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A Kinetic and Mechanistic Study on the Oxidation of Methyl Propyl Ketone by Cerium (IV) Perchlorate Catalysed by Ir (III) Chloride in Aqueous Perchloric Acid Medium

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ABSTRACT

A suitable kinetic and mechanistic study is proposed and reaction constants of different steps involved have been evaluated by a series of observation taken on the oxidation of methyl propyl ketone by Ir (III) chloride in aqueous perchloric acid medium and cerium (IV) perchlorate used as a catalyst here at temperature range of 293-308 K under conditions $[\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3] \gg [\text{Ce (IV)}]_{\text{T}} \gg [\text{Ir}]_{\text{T}}$. The reaction rate follows first order kinetics at low concentrations tending towards zero-order at higher concentrations with respect to ceric perchlorate and methyl propyl ketone. Order of reaction is unity with respect to [Ir (III)] in the concentration range studied. On increasing the concentrations of $[\text{H}^+]$ 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+} . Activation Parameters have also been analysed and calculated with respect to the slow step of the mechanism.

Keywords: Kinetics, Reaction mechanism, oxidations, cerium (IV) perchlorate methyl propyl ketone , Thermodynamic Parameters.

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INTRODUCTION

Absence of studies on the oxidation of methyl propyl ketone by Ce (IV) perchlorate has encouraged me to investigate the kinetic behaviour of title reaction as such kinetics of oxidation of some ketones and alcohols has been studied well by Ce(IV) and various other oxidant using ruthenium or palladium metal ions as homogeneous catalysts in acidic or alkaline medium[1-6]. Ir(III) catalysis in oxidation reactions by Ce (IV) in aqueous perchloric acid media has been reported in a very few cases. Reaction mechanism of various elementary reactions must be investigated to analyse the factors affecting the selectivity[7-9]. 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[10-13].

MATERIALS AND METHOD

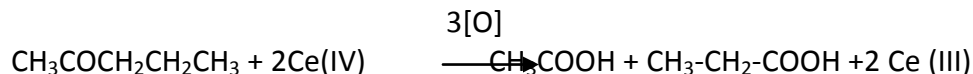
The titrant was prepared by taking appropriate amount of solution of ceric sulphate in 1:1 sulphuric acid. The mixture was heated with constant stirring and addition of small quantities of distilled water several times until measure part of the salt was dissolved. The estimation of ceric sulphate was 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 Matthey 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 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) sulphate 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 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 PRODUCT ANALYSIS

While performing a series of experiments the concentration of ceric perchlorate was kept in excess as compared to that of organic substrates in varying ratios. The number of reaction mixtures was studied at room temp (25°C) for twenty four hours. 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 confirms to the following stoichiometry:



RESULTS AND DISCUSSION

Dependence of rate on cerium (IV) concentration

When 0.75 mole dm^{-3} perchloric acid medium is taken and $[\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3]_{\text{T}} \gg [\text{Ce(IV)}]_{\text{T}} \gg [\text{Ir}]_{\text{T}}$ then 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 (in Table 1 and Fig. 1) 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. 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 dependence is given by

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

Table 1

	Temp. 25 ⁰ C
[Methyl propyl ketone]	= 1.00 x 10 ⁻³ M
[HClO ₄]	= 7.50 x 10 ⁻¹ M
[IrCl ₃]	= 4.00 x 10 ⁻⁷ M

[Ce(ClO ₄) ₄] x 10 ⁴ M	-dc/dt x 10 ⁶ M. Min ⁻¹	(a-x)* x 10 ⁴ M	K _{gr.} x 10 ² min ⁻¹	k _{cale.} (average) x 10 ² min ⁻¹
2.0	1.50	1.45	10.3	13.5
2.5	1.80	1.85	9.7	10.1
3.3	2.38	3.10	8.1	10.4
4.0	2.59	3.70	7.0	7.9
4.5	2.96	4.15	7.0	7.8
5.5	3.13	5.20	6.0	6.2
6.0	3.18	5.60	5.7	6.0
7.0	3.33	6.60	5.0	5.0
7.5	3.33	7.20	4.6	4.3
8.0	3.20	7.70	4.2	4.1

* Remaining concentration of Ce (ClO₄)₄ at which $-\text{dc}/\text{dt}$ values were calculated.

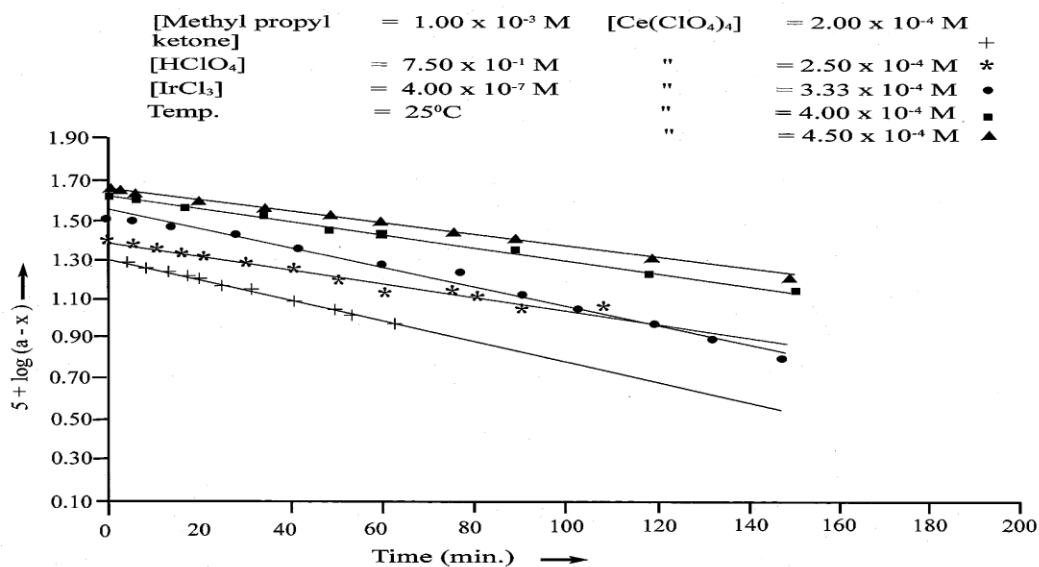


Fig 1: Individual plots showing change of [Ce(ClO₄)₄] in case of methyl propyl ketone.

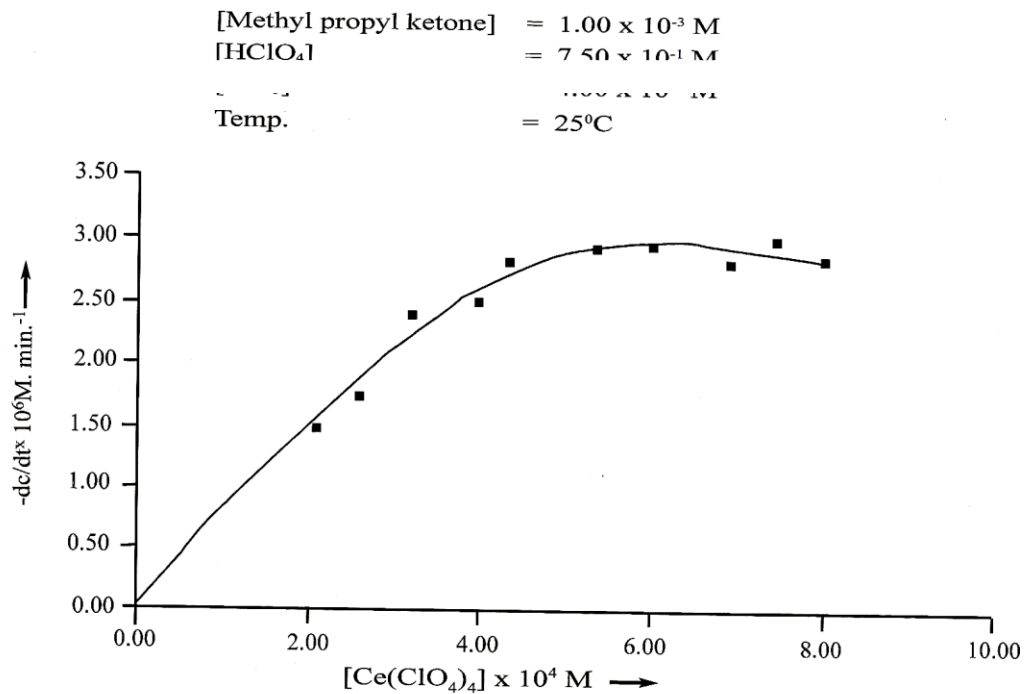


Fig 2: Effect of variation of cerium (IV) perchlorate concentration on the reaction velocity in the oxidation of methyl propyl ketone

[Ce(ClO₄)₄] = 4.00 x 10⁻⁴ M
 [HClO₄] = 7.50 x 10⁻¹ M
 [IrCl₃] = 4.00 x 10⁻⁷ M

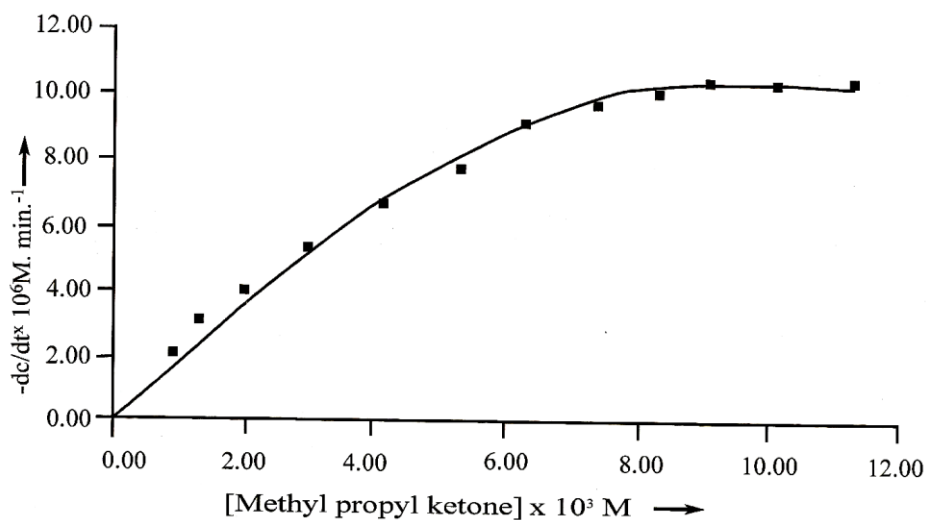


Fig 3: Effect of variation of [methyl propyl ketone] on the reaction velocity at 25^oC.

Dependence of rate on methyl propyl ketone concentration

Under this rate dependence -dc/dt values against methyl propyl ketone concentrations are plotted which shows that at lower concentration of methyl propyl ketone the reaction follows first order kinetics with respect to [methyl propyl ketone] which tends to become zero order at its higher concentration final confirmation comes from Table 2 and Fig. 3. we get straight line in the beginning which becomes parallel to the x-axis at higher concentration of Methyl propyl ketone . The dependence can be expressed as:

$$k_0 = \frac{m [\text{CH}_3\text{CO CH}_2\text{CH}_2\text{CH}_3]_T}{n + p [\text{CH}_3\text{CO CH}_2\text{CH}_2\text{CH}_3]_T} \dots\dots\dots(2)$$

(Where [CH₃COCH₂CH₂CH₃]_T give the total concentration of methyl propyl ketone ; m, n and p are constant). At high values of [CH₃COCH₂CH₂CH₃]_T, P [CH₃COCH₂CH₂CH₃] >> n and it explains the zero order dependence on substrate concentration.

Table 2
Temp. 25°C

[Ce(ClO₄)₄] = 4.00 x 10⁻⁴ M
 [HClO₄] = 7.50 x 10⁻¹ M

$$[\text{IrCl}_3] = 4.00 \times 10^{-7} \text{ M}$$

$$(a - x) = 3.00 \times 10^{-4} \text{ M}$$

[methyl propyl ketone] x 10 ³ M	-dc/dt x 10 ⁶ M. min ⁻¹	K _{gr.} x 10 ² min ⁻¹	K _{cale.} (average) x 10 ² min ⁻¹
0.75	1.78	0.59	0.58
1.00	2.59	0.86	0.84
2.00	4.00	1.33	1.26
3.00	5.38	1.79	1.59
4.00	6.43	2.14	1.96
5.00	7.50	2.50	2.50
6.00	8.80	2.93	2.83
7.00	9.44	3.15	3.10
8.00	10.00	3.33	3.33
9.00	10.56	3.52	3.45
10.00	10.76	3.59	3.35
11.00	10.83	3.61	3.24

Dependence of rate on catalyst concentration

Result estimation of rate dependence with respect to catalyst concentration is so efficient that the 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

$$\begin{aligned}
 [\text{Ce}(\text{ClO}_4)_4] &= 4.00 \times 10^{-4} \text{ M} \\
 [\text{Methyl propyl ketone}] &= 1.00 \times 10^{-3} \text{ M} \\
 [\text{HClO}_4] &= 7.50 \times 10^{-1} \text{ M}
 \end{aligned}$$

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

[methyl propyl ketone] x 10 ⁷ M	K _{gr.} x 10 ² min ⁻¹	K _{cale.} (average) x 10 ² min ⁻¹	$k = \frac{k_{gr.}}{[\text{IrCl}_3]} \times 10^4$ M ⁻¹ min ⁻¹
1.0	0.20	0.21	2.03
2.0	0.37	0.38	1.86
3.0	0.57	0.59	1.91
4.0	0.74	0.79	1.85
6.0	1.12	1.11	1.87
7.0	1.29	1.35	1.84
8.0	1.56	1.53	1.95

9.0	1.66	1.63	1.84
10.0	1.91	1.93	1.91
12.0	2.29	2.48	1.91

$[\text{Ce}(\text{ClO}_4)_4]$ = 4.00×10^{-4} M
 $[\text{Methyl propyl ketone}]$ = 1.00×10^{-3} M
 $[\text{HClO}_4]$ = 7.50×10^{-1} M
 $[\text{Slope}]$ = 1.01×10^0

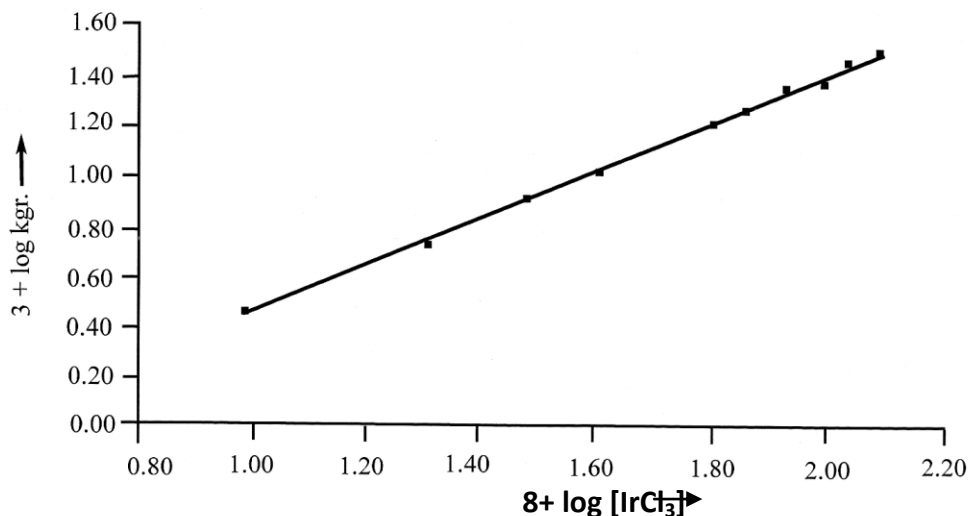


Fig. 4 : Effect of variation of $[\text{IrCl}_3]$ on the reaction velocity in the oxidation of Methyl propyl ketone at 25°C .

Dependence of rate on perchloric acid concentration

When perchloric acid concentration comes under consideration then it is seen that it is seen 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 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 clearly indicate that the rate of reaction follows first order kinetics in major part of the reaction.

Table 4

Temp. 25°C

$[\text{Ce}(\text{ClO}_4)_4]$ = 4.00×10^{-4} M
 $[\text{methyl propyl ketone}]$ = 1.00×10^{-3} M
 $[\text{IrCl}_3]$ = 4.00×10^{-7} M

$(a - x) = 3.20 \times 10^{-4}$ M

[HClO ₄] M	-dc/dt x 10 ⁶ M. min ⁻¹	K _{gr.} x 10 ² min ⁻¹	K _{cale.} (average) x 10 ² min ⁻¹
0.60	2.89	0.90	0.92
0.75	2.59	0.81	0.81
1.00	2.50	0.78	0.82
1.50	2.60	0.81	0.84
2.50	2.82	0.88	0.89
3.00	3.18	0.99	0.91
3.50	3.57	1.11	0.99
4.00	4.12	1.29	1.07
4.50	4.50	1.40	1.08
5.00	5.00	1.56	1.10

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

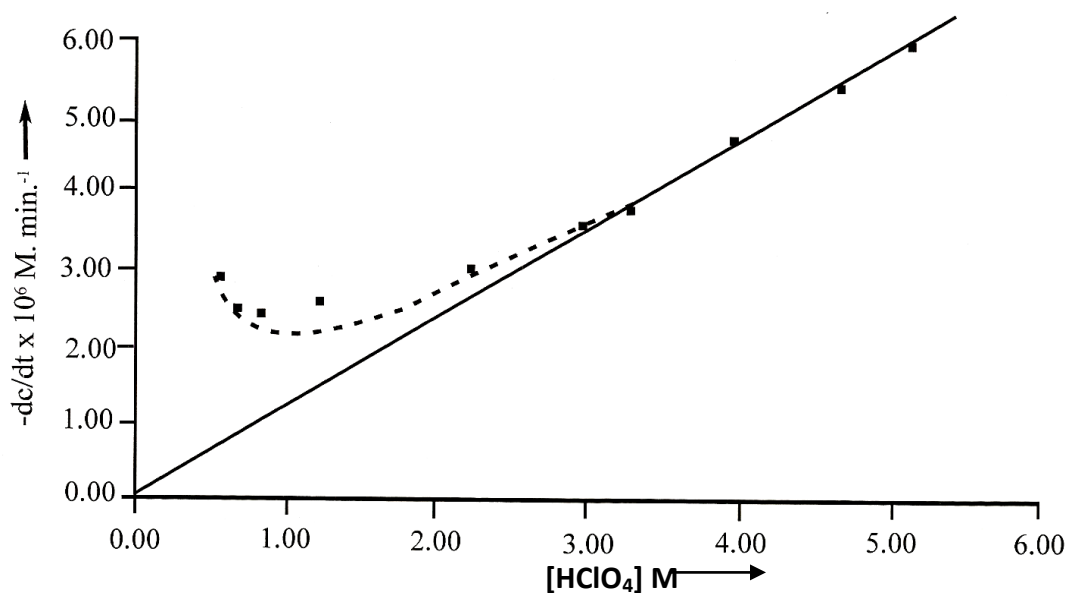


Fig 5: Effect of variation of $[\text{H}^+]$ on the reaction velocity in the oxidation of methyl propyl ketone at 25°C.

MECHANISM OF REACTION

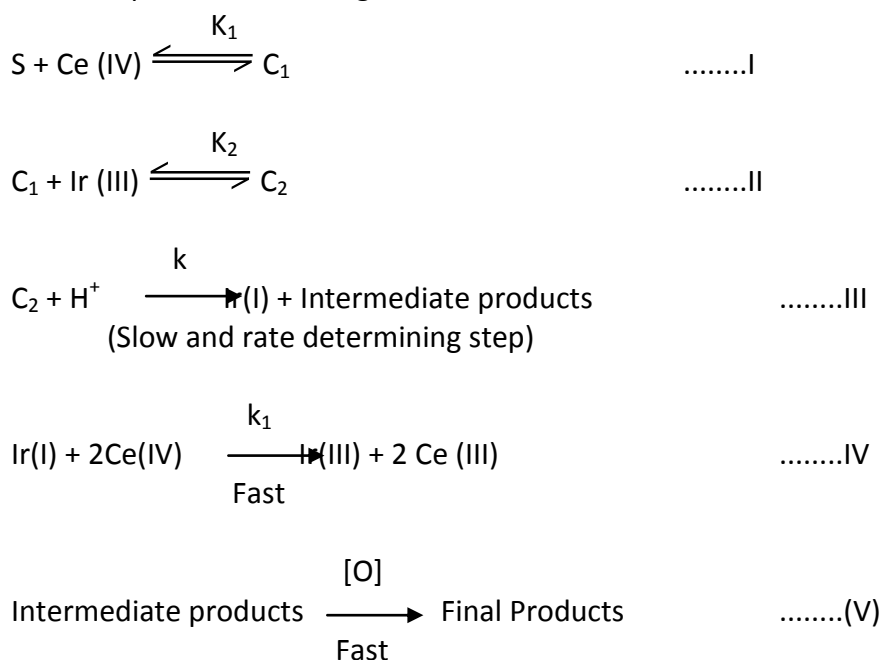
As the result estimated based on the concentration of methyl propyl ketone shows that the rate of oxidation follows first order kinetics at low concentrations tending toward zero order at higher concentrations with respect to methyl propyl ketone as shown in Fig. 1. At this higher concentration range of the substrate the reaction shows first order with respect to iridium (III) chloride concentration as shown in Fig. 4. A probable way of association of oxidant, substrate and catalyst is indicated in some pre-equilibrium steps. It was observed in all cases

that on increasing 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 feasible and clear from Fig. 6. The variation of ionic strength of the medium has tremendous effect on the reaction velocity was studied and it was 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 methyl propyl ketone .

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

Reaction scheme 1 (in which the substrate Methyl propyl 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.

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 –

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

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

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

Or

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

$$dt \quad 1 + K_1 K_2 [S] [Ce(IV)]$$

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 :

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

At low concentrations of cerium (IV) and methyl propyl 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

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

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

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

Equation 13 is found to be in good agreement with the experimental results. The final rate equation 11 may also be written as

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

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 :

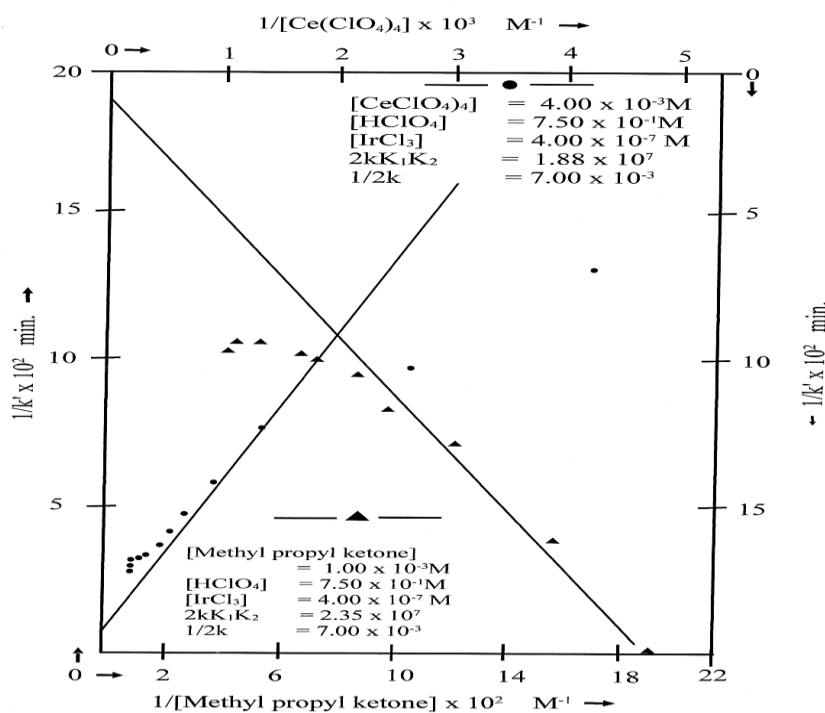
$$\frac{1}{V_i} = \frac{1}{k'} = \frac{1}{2 k K_1 K_2 [S] [Ce(IV)]} + \frac{1}{2k} \quad \dots\dots\dots 15$$

It is clear from this eq. that if we plot a graph between $1/k'$ versus $1/[\text{Substrate}]$ or $1/k'$ versus $1/[\text{cerium (IV)}]$, 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 K_1K_2 values were calculated and are given in Table 2. Fair and non ambiguous constancy of K and k K_1K_2 values obtained from two different graphs (Fig. 6 & 7) finally confirmed the proposed mechanism and the final rate law.

Table 5

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 $1/[\text{Ce(IV)}]$
methyl propyl ketone	9.40	11.75	71.43	71.43


Fig. 6

The values of various thermodynamic parameters obtained in the oxidation of methyl propyl ketone under investigation, are given in Table 6.

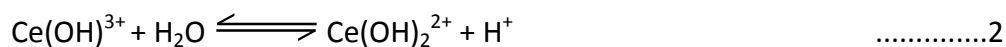
Table 6

The values of E_a , ΔS^\ddagger and ΔF^\ddagger calculated at 298K

Organic Substrate	ΔE_a K.Cal. mole ⁻¹	ΔS^\ddagger e.u.	ΔF^\ddagger K.Cal. mole ⁻¹	Kr x 10 ³ min ⁻¹
methyl propyl ketone	7.96	-43.57	20.94	7.40

REACTIVE SPECIES OF Ce (IV)

It has been optimized and reported that predominate species of cerium (IV) perchlorate in aqueous perchloric acid medium is monomeric and Ce (IV) exist in unhydrolysed as well as hydrolysed species. The various species of Ce (IV) which may exist in perchloric acid medium are governed by the following equilibrium.



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 $\text{Ce}(\text{OH})^{3+}$ refers to the hydrolysed species of Ce(IV).

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

H^+	Ce^{4+}	$\text{Ce}(\text{OH})^{3+}$
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 estimated and 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. The results indicate that both hydrolysed as well as unhydrolysed species are present at low acid concentrations in range of acid concentrations where the studies were performed while at higher concentrations of perchloric acid more and more hydrolysed species get converted into the unhydrolysed species. The concentration range in which my study was performed, only unhydrolysed species acted as the reactive species.



CONCLUSION

I like to conclude my study on A mechanistic study based on kinetics of the oxidation of methyl propyl 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 methyl propyl 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. 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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