

Kinetic Study of Oxidation of Cyclohexanol by Ceric Per Chlorate in Presence of Iridium (III) as a Catalyst



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ABSTRACT

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Iridium (III) chloride catalysed oxidation of Cyclohexanol by ceric per chlorate in aqueous perchloric acid medium was studied. Change in the concentration of perchloric acid shows a specific effect that the rate decreases in the beginning at low concentrations, then increases and it reaches to a maximum, probably due to conversion of hydrolysed to unhydrolyzed species of ceric perchlorate, which then accelerate the rate. Oxidation was highly selective as it oxidizes cyclohexanol to dicarboxylic acid. It is proposed that the complex formed between cerium (IV) and the organic substrate in first equilibrium step gives another complex in the presence of iridium (III) which ultimately gives rise to products of oxidation. Order of the reaction follows first order kinetics at low concentrations tending to become zero order at higher concentrations of organic substrate and oxidant. Rate of the reaction follows direct proportionality with respect to catalyst concentrations. No effect of change in ionic strength of the medium is observed. Energy of activation and entropy parameters were also calculated.

Keywords : Iridium (III) Chloride , Ceric per chlorate ,Oxidation, Cyclohexanol.

I. INTRODUCTION

Use of iridium (III) chloride amongst transition metal ions as a homogeneous catalyst in alkaline medium could attract little attention because in alkaline medium it is not supposed to be an efficient catalyst [1,2]. Its Potentiality as a homogeneous catalyst was

recognized when it was used in the acidic medium. The oxidation of a range of alcohols to ketones or carboxylic acids proceeds in good yield using catalytic quantities of cerium(IV) phosphonate modified silica and sodium bromate as the re-oxidant [3]. It may be pointed out that iridium(III)-cerium(IV) system in acidic medium is so efficient from the synthetic point

of view that it oxidizes cyclohexane and benzene also with the highest yields reported so far [4,5]. To find out the effect of iridium (III) chloride in catalysing the oxidation of hydrocarbons from kinetic point of view, we have studied the oxidation of cyclohexanol by ceric perchlorate in aqueous perchloric acid medium in the presence of iridium(III) chloride. This catalyst drew attention as it is being required hundred time less in comparison with Ruthenium (III) Chloride [6] and Osmium tetra oxide with hexacyanoferrate(III)[7].

2. Experiment

Sodium perchlorate, cerium(IV) sulphate (Loba chemie industrial Corporation), sulphuric acid, ferrous ammonium sulphate, ferroin, cyclohexanol (Koch-Light) were used as such without further purification and their solution were prepared by directly dissolving the weighted sample in distilled water. Solution of sodium hexachloro iridate(III) (Johnson Matthey and company) was prepared by dissolving the sample in the minimum amount of hydrochloric acid (A.R.); the final strength of acid and catalyst were 0.00624 and 3.35×10^{-3} M respectively. The strength of Cerium (IV) for sulphate prepared by dissolving the sample in 1:1 sulphuric dilute, was determined by titrating it against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. Solution of ceric perchlorate was prepared by precipitating the ceric hydroxide from the prepared solution of ceric ammonium nitrate with dilute solution of Ammonium hydroxide. The gelatinous precipitate thus, obtained was washed several times with distilled water till the complete removal of sulphate ion and after drying the precipitate, it was redissolve in perchloric acid. All other chemical used were either Analar or chemically pure substances. Progress of the reaction was measured (at constant temperature $\pm 0.1^\circ\text{C}$) at different intervals of time by transferring the aliquot to a fixed amount of ferrous ammonium sulphate solution (in slight excess to ceric perchlorate initially take) and titrating the remaining ferrous Ammonium Sulphate with a standard ceric

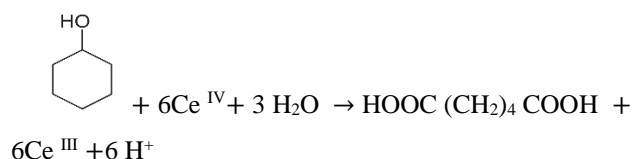
sulphate solution using ferroin as an indicator. In this way the titre values directly correspond to the amount of ceric perchlorate consumed in the reaction mixture.

2.1 Determination of kinetic orders and stoichiometry

Iridium (III) chloride oxidation of cyclohexanol by ceric perchlorate in perchloric acid was studied under the condition and range in which a catalysed reaction was negligible. Rate of reaction ($-dc/dt$) was obtained from the initial slopes of individual graphs plotted between the residual concentration of cerium (IV) at various intervals. In case of oxidant variation rate values were calculated at a fixed initial time while in remaining cases they were calculated at a fixed initial concentration. The rate values ($-dc/dt$) so obtained were finally plotted against the changing concentrations of the particular reactant for which order of reaction was to be obtained. Close similarity in the rate values obtained by two methods that is $k_{\text{calculated}}$ (by using integrated first order rate equation and taking average of values in a particular set and $k_{\text{graphical}}$ (by dividing $(-dc/dt)$ values with $(a-x)$ values that is the residual concentration of cerium (IV) at the point at which the rate were calculated), confirms reliability of the results. Orders, with respect to various reactants were confirmed by plotting graph between $\log(a-x)$ and 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 concentration (catalyst variation). The effect of ionic strength was studied separately, which shows its independence nature. Thus to save chemicals experiments were conducted without considering ionic strength into consideration.

Stoichiometry of the reaction was studied by taking ceric perchlorate in large excess in comparison with organic substrate in different ratios and thus complete oxidation of the provided organic substrate (cyclohexanol) was ensured. The final products was identified with the help of TLC and the spot test

method [8]. The stoichiometry of the reaction may be given according to the following equation.



Observations

Table 1. Effect of variations of [Cerium (IV)] on the rate at 25°C

[Ce ^{IV}] x 10 ⁻⁴ mol dm ⁻³	-dc/dt x 10 ⁻⁶ mol dm ⁻³ min ⁻¹	k _{gr} x 10 ⁻² min ⁻¹	k _{cal} x 10 ⁻² min ⁻¹
2.5	5.8	3.03	2.99
3.75	6.6	2.45	2.07
6.25	9.5	1.75	1.60
7.5	10.3	1.68	1.65
10.0	12.2	1.37	1.20
15.0	12.6	0.92	0.93

Table 2. Effect of variations of substrate (cyclohexanol) on the rate at 25°C

[Cyclohexanol] x 10 ⁻³ mol dm ⁻³	-dc/dt x 10 ⁻⁶ mol dm ⁻³ min ⁻¹	k _{gr} x 10 ⁻² min ⁻¹	k _{cal} x 10 ⁻² min ⁻¹
1.00	1.76	0.80	0.84
2.00	2.82	1.31	1.20
3.00	4.56	2.07	2.18
4.00	5.90	2.70	2.75
5.00	7.50	3.50	3.40
6.00	8.14	3.72	3.75

Table 3. Effect of variations of catalyst [Ir(III)] on the rate at 25°C

[Ir(III)] x 10 ⁻⁷ mol dm ⁻³	-dc/dt x 10 ⁻⁶ mol dm ⁻³ min ⁻¹	k _{gr} x 10 ⁻² min ⁻¹	k _{cal} x 10 ⁻² min ⁻¹
0.45	0.71	0.36	0.36
0.50	0.79	0.40	0.41
0.75	1.38	0.60	0.60
1.00	2.5	0.75	0.87
3.00	4.44	2.30	2.20
4.00	5.90	2.95	2.92

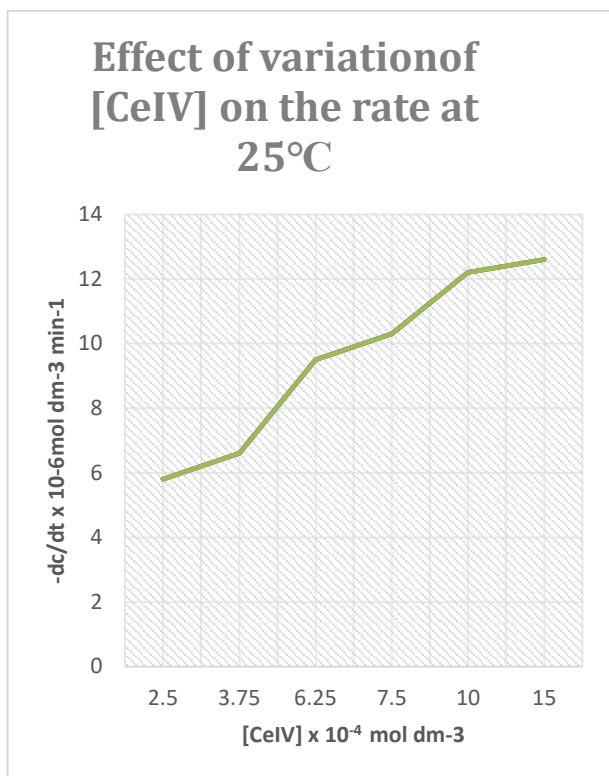
Table 4. Effect of variations of Acid [H⁺] on the rate at 25°C

[H ⁺] x M	-dc/dt x 10 ⁻⁶ mol dm ⁻³ min ⁻¹	k _{gr} x 10 ⁻² min ⁻¹	k _{cal} x 10 ⁻² min ⁻¹
1.25	2.96	3.29	3.28
2.00	2.27	2.52	2.63
3.00	2.06	2.29	2.35
4.50	2.50	2.78	2.76
5.00	2.90	3.20	3.44
6.00	3.57	3.97	3.94

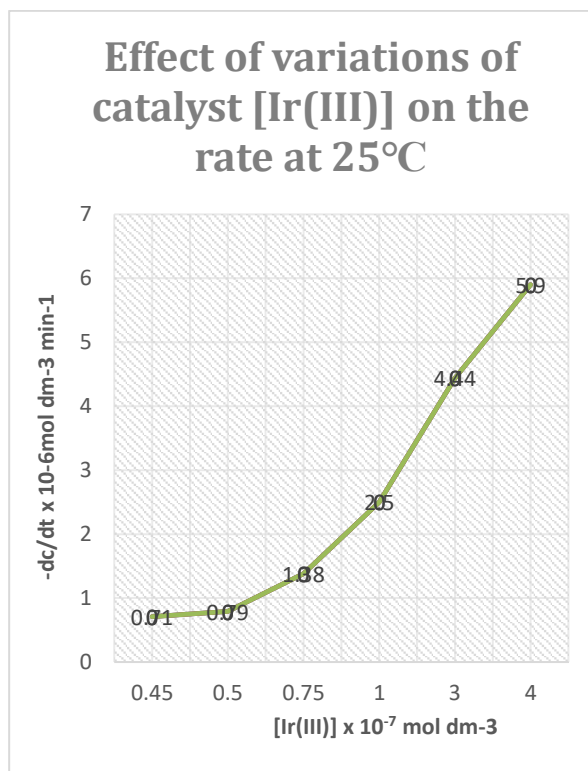
Using data from temperature variation following parameters were calculated using Arrhenius equation and thermodynamic relationship between reaction rate and entropy.

Table 5

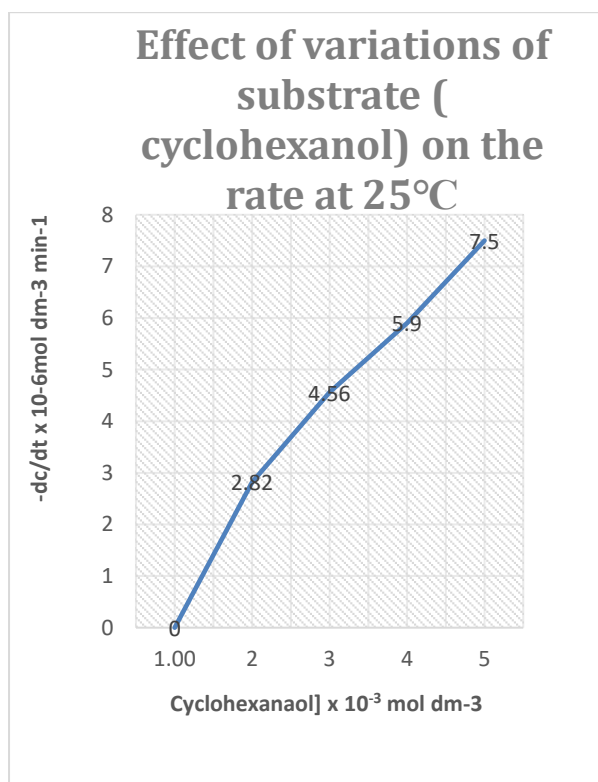
Organic Substrate	Δ E _a K.cal.mole ⁻¹	ΔS [‡] e.u.
Cyclohexanol	12.76	-26.66



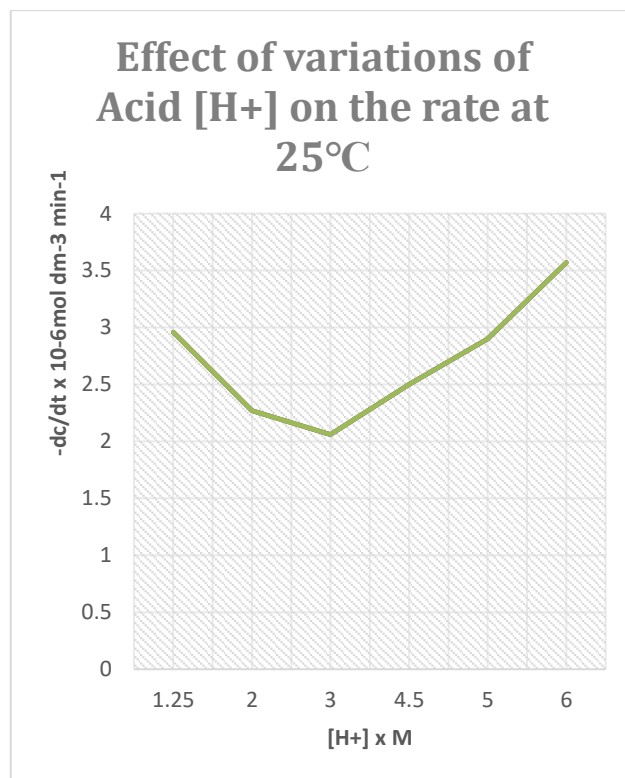
Graph 1 – [cyclohexanol] = $4.00 \times 10^{-3} \text{ M}$
 $[\text{HClO}_4] = 0.75 \text{ M}$, $[\text{IrCl}_3] = 4.00 \times 10^{-7} \text{ M}$



Graph 3 – [cyclohexanol] = $4.00 \times 10^{-3} \text{ M}$
 $[\text{HClO}_4] = 0.75 \text{ M}$, $[\text{Ce}(\text{ClO}_4)_4] = 2.5 \times 10^{-4} \text{ M}$



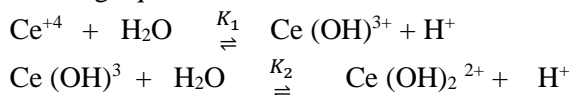
Graph 2 – $[\text{Ce}(\text{ClO}_4)_4] = 2.5 \times 10^{-4} \text{ M}$
 $[\text{HClO}_4] = 0.75 \text{ M}$, $[\text{IrCl}_3] = 4.00 \times 10^{-7} \text{ M}$



Graph 4 – [cyclohexanol] = $2.00 \times 10^{-3} \text{ M}$
 $[\text{IrCl}_3] = 5.00 \times 10^{-8} \text{ M}$, $[\text{Ce}(\text{ClO}_4)_4] = 1 \times 10^{-3} \text{ M}$

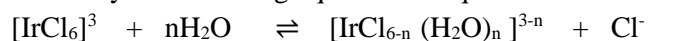
[HClO₄] = 0.75 M , [Ce(ClO₄)₄] = 2.5 x 10⁻⁴ M
 [IrCl₃] = 5.00 x 10⁻⁸ M , [Ce(ClO₄)₄] = 1 x 10⁻³ M

As we know Perchloric acid is a strong oxidant but concentration less than 50% and temperature up to 50-60 °C , it is not capable of releasing oxygen , therefore it will not behave as oxidant under our required conditions for performing experiments . Cerium (IV) in perchloric acid exit [9] in hydrolysed and unhydrolysed forms as per the following equilibrium:

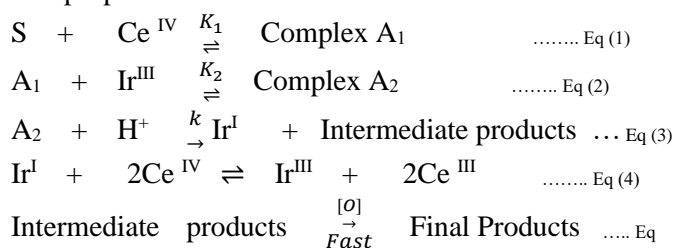


Dominant species of ceric per chlorate in aqueous perchloric acid medium is monomeric [10]. On increasing concentration of H⁺ ions from 1.25 to 6.0 M concentration of unhydrolyzed species increases continuously on the other hand the concentration of hydrolysed species first increases and then starts decreasing [11]. The range in which we performed our experiment , clearly give indication regarding presence of both hydrolysed as well unhydrolysed species , but at higher concentration mainly unhydrolysed species predominate the scene.

It was reported that IrCl₃ in HCl gives IrCl₆⁻³ species [12]. It has also been well established from various sources that Iridium (III) and Iridium (I) ions are the stable species of iridium [13]. The aquation of [IrCl₆]³⁻ has been shown by the following equilibrium equation.



Formation of 1:1 complexes was well documented between cerium (IV) and alcohol [14-17] and ketones [18-20]. On the bases of above data following scheme was proposed for the above reaction



(5)

Deriving rate law

$$\text{A}_1 = K_1[\text{CeIV}] [\text{S}] \quad \dots\dots\dots \text{Eq (a)}$$

$$\text{A}_2 = K_2 \text{A}_1 [\text{Ir}^{\text{III}}] \quad \dots\dots\dots \text{Eq (b)}$$

$$[\text{Ir}^{\text{III}}] = \frac{\text{A}_2}{\text{A}_1 K_2} = \frac{\text{A}_2}{K_1 K_2 [\text{Ce IV}] [\text{S}]} \quad \dots\dots \text{Eq (c)}$$

$$[\text{Ir}^{\text{III}}]_{\text{T}} = \text{A}_2 + [\text{Ir}^{\text{III}}] \quad \dots\dots\dots \text{Eq (d)}$$

$$[\text{Ir}^{\text{III}}]_{\text{T}} = \text{A}_2 + \frac{\text{A}_2}{K_1 K_2 [\text{Ce IV}] [\text{S}]} \quad \dots\dots \text{Eq (e)}$$

$$[\text{Ir}^{\text{III}}]_{\text{T}} = \text{A}_2 \left[\frac{1}{K_1 K_2 [\text{Ce IV}] [\text{S}]} + 1 \right] \quad \dots \text{Eq (f)}$$

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

$$\frac{-d[\text{CeIV}]}{dt} = k \text{A}_2 [\text{H}^+] \quad \dots\dots \text{Eq (h)}$$

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

II. CONCLUSION

At low concentration of Cerium and substrate above equation becomes as 1 is far greater than K₁ K₂ [Ce IV] [S]

$$\frac{-d[\text{CeIV}]}{dt} = 2kK_1 K_2 [\text{Ce IV}] [\text{S}] [\text{Ir}^{\text{III}}]_{\text{T}} [\text{H}^+] \quad \dots\dots \text{Eq (j)}$$

At low concentration order with respect to oxidant , substrate , catalyst and acid is first order.

At high concentration of Cerium and substrate above equation becomes as 1 is far smaller than K₁ K₂ [Ce IV] [S]. Therefore equation becomes

$$\frac{-d[\text{CeIV}]}{dt} = 2k[\text{Ir}^{\text{III}}]_{\text{T}} [\text{H}^+] \quad \dots\dots\dots \text{Eq (k)}$$

At high concentration order with respect to catalyst and acid is first order and oxidant and substrate becomes zero order . This justify our experimental results and assume the validity of the final rate law .

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