



Graphical separation of un-catalyzed and catalyzed reactions in iridium(III) catalyzed oxidation of cinnamaldehyde by cerium(IV) in aqueous acidic medium

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ABSTRACT

When used as a homogeneous catalyst, iridium trichloride was found to change order of the reaction with respect to cerium(IV) sulphate concentrations in the oxidation of 3-phenyl propanal in aqueous acidic medium. Cerium(IV) and organic substrate form complex in the first equilibrium step. This complex decomposes in the rate determining step when iridium(III) is not present in the system while in the presence of iridium(III), it gives rise to another complex, which ultimately gives rise to cinnamic acid as product of reaction. Order of the reaction in the absence of iridium(III) was found to be one with respect to cerium(IV) sulphate concentrations while the reaction follows first order kinetics at low concentrations becoming to zero order at higher concentrations of the oxidant in the presence of catalyst. Both in the presence and the absence of catalyst, after showing first order kinetics in the beginning reaction tends to become independent of organic substrate at its higher concentrations. Rate of the reaction follows direct proportionality with respect to catalyst concentrations. Change in the ionic strength of the medium or concentrations of hydrogen ions, cerium(III) and acetic acid have no effect on the rate. Interestingly with fair degree of accuracy, the rate of un-catalyzed path may be separated graphically with the help of the intercept of catalyst graph. IR spectrum of the product confirmed cinnamic acid as the final oxidation product. Energy of activation, free energy of activation and entropy parameters were calculated.

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1. Introduction

Iridium(III) chloride does not show efficient catalytic activity in alkaline medium [1,2]. Cerium(IV) has been reported to oxidize various aromatic compounds having different functional groups, but these oxidations have been studied mainly from the synthetic point of view [3]. Redox reactions of aromatic compounds are very important from the synthetic point of view because most of the industries are based on the oxidation products of various aromatics. Kinetic study of the oxidation of various aromatic compounds helps to find out the optimum conditions or concentrations under which maximum yield of the product may be obtained under most economical conditions. Powerful catalytic activity of iridium(III)–cerium(IV) system in acidic medium has been reported in the oxidation of aliphatic ketones and alcohols [4–8]. This system oxidizes various aromatic organic compounds in excellent yields, including cyclohexane and benzene with the highest yields reported so far [9,10].

In continuation of these studies we hereby report the effect of iridium(III) chloride in catalyzing the oxidation of cinnamaldehyde by cerium(IV) sulphate in aqueous sulphuric acid medium in the presence and absence of iridium(III) chloride.

2. Experimental

Cerium(IV) sulphate, cinnamaldehyde (Lancaster), sulphuric acid, acetic acid, ferroin (E. Merck) and cerium(III) sulphate (Fluka A.G.) were used as supplied without further purification by preparing their solutions in double distilled water. Strength of sodium hexachloroiridate(III) (Johnson Matthey & Co.) was 3.35×10^{-3} M which was prepared by dissolving the sample in minimum amount of AR HCl (0.62×10^{-2} M). Ferrous ammonium sulphate (FAS) solution was standardized by titrating it against a standard solution of potassium dichromate (E. Merck) using *N*-phenyl anthranilic acid as an internal indicator. Stock solution of cerium(IV) sulphate was prepared by dissolving the sample in AR sulphuric acid (diluted with distilled water in 1:1 ratio) and its strength was checked by titrating it against a standard ferrous ammonium sulphate solution using ferroin as an internal indicator. Strength of sulphuric acid present in cerium(IV) sulphate was adjusted in

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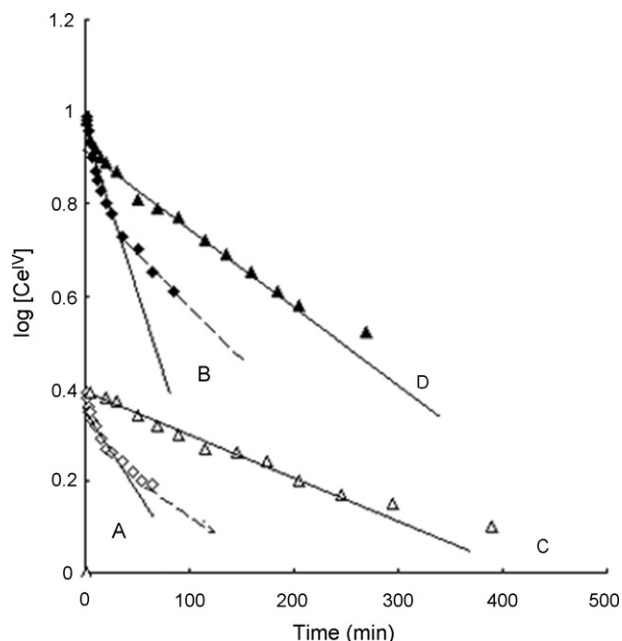


Fig. 1. Sample individual time plots for the consumption of Ce^{IV} at 30°C . $[\text{H}_2\text{SO}_4]=0.15\text{ M}$, $[\text{cinnamaldehyde}]=1.00 \times 10^{-3}\text{ M}$, $[\text{acetic acid}]=0.09\text{ M}$, $[\text{IrCl}_3]=0.67 \times 10^{-6}\text{ M}$ (for catalyzed reactions only) and $[\text{Ce}(\text{SO}_4)_2]=\text{A}$ and $\text{C}-0.40$; B and $\text{D}-1.00 (\times 10^{-3}\text{ M})$. (Concentrations are the initial concentration of reactants.)

maintaining sulphuric acid concentration in the reaction mixture. All other chemicals used were of either AR grade or chemically pure substances. Cinnamaldehyde was insoluble in aqueous medium therefore its stock solution was prepared by dissolving the sample in minimum amount of acetic acid and then diluting the solution to the desired volume. Concentration of acetic acid was kept constant in all the variations except while studying the effect of acetic acid concentration on the rate. Progress of the reaction was measured (constant temperature $\pm 0.1^\circ\text{C}$) at different intervals of time by transferring 5.0 ml of aliquot of reaction mixture to the fixed amount of ferrous ammonium sulphate solution (volume or strength of FAS solution should be slightly in excess to the total cerium(IV) initially taken in the reaction mixture) and estimating the excess 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 cerium(IV) consumed in the reaction mixture. In all kinetic runs cinnamaldehyde concentration was kept in excess.

2.1. Determination of kinetic orders

Oxidation of cinnamaldehyde by cerium(IV) sulphate in acidic medium takes place even in the absence of iridium(III) chloride. Therefore, un-catalyzed and catalyzed reactions were studied separately under similar conditions. In the case of oxidant variation $-dc/dt$ values were calculated at a fixed initial time from the individual plots, 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. Orders, with respect to various reactants were confirmed by plotting log of remaining concentration of oxidant 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). Study could not be made at constant ionic strength of the medium due to large volumes of potassium chloride 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 potassium chloride.

2.2. Product study and stoichiometry

To find out stoichiometry, reactions were studied under the conditions when cerium(IV) sulphate was in large excess compared to organic substrate. Reaction mixtures were kept at 30°C for a long period to ensure complete oxidation of the organic substrate. After completion of the reaction, solution was concentrated on a water bath. Reaction mixture was then extracted with diethyl ether ($5 \times 25\text{ ml}$) and the solvent evaporated under reduced pressure. After re-crystallization with hot water compound was obtained as white solid (mp 130°C , reported 133°C), which gave the test for unsaturation [11]. The compound was finally identified by chromatographic technique [12] and also by taking IR spectra of the product. Peaks at 3027 cm^{-1} ($\nu\text{O-H}$); 1680 cm^{-1} ($\nu\text{C=O}$); 1494 cm^{-1} ($\nu\text{C=C}$) in the IR spectrum (ABB Bomen, FTLA 2000 104) of the product confirmed the formation of cinnamic acid in the reaction mixture. Lowering of the peak (observed at 3027 cm^{-1}) of hydroxyl group in acids is mainly due to overlap of C-H stretch. [13] Stoichiometry of the reaction may be given by the following equation:

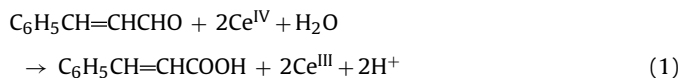


Table 1
Effect of variation of [cerium(IV)] and [cinnamaldehyde] on the rate at 30°C

[Ce^{IV}] [#] ($\times 10^3\text{ M}$)	$-dc/dt$ ($\times 10^5\text{ M min}^{-1}$)		$k((-\text{dc}/dt)/[\text{Ce}^{\text{IV}}])$ ($\times 10^2\text{ min}^{-1}$)		[Cinnamaldehyde] [*] ($\times 10^3\text{ M}$)	$-dc/dt$ ($\times 10^5\text{ M min}^{-1}$)		$k((-\text{dc}/dt)/[\text{cinnamaldehyde}])$ ($\times 10^3\text{ min}^{-1}$)	
	(A)	(B)	(A)	(B)		(A)	(B)	(A)	(B)
0.40	0.54	0.10	1.35	0.25	1.00	0.50	0.34	5.00	3.40
0.50	0.62	0.12	1.24	0.24	1.25	0.58	0.36	4.64	2.88
0.60	0.63	0.14	1.05	0.23	1.50	0.63	0.38	4.20	2.53
0.70	0.65	0.18	0.92	0.25	2.00	0.63	0.42	3.45	2.10
0.80	0.68	0.20	0.85	0.25	2.50	0.72	0.50	2.88	2.00
0.90	0.71	0.23	0.78	0.25	3.30	0.82	0.67	2.48	2.00
1.00	0.71	0.24	0.70	0.24	4.00	0.88	0.80	2.20	2.00
–	–	–	–	–	5.00	1.14	0.88	2.28	1.76

[$\text{Ce}(\text{SO}_4)_2$] $=1.00 \times 10^{-3}\text{ M}$ (for * only), [cinnamaldehyde] $=1.0 \times 10^{-3}\text{ M}$ (for # only), $[\text{H}_2\text{SO}_4]=0.15\text{ M}$, $[\text{IrCl}_3]=0.67 \times 10^{-6}\text{ M}$ (for A only), [acetic acid] $=0.50\text{ M}$ (for *); 0.09 M (for #). (Concentrations are the initial concentration of reactants.)

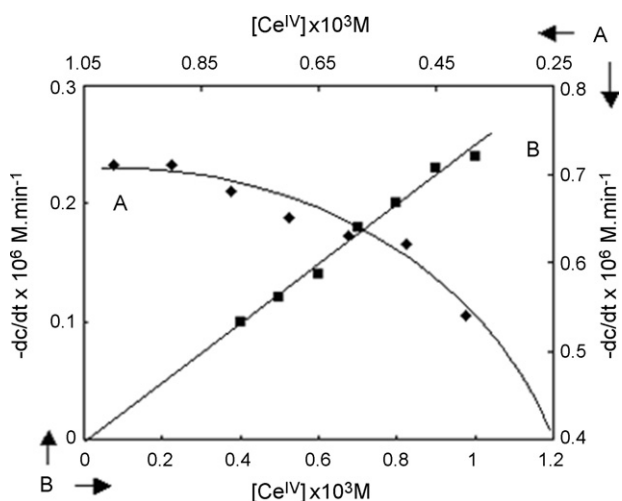


Fig. 2. Effect of variation of [cerium(IV)] on the rate at 30 °C. $[\text{H}_2\text{SO}_4]=0.15\text{ M}$, $[\text{cinnamaldehyde}]=1.00 \times 10^{-3}\text{ M}$, $[\text{acetic acid}]=0.09\text{ M}$ and $[\text{IrCl}_3]=0.67 \times 10^{-6}\text{ M}$ (for catalyzed reactions only). (Concentrations are the initial concentration of reactants.)

3. Results

First order plots between the log of residual oxidant concentration in the reaction mixture versus time in case of uncatalyzed reactions show parallel straight lines, however, probably due to the formation of complex, in the case of catalyzed reaction, deviations in the later part of the reaction at higher concentrations of the oxidant are more pronounced (Fig. 1). In the case of un-catalyzed reaction $-\text{dc}/\text{dt}$ values increase proportionately with increasing concentration of the oxidant, while in the case of catalyzed reaction $-\text{dc}/\text{dt}$ values increase proportionately with concentration only in the beginning and the increase becomes less prominent at higher concentrations (Table 1). First order rate constant values for molar concentrations of the oxidant show fair constancy in the case of un-catalyzed reaction, while these values remain constant only in the beginning in the case of catalyzed reaction. On plotting $-\text{dc}/\text{dt}$ values versus concentration of the oxidant straight lines passing through the origin are obtained in the case of both catalyzed and un-catalyzed reactions. In the case of un-catalyzed reaction deviation from linearity in the graph was not observed even at higher concentrations of the oxidant, while in the case of catalyzed reaction the straight line passing through the origin becomes parallel to x -axis at higher concentrations of the oxidant (Fig. 2). All these facts collectively confirm that rate of the reaction through out fol-

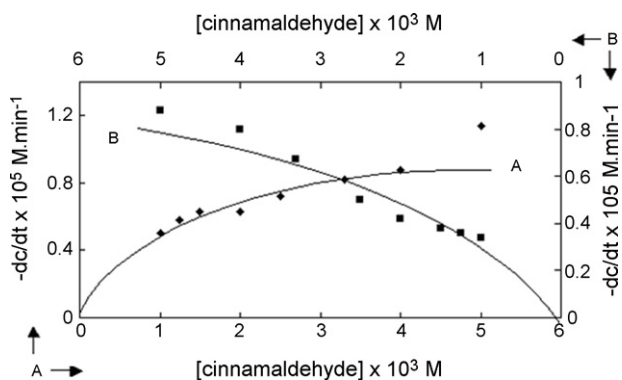


Fig. 3. Effect of variation of [cinnamaldehyde] on the rate at 30 °C. $[\text{Ce}(\text{SO}_4)_2]=1.00 \times 10^{-3}\text{ M}$, $[\text{H}_2\text{SO}_4]=0.15\text{ M}$, $[\text{acetic acid}]=0.50\text{ M}$ and $[\text{IrCl}_3]=0.67 \times 10^{-6}\text{ M}$ (for catalyzed reactions only). (Concentrations are the initial concentration of reactants.)

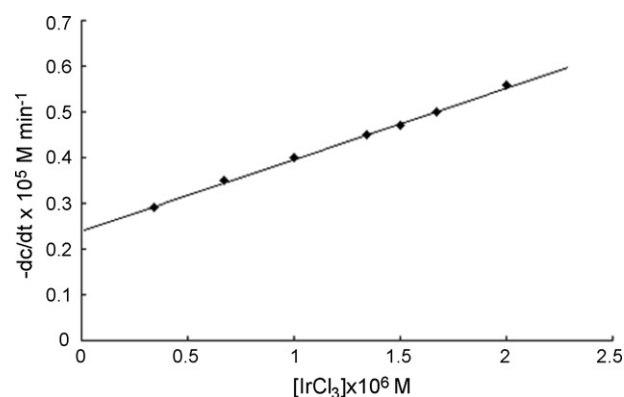


Fig. 4. Effect of variation of [catalyst] on the rate at 30 °C. $[\text{Ce}(\text{SO}_4)_2]=0.67 \times 10^{-3}\text{ M}$, $[\text{cinnamaldehyde}]=2.00 \times 10^{-3}\text{ M}$, $[\text{H}_2\text{SO}_4]=0.15\text{ M}$ and $[\text{acetic acid}]=0.15\text{ M}$. (Concentrations are the initial concentration of reactants.)

lows first order kinetics in the case of un-catalyzed reaction while in the case of catalyzed reaction, the rate shows direct proportionality with respect to oxidant only at its low concentrations and tends to become independent of concentration at higher concentrations of the oxidant. In Table 1, $-\text{dc}/\text{dt}$ values increase with increasing concentration of organic substrate in the beginning but at higher concentrations the increase is not so prominent. This trend becomes clear on plotting $-\text{dc}/\text{dt}$ values versus $[\text{ketone}]$ in which line appears to be passing through the origin in the beginning at low concentrations. At higher concentrations of organic substrates the line tends to become parallel to the x -axis (Fig. 3). These facts indicate that in both cases, order of the reaction with respect to organic substrate is one at low concentrations but tends to become zero at higher concentrations of the organic substrate. Study at still lower concentrations of organic substrate could not be performed due to practical difficulties as the reaction becomes too slow to be measured properly, moreover, lowering the concentrations further, may not be in accordance with the Ostwald's isolation method, yet the trend of lines is quite clear from Fig. 3.

On plotting $-\text{dc}/\text{dt}$ values versus concentration of $[\text{IrCl}_3]$ (Fig. 4), a straight line was obtained with a positive intercept at y -axis. Slope of this line shows the rate of catalyzed reaction while the positive intercept gives the extent of the reaction, which takes place even in the absence of the catalyst. Proportionate increase in $-\text{dc}/\text{dt}$ values with increasing catalyst concentrations and fair constancy in the first order rate constant k values indicate that the reaction follows first order kinetics with respect to iridium(III) chloride concentrations (Table 2). On plotting double logarithmic graphs between $\log -\text{dc}/\text{dt}$ and $\log [\text{IrCl}_3]$ straight lines with slope value 0.95 was obtained, which further supports direct proportionality of the reaction velocity with respect to iridium(III) chloride concentrations.

$-\text{dc}/\text{dt}$ values remain practically constant at 0.59 ± 0.03 and 0.36 ± 0.02 ($\times 10^{-5}\text{ M min}^{-1}$) in the case of catalyzed

Table 2
Effect of variation of [iridium(III)] on the rate at 30 °C

$[\text{Ir}^{\text{III}}] (\times 10^6\text{ M})$	$-\text{dc}/\text{dt} (\times 10^5\text{ M min}^{-1})$	$k((-\text{dc}/\text{dt})/[\text{Ir}^{\text{III}}]) (\text{min}^{-1})$
0.34	0.29	8.50
0.67	0.35	5.20
1.00	0.40	4.00
1.34	0.45	3.35
1.50	0.47	3.13
1.67	0.50	2.94
2.00	0.56	2.73

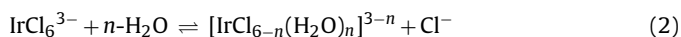
$[\text{Ce}(\text{SO}_4)_2]=0.67 \times 10^{-3}\text{ M}$, $[\text{cinnamaldehyde}]=2.00 \times 10^{-3}\text{ M}$, $[\text{H}_2\text{SO}_4]=0.15\text{ M}$, $[\text{acetic acid}]=0.15\text{ M}$. (Concentrations are the initial concentration of reactants.)

and un-catalyzed reactions respectively on changing sulphuric acid concentrations from 0.20 to 0.75 M (under the conditions $[\text{IrCl}_3]=0.67 \times 10^{-6} \text{ M}$ (in case of catalyzed reaction only) $[\text{Ce}(\text{SO}_4)_2]=1.00 \times 10^{-3} \text{ M}$; $[\text{cinnamaldehyde}]=2.0 \times 10^{-3} \text{ M}$ and $[\text{acetic acid}]=0.15 \text{ M}$). On changing the concentration of externally added $\text{Ce}_2(\text{SO}_4)_3$ from 1.00 to $2.00 \times 10^{-3} \text{ M}$ the rate values remain constant at 0.72 ± 0.02 and 0.41 ± 0.01 ($\times 10^{-5} \text{ M min}^{-1}$) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[\text{IrCl}_3]=0.67 \times 10^{-6} \text{ M}$ (in case of catalyzed reaction only), $[\text{Ce}(\text{SO}_4)_2]=1.00 \times 10^{-3} \text{ M}$; $[\text{cinnamaldehyde}]=2.0 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4]=0.25 \text{ M}$ and $[\text{acetic acid}]=0.15 \text{ M}$). Constancy in the rate values shows that changes in the concentration of hydrogen ions or Ce(III) ions do not effect the reaction velocity. These observations show that these ions are not given out before the rate determining slow step. Similarly on changing the concentration of acetic acid from 0.15 to 0.75 M (in case of un-catalyzed reaction 0.25 to 1.00 M), the rate values remain constant at 0.58 ± 0.028 and 0.33 ± 0.019 ($\times 10^{-5} \text{ M min}^{-1}$) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[\text{IrCl}_3]=0.67 \times 10^{-6} \text{ M}$ (in case of catalyzed reaction only), $[\text{Ce}(\text{SO}_4)_2]=1.00 \times 10^{-3} \text{ M}$; $[\text{cinnamaldehyde}]=2.00 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4]=0.15 \text{ M}$ and $[\text{acetic acid}]=0.15 \text{ M}$). Large volumes of potassium chloride 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 potassium chloride does not affect the reaction velocity and the rate values ($-dc/dt$) remain constant at 0.58 ± 0.017 and 0.40 ± 0.02 ($\times 10^{-5} \text{ M min}^{-1}$) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[\text{IrCl}_3]=0.67 \times 10^{-6} \text{ M}$ (in case of catalyzed reaction only), $[\text{Ce}(\text{SO}_4)_2]=1.00 \times 10^{-3} \text{ M}$; $[\text{cinnamaldehyde}]=2.00 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4]=0.15 \text{ M}$, $[\text{acetic acid}]=0.15 \text{ M}$). This observation shows that changes in the ionic strength of the medium and the concentration of chloride ions have no effect on the reaction velocity. Arrhenius equation was found to be applicable and from the slopes of the Arrhenius plots and by using Eyring equation, dif-

ferent 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 12.6 and 8.64 (Kcal), -48.00 and -57.00 (e.u.), 17.28 and 14.55 ($\text{kcal g}^{-1} \text{ mole}^{-1}$) for un-catalyzed and catalyzed reactions, respectively.

4. Reactive species of iridium(III) chloride

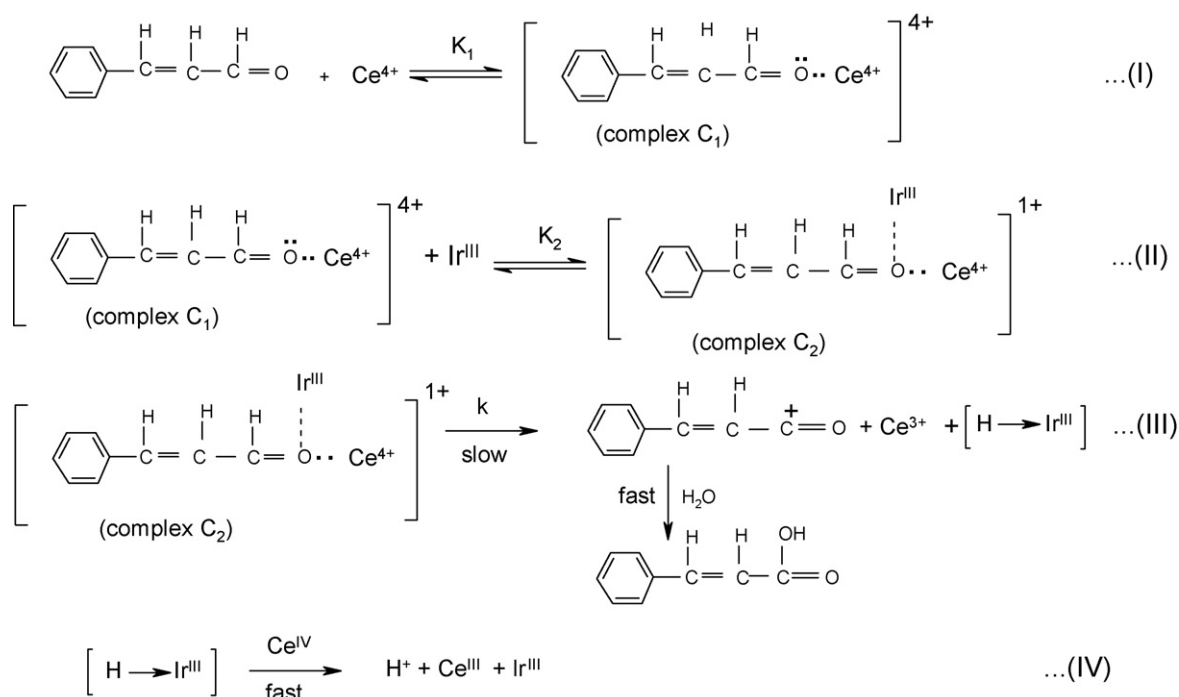
It is known that IrCl_3 in hydrochloric acid gives IrCl_6^{3-} species [14]. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [15]. Further, the aquation of $[\text{IrCl}_6^{3-}]$ gives $[\text{IrCl}_5(\text{H}_2\text{O})^{2-}]$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ species [16–18]. This equilibrium may be shown in general by the following equation:



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 [1,2]. Therefore, considering our experimental results, IrCl_6^{3-} has been considered to be the reactive species of iridium(III) chloride in the present study, which has been considered to be the active species previously also [1,2,6]. 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 also may not be possible.

5. Discussion

Formation of 1:1 complexes between cerium(IV) and alcohols [19] and ketones [20] are well documented. Complex formation between cerium(IV) and alcohols to give complexes of composition $[\text{ROH-cerium(IV)}]^{4+}$ and Michaelis–Menten type of kinetics has



Scheme 1. Proposed steps in the oxidation of cinnamaldehyde by cerium(IV) in aqueous acidic medium in the presence of iridium(III) chloride.

been reported [21]. While similar results have been reported in the case of ketones also [22–24].

5.1. Mechanism in the presence of iridium(III) chloride

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 gives rise to the intermediate product, which ultimately converts into *p*-methoxy benzoic acid. Electron of the hydrogen atom is quickly taken up by another cerium(IV), giving rise to the original iridium(III) species.

5.2. Mechanism in the absence of iridium(III) chloride

In the case of un-catalyzed path all the results were similar except of the order with respect to cerium(IV) concentrations, in which the reaction shows direct proportionality with respect to oxidant even at higher concentrations of the oxidant. Thus on the basis of similar results reaction path in the absence of catalyst may be given as according to Scheme 2.

6. Rate laws

6.1. Derivation of rate law for the catalyzed path

Considering the equilibrium concentrations of complexes C_1 and C_2 in steps (I) and (II) of the mechanism 1 and putting concentration of C_1 from step (I) into the concentration of $[Ir^{III}]$ obtained from step (II), total concentration of catalyst may be given as according to the following equation:

$$[Ir^{III}]_{\text{Total}} = \frac{[C_2]}{K_1 K_2 [S][Ce^{IV}]} + [C_2] \quad (3)$$

From Eq. (3) concentration of complex C_2 is given as

$$[C_2] = \frac{K_1 K_2 [Ce^{IV}][S][Ir^{III}]_T}{1 + K_1 K_2 [Ce^{IV}][S]} \quad (4)$$

Rate in terms of decreasing concentration of cerium(IV) from step (III) of the mechanism may be given as

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

This equation explains all experimental findings. At low concentrations of oxidant and organic substrate the inequality $1 \gg K_1 K_2 [Ce^{IV}][S]$ may hold and Eq. (5) reduces to (6) which, explains the nature shown by various reactants.

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

At higher concentrations of oxidant and substrate the reverse inequality $1 \ll kK_1 K_2 [Ce^{IV}][S]$ holds good and the equation becomes as

$$-\frac{d[Ce^{IV}]}{dt} = k[Ir^{III}]_T \quad (7)$$

Further verification of the rate law (5) may be given by rewriting Eq. (8) as

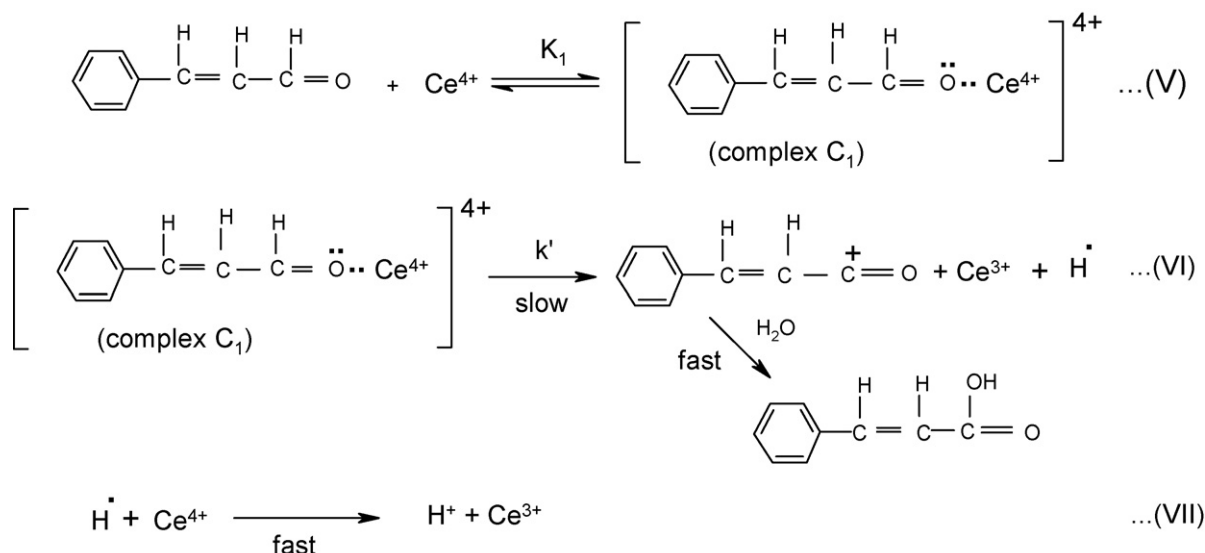
$$\frac{1}{-d[Ce^{IV}]/dt} = \frac{1}{kK_1 K_2 [Ce^{IV}][S]} + \frac{1}{k[Ir^{III}]} \quad (8)$$

Values of $kK_1 K_2$ were calculated from the slopes of the graphs between $1/\text{rate}$ versus $1/[Ce^{IV}]$, $1/[\text{substrate}]$ and $1/[Ir^{III}]$, which comes out to be 3.15, 1.49 and $1.67 (\times 10^7)$ respectively. Fair constancy in the $kK_1 K_2$ values calculated from three different graphs further indicates the validity of the Scheme 1 and the rate law (5). It may be pointed out that the intercept of the catalyst graph gives the extent of the reaction, which takes place even in the absence of iridium(III) chloride. This value was calculated and was found to be 1.64 for the un-catalyzed reaction.

6.2. Derivation of rate law for un-catalyzed path

Similarly for the un-catalyzed path total concentration of cerium(IV) may be given as

$$[Ce^{IV}] = \frac{[C_1]}{K_1 [S]} \quad (9)$$



Scheme 2. Proposed steps in the oxidation of cinnamaldehyde by cerium(IV) in aqueous acidic medium in the absence of iridium(III) chloride.

and considering equilibrium in step 1 of the mechanism 2 concentration of cerium(IV) may be given as

$$[\text{Ce}^{\text{IV}}]_{\text{Total}} = [\text{Ce}^{\text{IV}}] + [\text{C}_1] \quad (10)$$

Putting the value of $[\text{Ce}(\text{IV})]$ from Eq. (9) into Eq. (10) $[\text{C}_1]$ comes out to be

$$[\text{C}_1] = \frac{K'_1[\text{S}][\text{Ce}^{\text{IV}}]_{\text{T}}}{1 + K'_1[\text{S}]} \quad (11)$$

and the rate in terms of decreasing concentrations of cerium(IV) sulphate may be given as

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = k'[\text{C}_1] = \frac{k'K'_1[\text{S}][\text{Ce}^{\text{IV}}]_{\text{T}}}{1 + K'_1[\text{S}]} \quad (12)$$

This equation explains first order kinetics with respect to organic substrate, which tends to become zero order at higher concentrations of organic substrate, and the first order kinetics with respect to cerium(IV) concentrations even at its higher concentrations. Deviations from the straight line at higher concentrations of oxidant as observed in Fig. 2 are also explained due to the formation of complex between the oxidant and organic substrate in the first step of the mechanism 2. Rate law given by Eq. (13) reduces to as given in Eq. (14) if the inequality $1 \gg K'_1[\text{S}]$ is considered at low concentrations of organic substrate.

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = k'K'_1[\text{S}][\text{Ce}^{\text{IV}}]_{\text{T}} \quad (13)$$

Eq. (13) may also be written in the form

$$\frac{1}{\text{rate}} = \frac{1}{k'K'_1[\text{Ce}^{\text{IV}}][\text{S}]} + \frac{1}{k'[\text{Ce}^{\text{IV}}]} \quad (14)$$

On plotting graphs between $1/\text{rate}$ versus $1/[\text{S}]$ or $1/[\text{Ce}^{\text{IV}}]_{\text{T}}$ with the help of Eq. (14) we should get straight lines with positive intercepts at y -axis. The values of $k'K'_1$ were calculated from two graphs and were found to be 2.20 and 1.12, while this value calculated from the intercept of the catalyst graph in the catalyzed reaction was found to be 1.64. Close similarity in the rate values calculated from two separately studied reactions finally confirm the validity of the mechanisms and the rate laws proposed for both the reactions. The study also provides a method by which with fair degree of accuracy, the rate and extent of the un-catalyzed reaction can be calculated by studying the catalyzed reaction only.

Absence of any reaction between the organic substrate and iridium(III) giving rise to the complex C_1 in first step of Scheme 1 rules out the possibility of interaction between these two. 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 and at least formation of the complexes before the rate determining step.

7. Conclusion

The present study shows that iridium(III) chloride acts as a very effective catalyst for the oxidation of aromatic aldehydes in acidic

medium when used in conjunction with cerium(IV) sulphate. The present iridium(III)–cerium(IV) system is especially useful in the synthetic reaction of industrial importance. The present study also proves that the rate and extent of un-catalyzed reaction can be calculated with fair degree of accuracy by the intercept of the catalyst graph by studying the catalyzed reaction only.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.07.007.

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