{-3} \text{ M} \\
 [\text{IrCl}_3] &= 2.00 \times 10^{-7} \text{ M}
 \end{aligned}$$

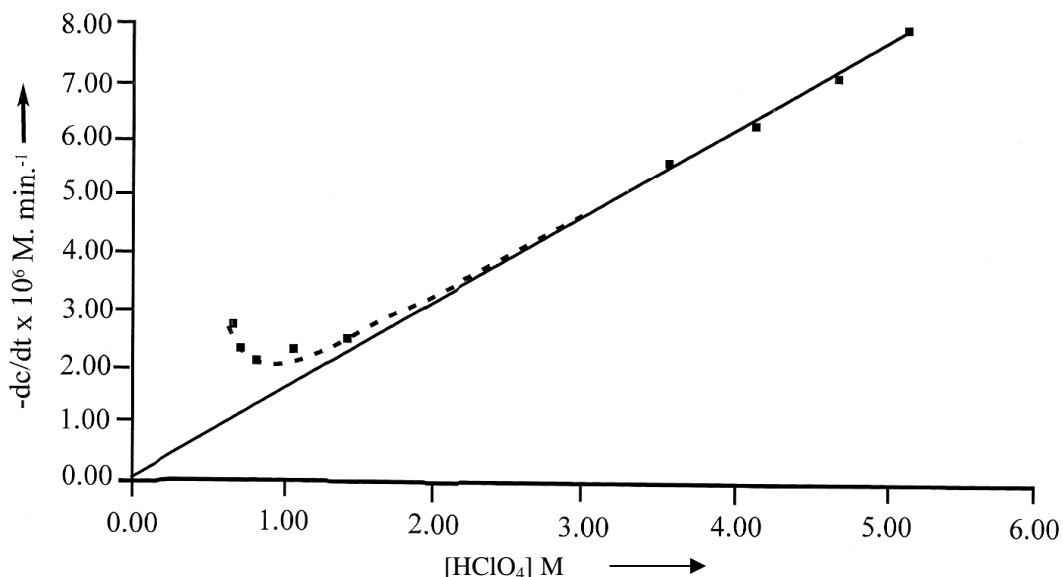
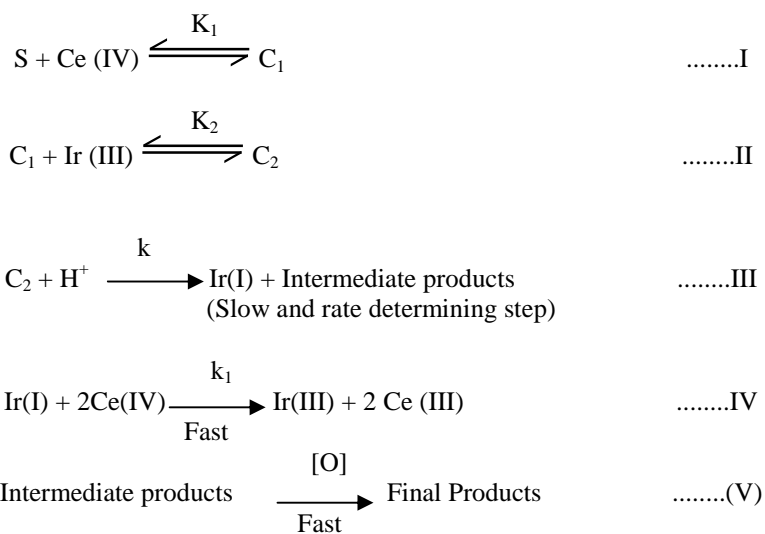


Fig. 5 : Effect of variation of $[\text{H}^+]$ on the reaction velocity in the oxidation of diethyl ketone at 25°C .

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 Diethyl Ketone .

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

Reaction scheme 1 (in which the substrate Diethyl Ketone is denoted by S) is reasonable to explain the experimental findings



Formation of 1:1 complexes between ceric perchlorate and ketones is well documented[13].

Our experimental data also support the formation of complex C_1 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 was not prominent at low concentrations, both the ceric variation as well as in the substrate variation. while deviations from the straight line became 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 C_1 and C_2 their concentrations may be given as

$$[C_1] = K_1 [S] [Ce(IV)] \quad \dots\dots 2$$

$$[C_2] = K_2 [C_1] [Ir(III)] \quad \dots\dots 3$$

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

$$[Ir(III)] = \frac{[C_2]}{K_2 [C_1]} \quad \dots\dots 4$$

on putting the concentration of complex C_1 from the eq. 2 we get.

$$[Ir(III)] = \frac{[C_2]}{K_1 K_2 [S] [Ce(IV)]} \quad \dots\dots 5$$

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

$$[Ir(III)]_T = [Ir(III)] + [C_2] \quad \dots\dots 6$$

Putting the concentration of $[Ir(III)]$ from eq. 5 into 6 we get.

$$[Ir(III)]_T = \frac{[C_2]}{K_1 K_2 [S] [Ce(IV)]} + [C_2] \quad \dots\dots 7$$

From eq. 7 concentration of complex C_2 may be given as –

$$[C_2] = \frac{K_1 K_2 [S] [Ce(IV)] [Ir(III)]_T}{1 + K_1 K_2 [S] [Ce(IV)]} \quad \dots\dots 8$$

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

$$\frac{-d [Ce(IV)]}{dt} = K [C_2] [H^+] \quad \dots\dots 9$$

Or

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

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

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

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

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

This equation clearly explains first order kinetics with respect to [Ce(IV)] and [Diethyl Ketone]. 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 Diethyl Ketone the reverse inequality $1 \ll K_1 K_2 [\text{S}] [\text{Ce(IV)}]$ may hold good and the final rate law 11 takes the form.

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

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

The final rate equation 11 may also be written as

$$\frac{-d [\text{Ce (IV)}]}{dt} = k' = \frac{2 k K_1 K_2 [\text{S}] [\text{Ce(IV)}]}{1 + K_1 K_2 [\text{S}] [\text{Ce (IV)}]} \quad \dots\dots 14$$

Where K' is first order rate constant. Further verification of the final rate eq. 11 may be done by rewriting the eq. 14 in the form as :

$$\frac{1}{V_i} = \frac{1}{k'} = \frac{1}{2 k K_1 K_2 [\text{S}] [\text{Ce(IV)}]} + \frac{1}{2k} \quad \dots\dots 15$$

It is clear from this eq. that if we plot a graph between 1/k' versus 1/[Substrate] or 1/k' versus 1/[cerium (IV)], we should get a straight line with a positive intercept at Y-axis this graph is shown in Fig. 6.

From the slope and intercept of the straight line, K and k K₁K₂ values were calculated and are given in Table- 2. Fair constancy of K and k K₁K₂ values obtained from two different graphs (Fig. 6 & 7) finally confirmed and concede the proposed mechanism and the final rate law[11].

TABLE- 5

Substrate	kK ₁ K ₂ from the slope of 1/k' versus 1/[sub] x10 ⁶	kK ₁ K ₂ the slope of 1/k' versus 1/[Ce(IV)] x10 ⁶	k from the intercept of 1/k' versus 1/[sub]	k from the intercept of 1/k' versus 1/[Ce(IV)]
Diethyl Ketone	1.80	1.60	62.50	62.5

The values of various thermodynamic parameters obtained in the oxidation of Diethyl Ketone under investigation, are given in Table- 6.

Table- 6
The values of Ea, ΔS[‡] and ΔF[‡] calculated at 298K

Organic Substrate	ΔEa K.Cal. mole ⁻¹	ΔS [‡] e.u.	ΔF [‡] K.Cal. mole ⁻¹	Kr x 10 ³ min ⁻¹
Diethyl Ketone	9.15	-39.93	21.05	6.17

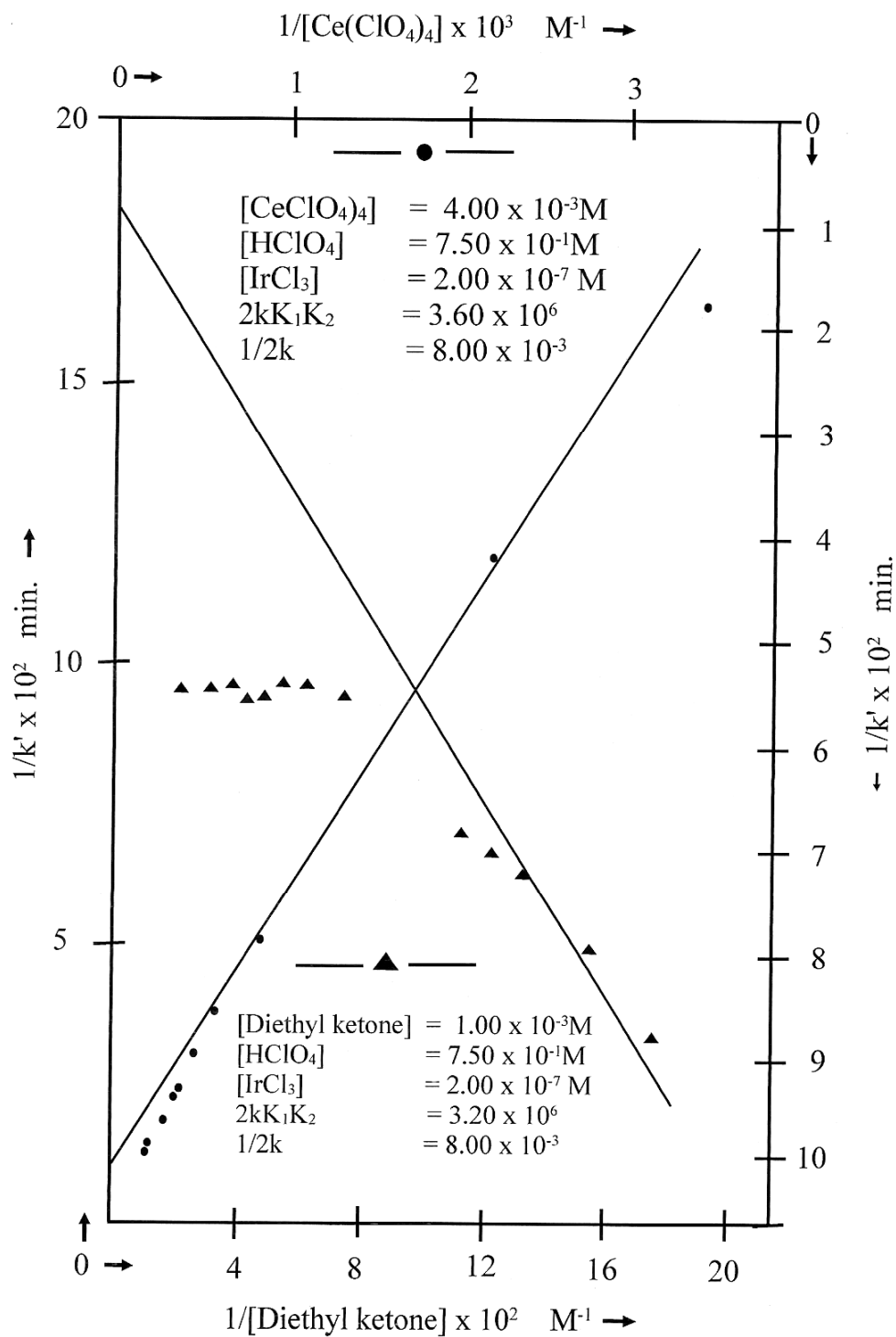
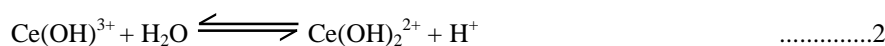
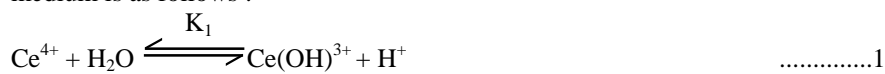


Fig. 6

Reactive species of Ce (IV):-

The equilibrium which governed and reveal the various species of Ce (IV) which may exist in perchloric acid medium is as follows :



In perchloric acid medium Ce(IV) exist in Unhydrolysed and hydrolysed species it has been reported that predominant species of cerium (IV) perchlorate in aqueous perchloric acid medium is monomeric.

The following Table- 7 gives the values of both species at different concentrations of hydrogen ions. Ce^{4+} refers to the unhydrolysed Ce^{4+} species, and $Ce(OH)^{3+}$ refers to the hydrolysed species of Ce(IV).

Table- 7
Values of Ce^{4+} and $Ce(OH)^{3+}$ at different $[H^+]$

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

Thus the concentration range in which our analysed and estimated studies were performed regards only unhydrolysed species acted as reactive species. It has been reported that high perchloric acid concentration decreases the amount of hydrolysed 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- 7. In the range of acid concentrations where the studies were performed, our results indicate that both hydrolysed as well as unhydrolysed species are present a low acid concentrations, while at higher concentrations of perchloric acid more and more hydrolysed species get converted into the unhydrolysed species.

CONCLUSION

I like to conclude my study on A mechanistic study based on kinetics of the oxidation of diethyl ketone by Ir (III) chloride in aqueous perchloric acid medium when cerium (IV) perchlorate is used as a catalyst with the specifications that the reaction constants of different steps involved have been evaluated with great ease and accuracy the rate of reaction tends towards zero-order at higher concentration and first order at lower concentration with respect to ceric perchlorate and diethyl ketone. Order of reaction is unity with respect to $[Ir(III)]$ in the concentration range studied. On increasing the concentrations of $[H^+]$ the rate decreases slightly. The effect of ionic strength and the dielectric constant on reaction rate has also been studied. The active species of oxidant is indicated to be Ce^{4+} and $Ce(OH)^{3+}$. Thus the concentration range in which our analysed and estimated studies were performed regards only unhydrolysed species acted as reactive species. In the range of acid concentrations where the studies were performed, our results indicate that both hydrolysed as well as unhydrolysed species are present a low acid concentrations, while at higher concentrations of perchloric acid more and more hydrolysed species get converted into the unhydrolysed species. Endowment of such reactions forced me to do the analysis on the topic. The calculation of activation parameters is done with tremendous analysis with respect to slow step of mechanism.

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