Un-catalyzed and iridium(III) catalyzed oxidation of *p*-methoxy benzaldehyde by cerium(IV)

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Abstract

Apart from being an efficient catalyst in acidic medium iridium trichloride, was found to change order of the reaction with respect to cerium(IV) sulphate concentrations in the oxidation of *p*-methoxy benzaldehyde 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 *p*-methoxy benzoic 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 calculated graphically with the help of the intercept of the catalyst graph. Product of oxidation was identified to be anisic acid. Energy of activation, free energy of activation and entropy parameters were calculated.
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1. Introduction

Homogeneous catalysis by iridium(III) chloride has been given little attention due to its sluggish catalytic activity in alkaline medium [1,2]. Oxidation of aromatic compounds by cerium(IV) having different functional groups has been reported from the synthetic point of view [3]. Un-catalyzed oxidation of various organic compounds by cerium(IV) like alcohols [4] and ketones [5–7] has been reported by us. From the synthetic point of view, cerium(IV) oxidation of aromatic compounds in the presence and absence of metal ion catalysts has frequently been reported, but from the kinetic point of view these oxidations, in the presence of transition metal ions, have not been given much attention. To find out the effect of iridium(III) chloride in catalyzing the oxidation of aromatic aldehydes, we have studied the oxidation of *p*-methoxy benzaldehyde by cerium(IV) sulphate in aqueous sulphuric acid medium in the presence and absence of iridium(III) chloride.

2. Experimental

Cerium(IV) sulphate, *p*-methoxy benzaldehyde (Loba Chemie Indaustranal Co.), 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 doubly distilled water. Strength of sodium hexachloroiridate(III) (Johonson Matthay & Co.), prepared by dissolving the sample in minimum amount of A.R. HCl (0.62×10^{-2} mol dm^{-3}), was 3.35×10^{-3} mol dm^{-3}. Ferrous ammonium sulphate solution was standardized by titrating it against a standard solution of potassium dichromate (E. Merck) using *N*-phenyl anthranilic acid as an internal indicator. Cerium(IV) sulphate, prepared by dissolving the sample in 1:1 sulphuric acid, was titrated against the standard ferrous ammonium sulphate solution using ferroin as an internal indicator. All other chemicals used were either Analar or chemically pure substances. Anisaldehyde was

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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 ±0.1 °C) at different intervals of time by transferring the aliquot to a fixed amount of ferrous ammonium sulphate solution (in slight excess to cerium(IV) sulphate initially taken) and estimating the remaining 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 anisaldehyde concentration was kept in excess.

2.1. Determination of kinetic orders

Oxidation of anisaldehyde 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 rate values ($-d[Ce(IV)]/dt$ hereafter denoted as $-dc/dt$, the remaining concentration of cerium(IV) in the reaction mixture at various time intervals) 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 $\ln(a - x)$ 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). Tables and figures contain initial concentrations of the reactants. 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

Product study was performed by taking a number of reaction mixtures in which cerium(IV) sulphate was kept in large excess compared to that of organic substrate in different ratios. The reaction mixture was 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× 25 ml) and the solvent evaporated under reduced pressure. After re-crystallization with ethanol the compound was identified by spot test methods [8] and chromatographic techniques [9] and also by taking IR spectra of the product. Melting point of the product was found to be 180 °C (reported 182 °C). Peaks at 2982–2942 nm (ν_{-OH}), 1683 nm ($\nu_{-C=O}$) and 1299–1256 nm
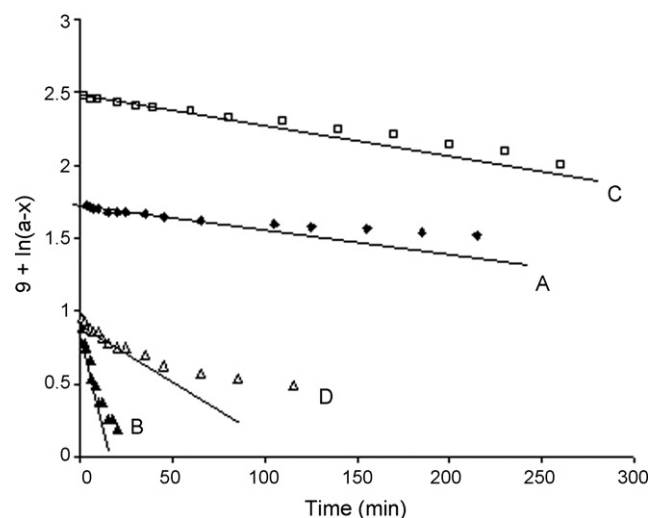

Fig. 1. Sample individual time plots for the consumption of Ce^{IV} at 30 °C. $[H_2SO_4] = 0.50 \, mol \, dm^{-3}$, $[anisaldehyde] = 5.00 \times 10^{-3} \, mol \, dm^{-3}$, $[acetic \, acid] = 0.35 \, mol \, dm^{-3}$, $[IrCl_3] = 1.67 \times 10^{-6} \, mol \, dm^{-3}$ (for catalyzed reactions only) and $[Ce(SO_4)_2] = $ (A) 1.50, (B) 0.33, (C) 5.00 and (D) 0.33 ($\times 10^{-3} \, mol \, dm^{-3}$). Catalyzed (A and B); un-catalyzed (C and D).

($\nu_{-C=C}$) in the IR spectrum (ABB Bomen, FTLA 2000 104) of the product confirmed the formation of anisic acid in the reaction mixture. Stoichiometry of the reaction may be given by the following equation:

$$H_3CO \cdot C_6H_4CHO + 2Ce^{IV} + H_2O$$
$$\rightarrow H_3CO \cdot C_6H_4COOH + 2Ce^{III} + 2H^+ \qquad (1)$$
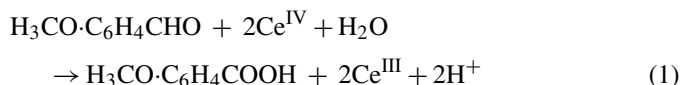
3. Results

First order plots, $\ln(a - x)$ versus time (where $(a - x)$ is remaining concentration of oxidant) in the case of catalyzed (Fig. 1A and B) and un-catalyzed (Fig. 1C and D) reactions for their highest (A and C) and lowest concentrations (B and D) show straight lines in major part of the reaction. Deviations from linearity are observed at about 90% completion of the reaction when initial oxidant concentration is low while they become apparent early at about 70% completion of reaction when the initial oxidant concentration is high. Deviation from linearity, which is more pronounced at higher concentrations of the oxidant, is probably due to the formation of complex between the oxidant and substrate during the course of reaction. In the case of un-catalyzed reaction rate values $-dc/dt$ ($-d[Ce(IV)]/dt$) increase proportionately with increasing concentration of the oxidant, while in the case of catalyzed reaction $-dc/dt$ values increase proportionately with concentration only in the beginning and the increase becomes less prominent at higher oxidant concentrations (Table 1). First order rate constant values for molar concentration of 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 rate values ($-dc/dt$) 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

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

$[Ce^{IV}]^a$ ($\times 10^3$ mol dm^{-3})	$-dc/dt$ ($\times 10^5$ mol dm^{-3} min^{-1})		k ($\times 10^2$ min^{-1})		[Anisaldehyde]^b ($\times 10^3$ mol dm^{-3})	$-dc/dt$ ($\times 10^5$ mol dm^{-3} min^{-1})		k ($\times 10^3$ min^{-1})	
	(A)	(B)	(A)	(B)		(A)	(B)	(A)	(B)
0.33	1.09	0.18	3.33	0.54	2.50	–	0.18	–	0.72
0.40	1.20	0.20	3.00	0.50	3.30	2.50	0.20	7.57	0.60
0.50	–	0.30	–	0.60	4.00	2.60	0.23	6.50	0.57
0.60	1.50	0.32	2.50	0.53	5.00	2.65	0.25	5.30	0.50
0.65	–	0.35	–	0.53	6.67	2.80	0.27	4.10	0.40
0.80	–	0.41	–	0.51	8.00	3.05	0.28	3.80	0.35
1.20	2.00	0.56	1.67	0.46	10.0	3.10	0.30	3.10	0.30
1.50	2.15	0.68	1.43	0.45	–	–	–	–	–
2.00	2.25	–	1.12	–	–	–	–	–	–
2.50	2.35	–	0.94	–	–	–	–	–	–
3.50	2.50	–	0.71	–	–	–	–	–	–
5.00	2.60	–	0.52	–	–	–	–	–	–

^{a} [Anisaldehyde] $= 5.0 \times 10^{-3}$ mol dm^{-3}, [H$_2$SO$_4$] $= 0.50$ mol dm^{-3}, [acetic acid] $= 0.35$ mol dm^{-3}.
^{b} [Ce(SO$_4$)$_2$] $= 2.00 \times 10^{-3}$ mol dm^{-3}, [H$_2$SO$_4$] $= 0.50$ mol dm^{-3}, [acetic acid] $= 0.75$ mol dm^{-3}.
[IrCl3] $= 1.67 \times 10^{-5}$ mol dm^{-3} (only for entries in (B)).

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 follows 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, $-dc/dt$ 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 rate values ($-dc/dt$) versus concentration of 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

Fig. 3. Effect of variation of [anisaldehyde] on the rate at 30 °C. Captions are same for (A) un-catalyzed reaction and (B) catalyzed reaction: [Ce(SO$_4$)$_2$] $= 2.00 \times 10^{-3}$ mol dm^{-3}, [H$_2$SO$_4$] $= 0.50$ mol dm^{-3}, [acetic acid] $= 0.75$ mol dm^{-3} and [IrCl$_3$] $= 1.67 \times 10^{-6}$ mol dm^{-3} (only for catalyzed reactions).

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 to maintain the validity of the Ostwald's isolation method and also due to practical difficulties as the reaction becomes too slow to be measured properly, yet the trend of lines is quite clear from Fig. 3.

Interestingly, on plotting $-dc/dt$ values versus concentration of 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 $-dc/dt$ values with increasing catalyst concentrations and fair constancy in k_1 values indicate that the reaction follows first order kinetics with respect to iridium(III) chloride concentrations (Table 2). On plotting double logarithmic graphs between $-dc/dt$ and concentration of IrCl$_3$, straight lines with slope value 0.95 was obtained, which further supports direct proportionality of the reaction velocity with respect to IrCl$_3$ concentrations.
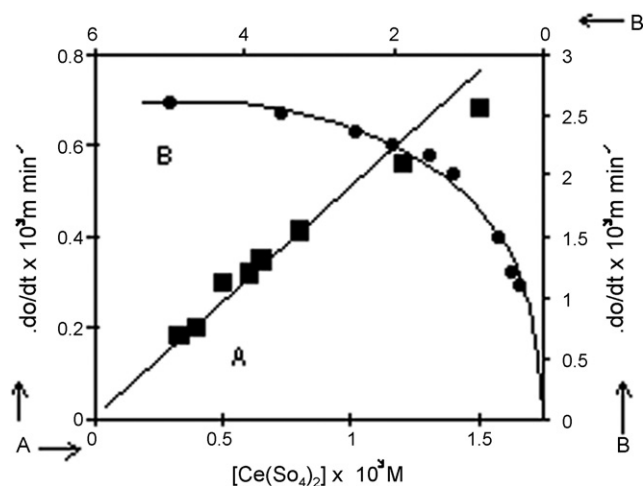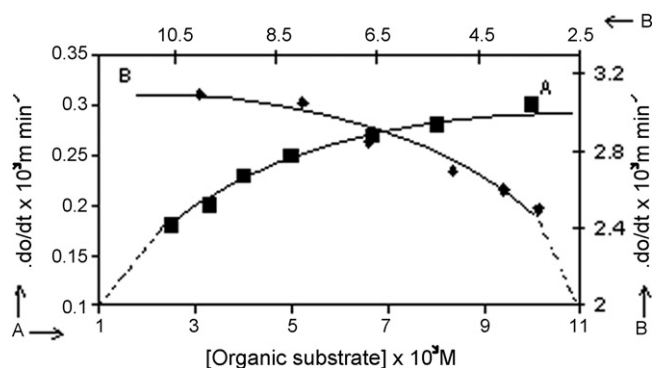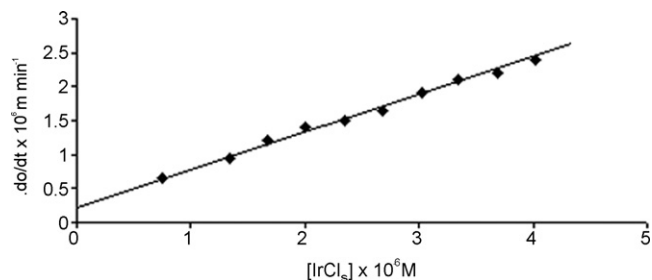

Fig. 2. Effect of variation of [cerium(IV)] on the rate at 30 °C. (A) Un-catalyzed reaction and (B) catalyzed reaction captions are same as in Fig. 1 (except for [Ce(SO$_4$)$_2$]).

Fig. 4. Effect of variation of [catalyst] on the rate at 30 °C. $[Ce(SO_4)_2] = 2.00 \times 10^{-3}$ mol dm^{-3}, [anisaldehyde] = 5.00×10^{-3} mol dm^{-3}, $[H_2SO_4] = 0.50$ mol dm^{-3} and [acetic acid] = 0.35 mol dm^{-3}.

$-dc/dt$ values remain practically constant at 1.00 ± 0.01 and 0.25 ± 0.01 ($\times 10^{-5}$ M min^{-1}) in the case of catalyzed and un-catalyzed reactions respectively on changing sulphuric acid concentrations from 0.15 to 0.75 M (under the conditions $[IrCl_3] = 1.67 \times 10^{-6}$ M (in case of catalyzed reaction only), $[Ce(SO_4)_2] = 1.20 \times 10^{-3}$ M, [anisaldehyde] = 5.0×10^{-3} M and [acetic acid] = 0.35 M). On changing the concentration of externally added $Ce_2(SO_4)_3$ from 0.67 to 2.00×10^{-3} M the rate values remain constant at 1.05 ± 0.03 and 0.30 ± 0.005 ($\times 10^{-5}$ M min^{-1}) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[IrCl_3] = 1.67 \times 10^{-6}$ M (in case of catalyzed reaction only), $[Ce(SO_4)_2] = 1.20 \times 10^{-3}$ M, [anisaldehyde] = 5.0×10^{-3} M, $[H_2(SO_4)_2] = 0.50$ M and [acetic acid] = 0.35 M). Constancy in the rate values shows that change in the concentration of hydrogen ions or Ce(III) ions does 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 0.25 to 1.00 M, the rate values remain constant at 0.63 ± 0.01 and 0.24 ± 0.016 ($\times 10^{-5}$ M min^{-1}) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[IrCl_3] = 1.67 \times 10^{-6}$ M (in case of catalyzed reaction only), $[Ce(SO_4)_2] = 1.20 \times 10^{-3}$ M, [anisaldehyde] = 3.30×10^{-3} M and $[H_2SO_4] = 0.25$ 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'

Table 2
Effect of variation of [iridium(III)] on the rate at 25 °C

$[Ir^{III}]$ ($\times 10^6$ mol dm^{-3})	$-dc/dt$ ($\times 10^5$ mol dm^3 min^{-1})	k (min^{-1})
0.75	0.65	8.66
1.34	0.95	7.08
1.67	1.20	7.18
2.01	1.40	6.96
2.35	1.50	6.40
2.68	1.65	6.15
3.02	1.90	6.30
3.35	2.10	6.30
3.69	2.20	6.00
4.02	2.40	6.00

$[Ce(SO_4)_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, [anisaldehyde] = 5.0×10^{-3} mol dm^{-3}, $[H_2SO_4] = 0.50$ mol dm^{-3} and [acetic acid] = 0.35 mol dm^{-3}.

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 1.04 ± 0.05 and 0.11 ± 0.0075 ($\times 10^{-5}$ M min^{-1}) in the case of catalyzed and un-catalyzed reactions respectively (under the conditions $[IrCl_3] = 1.67 \times 10^{-6}$ M (in case of catalyzed reaction only), $[Ce(SO_4)_2] = 0.40 \times 10^{-3}$ M, [anisaldehyde] = 5.00×10^{-3} M, $[H_2SO_4] = 0.50$ M and [acetic acid] = 0.35 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, different 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 13.8 and 6.34 kcal, -35.91 and -63.26 e.u., 10.61 and 19.08 kcal g^{-1} mol^{-1}) for catalyzed and un-catalyzed reactions, respectively.

4. Reactive species of iridium(III) chloride

It is known that $IrCl_3$ in hydrochloric acid gives $IrCl_6^{3-}$ species [10]. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [11]. Further, the aquation of $[IrCl_6^{3-}]$ gives $[IrCl_5(H_2O)^{2-}]$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_3(H_2O)_3]$ species [12–14]. This equilibrium may be shown by the following general equation:

$$IrCl_6^{3-} + n - H_2O \rightleftharpoons [IrCl_{6-n}(H_2O)_n]^{3-n} + Cl^- \qquad (2)$$
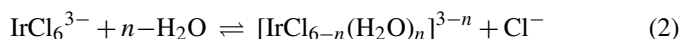
No effect of chloride ions on the reaction rate in the present study indicates that the above equilibrium is shifted more towards the left side and $IrCl_5(H_2O)^{2-}$ cannot be considered as the reactive species [1,2]. Therefore, considering our experimental results, $IrCl_6^{3-}$ has been considered to be the reactive species of iridium(III) chloride in the present study, which has been considered to be the active species previously also [1,2,7]. 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 [15] and ketones [16] are well documented. Complex formation between Cerium(IV) and alcohols to give complexes of composition [ROH.Cerium(IV)]$^{4+}$ and Michaelis–Menten type of kinetics has been reported [17]. While similar results have been reported in the case of ketones also [18–20].
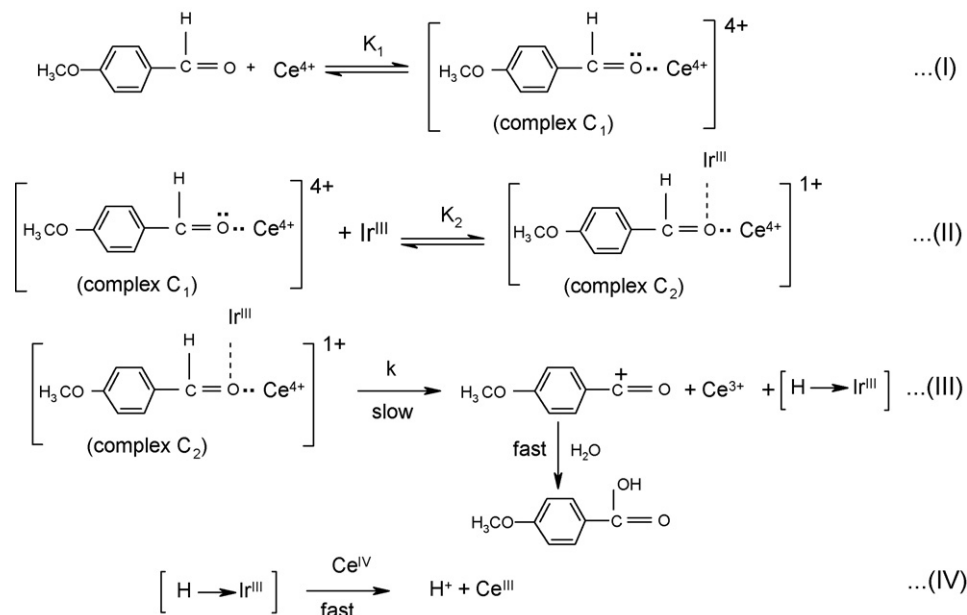
5.1. Mechanism in the presence of iridium(III) chloride

Thus, according to Scheme 1, cerium(IV) species combines with organic substrate to give complex C_1, which in turn com-

Scheme 1.

bines 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:

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

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

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

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

$$-\frac{d[Ce^{IV}]}{dt} = \frac{k K_1 K_2 [Ce^{IV}][S][Ir^{III}]}{1 + K_1 K_2 [Ce^{IV}][S]} \tag{5}$$

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 the Eq. (5) reduces to (6) which, explains the nature shown by various reactants.

$$-\frac{d[Ce^{IV}]}{dt} = k K_1 K_2 [Ce^{IV}][S][Ir^{III}] \tag{6}$$

At higher concentrations of oxidant and substrate the reverse inequality $1 \ll k K_1 K_2 [Ce^{IV}][S]$ holds good and the equation becomes as

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

Further verification of the rate law (5) may be given by rewriting the following equation as

$$\frac{1}{-d[Ce^{IV}]/dt} = \frac{1}{k K_1 K_2 [Ce^{IV}][S]} + \frac{1}{k[Ir^{III}]} \tag{8}$$

Values of $k K_1 K_2$ were calculated from the slopes of the graphs between 1/rate versus $1/[Ce^{IV}]$, 1/[substrate] and $1/[Ir^{III}]$, which comes out to be 0.92, 0.67 and 0.17 ($\times 10^5\,M^{-2}\,s^{-1}$), respectively. Fair constancy in the $k K_1 K_2$ values calculated from three different graphs further indicates the validity of 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 $4.16 \times 10^{-3}\,s^{-1}$ for the un-catalyzed reaction.
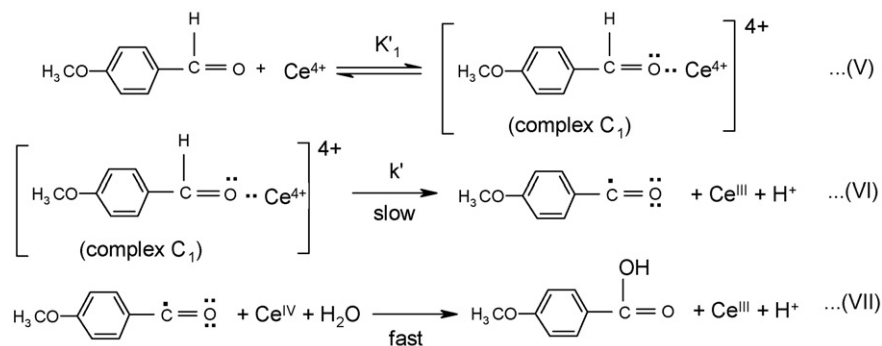
Scheme 2.

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

$$[Ce^{IV}] = \frac{[C_1]}{K_1'[S]} \tag{9}$$

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

$$[Ce^{IV}]_{Total} = [Ce^{IV}] + [C_1] \tag{10}$$

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

$$[C_1] = \frac{K_1'[S][Ce^{IV}]_T}{1 + K_1'[S]} \tag{11}$$

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

$$-\frac{d[Ce^{IV}]}{dt} = k'[C_1] = \frac{k'K_1'[S][Ce^{IV}]_T}{1 + K_1'[S]} \tag{12}$$

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. It may be pointed out that step I in the catalyzed mechanism and step V of the un-catalyzed mechanism are same and may be denoted by the same equilibrium constant, but as the value of constant K_1 could not be determined separately therefore, for distinguishing the constant of catalyzed and un-catalyzed reactions different symbols have been given. Rate law given by Eq. (12) reduces to as given in Eq. (13) if the inequality $1 \gg K_1$ [S] is considered at low concentrations of organic substrate

$$-\frac{d[Ce^{IV}]}{dt} = k'K_1'[S][Ce^{IV}]_T \tag{13}$$

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

$$\frac{1}{rate} = \frac{1}{k'K_1'[Ce^{IV}][S]} + \frac{1}{k'[Ce^{IV}]} \tag{14}$$

On plotting graphs between 1/rate versus 1/[S] or $1/[Ce^{IV}]_T$ 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 10.0 and 5.3 ($\times 10^{-3}$ s^{-1}), while this value calculated from the intercept of the catalyst graph in the catalyzed reaction was found to be 4.16×10^{-3} s^{-1}. 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, which is otherwise considered to be a sluggish catalyst in alkaline medium, acts as a very effective catalyst for the oxidation of aromatic aldehydes in acidic medium when used in conjunction with cerium(IV) sulphate. The study also gives a method by which without studying the un-catalyzed reaction separately, its rate and extent can be calculated with fair degree of accuracy by the intercept of the catalyst graph by studying the catalyzed reaction only. The present study is very useful in synthesis for which the work is in progress.

Appendix A. Supplementary data

References

[1] Manibala, H.S. Singh, B. Krishna, P.K. Tandon, J. Indian Chem. Soc. LXII (1985) 434–437.

[2] M.P. Singh, P.K. Tandon, R.M. Singh, A. Mehrotra, J. Indian Chem. Soc. 67 (1990) 458–462.

[3] T.L. Ho, in: W.J. Mijs, C.R.H. de Jonge (Eds.), Organic Synthesis by Oxidation with Metal Compounds, 569, Plenum, 1986.

[4] P.K. Tandon, B. Krishna, Kinetika i Kataliz USSR 26 (1985) 607–614.

[5] P.K. Tandon, S. Sahgal, A.K. Singh, Gayatri, M. Purwar, J. Mol. Catal. A: Chem. 232 (2005) 83–88.

[6] P.K. Tandon, S. Sahgal, Gayatri, M. Purwar, M. Dhusia, J. Mol. Catal. A: Chem. 250 (2006) 203–209.

[7] P.K. Tandon, S. Sahgal, A.K. Singh, S. Kumar, M. Dhusia, J. Mol. Catal. A: Chem. 258 (2006) 320–326.

[8] F. Feigl, Spot Tests in Organic Chemistry, Elsevier, New York, 1960, p. 369.

[9] O. Mikes, Laboratory Handbook of Chromatographic Methods (Eng. Ed.), D. Van Nostrand Co. Ltd., London, 1966, p. 96 (Chapter 2).

[10] J.C. Chang, C.S. Garner, Inorg. Chem. 4 (1965) 209–215.

[11] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley-Interscience, 1999, p. 1039.

[12] V.I. Kravtsov, G.M. Petrova, Russ. J. Inorg. Chem. (Engl. Transl.) 9 (1964) 552–556.

[13] I.A. Poulsen, C.S. Garner, J. Am. Chem. Soc. 84 (1962) 2032–2037.

[14] A.P.J. Domingos, A.M.T.S. Domingos, J.M.P. Gabral, J. Inorg. Nucl. Chem. 31 (1969) 2568–2573.

[15] L.B. Young, W.S. Trahanovsky, J. Am. Chem. Soc. 91 (1969) 5060–5068.

[16] J.S. Littler, J. Chem. Soc. (1962) 832–837.

[17] S.S. Muhammad, K.V. Rao, Bull. Chem. Soc. Jpn. 36 (1963) 943–949; ibid, 949–953.

[18] J. Shorter, J. Chem. Soc. (1950) 3425–3431.

[19] R.N. Mehrotra, Indian J. Chem. 22 A (1983) 169–172.

[20] J. Shorter, C.N. Hinshelwood, J. Chem. Soc. (1950) 3276–3283.