



Iridium(III) catalyzed oxidation of toluene and ethyl benzene by cerium(IV) in aqueous acidic medium

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ABSTRACT

Iridium(III) chloride catalyzed oxidation of toluene and ethyl benzene by cerium(IV) sulphate in aqueous sulphuric acid medium was studied. Change in the concentration of oxidant shows a specific effect that the rate increases in the beginning at low concentrations, it reaches to a maximum and further increase in oxidant concentration decreases the rate. Oxidation was highly selective as it oxidizes toluene to benzaldehyde and ethyl benzene acetophenone. 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 in both the cases. Rate of the reaction follows direct proportionality with respect to catalyst concentrations, while the rate decreases sharply with increasing hydrogen ion and cerium(III) concentrations. Change in ionic strength of the medium and the effects of changing concentrations of acetic acid, Cl^- ions, and HSO_4^- ions on the rate were studied. Energy of activation, free energy of activation and entropy parameters were also calculated.

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1. Introduction

Recently unparalleled utility of various species of cerium(IV), specially ceric ammonium nitrate (CAN), in a variety of organic transformations of synthetic importance has been reported in the absence of metal ion catalysts [1–3]. Recently mechanistic study of the aerobic oxidation of primary and secondary alcohols using a simple cyclopentadienyl iridium(III) complex ($[\text{Cp}^*\text{IrCl}_2]_2$) as the catalyst has been reported [4]. In this study it has been suggested that the transition metal maintains its (+3) oxidation state throughout the entire catalytic cycle and iridium hydride is the key intermediate in the catalytic cycle. Iridium(III) catalyzed oxidation of aliphatic and substituted alcohols and diols [5–8] by cerium(IV) in acidic medium has been investigated. Kinetic study of transition metal ion catalyzed oxidation of aromatic compounds by cerium(IV) has not been given much attention till now. Amongst transition metal ions, use of iridium(III) chloride as a homogeneous catalyst in alkaline medium could attract little attention because it is not an efficient catalyst in alkaline medium [9,10]. Potential of iridium(III) chloride 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 [11]. 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 [12,13]. To find out the effect of iridium(III) chloride in catalyzing the oxidation of hydrocarbons from kinetic point of view, we have studied the oxidation of toluene and ethyl benzene by cerium(IV) sulphate in aqueous sulphuric acid medium in the presence of iridium(III) chloride.

2. Experimental

Cerium(IV) sulphate (E. Merck) was dissolved in 1:1 sulphuric acid and was titrated against the standard ferrous ammonium sulphate solution using ferroin as an internal indicator. Sodium hexachloroiridate(III) (J.M.) was dissolved in minimum amount of HCl. In the stock solution final strengths of acid and the catalyst were 0.62×10^{-2} and 3.35×10^{-3} M, respectively. Ferrous ammonium sulphate solution was standardized with potassium dichromate (E. Merck) using *N*-phenyl anthranilic acid as an internal indicator. All other chemicals used were of analytical grade reagents or chemically pure substances. Toluene and ethyl benzene (E. Merck) are insoluble in aqueous medium therefore these aromatic hydrocarbons were initially dissolved in minimum amount of acetic acid and then stock solution was prepared by diluting the solution. Concentration of acetic acid was kept constant in all the variations except

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in the study to see the effect of change 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 aliquot of reaction mixture to a fixed amount of ferrous ammonium sulphate solution (in slight excess to cerium(IV) sulphate initially taken). Remaining amount of ferrous ammonium sulphate was estimated with a standard cerium(IV) sulphate solution using ferroin as an internal indicator. In all kinetic runs concentration of aromatic hydrocarbon was kept in excess.

2.1. Determination of kinetic orders

Rate values ($-dc/dt$) were obtained from the initial slopes of individual time plots. In the case of oxidant variation, $-dc/dt$ values were calculated at a fixed initial time in the individual plots while in all other cases these values were calculated at a fixed initial concentration. First order rate constants for molar concentrations (k) were calculated by dividing $-dc/dt$ values with the concentration of oxidant, organic substrate or the catalyst, as the case may be. Orders, with respect to various reactants were confirmed by four different methods. 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

Stoichiometry of the reaction was calculated after ensuring complete oxidation of organic substrate by the oxidant in different ratios. After completion of the reaction, reaction mixture was extracted with diethyl ether (5×25 ml) and the solvent was evaporated under the reduced pressure. After evaporating the solvent calculated amount of 2,4-dinitrophenyl hydrazine solution was added to the extract. Yellowish-orange precipitate of 2,4-dinitrophenyl hydrazone was obtained indicating the presence of carbonyl group in the product. Oxidation products in case of toluene and ethyl benzene were identified as benzaldehyde and acetophenone by the spot test methods [14], chromatographic technique [15] and also by taking NMR spectra of the products. Melting points of the DNP derivatives of the products were found to be 232 and 244°C (reported 241 and 250°C for benzaldehyde and acetophenone, respectively). In NMR spectra (Bruker, DRX 300) in case of hydrazone of benzaldehyde signals were found at δ 11.2 (1H, s), δ 4.0 (1H, s), δ 9.1 (1H, d), δ 8.1–8.3 (2H, m), δ 7.1–7.9 (5H, m) [S.I. 1] while in the case of hydrazone of acetophenone signals were found at δ 1.55 (3H, s), δ 7.26 (1H, s), δ 8.77–8.76 (1H, d), δ 8.42–8.41 (2H, d), δ 8.39–8.38 (1H, d), δ 7.88–7.82 (2H, d), δ 7.48–7.46 (1H, t), δ 4.0 (1H, s) [S.I. 2]. Stoichiometry of the reaction in case of benzaldehyde may be given by Eq. (1)



3. Results and discussion

3.1. Results

Effect of variation of concentration of oxidant on the rate showed a specific nature. First order plots between $\log(a-x)$ versus time for the consumption of cerium(IV) sulphate in the case of both toluene and ethyl benzene, show straight lines at low concentrations of the oxidant. However, deviations in later part of the reaction at higher concentrations of the oxidant become pronounced. On plotting $-dc/dt$ values versus [oxidant], rate values increase proportionately with increasing [oxidant] in the

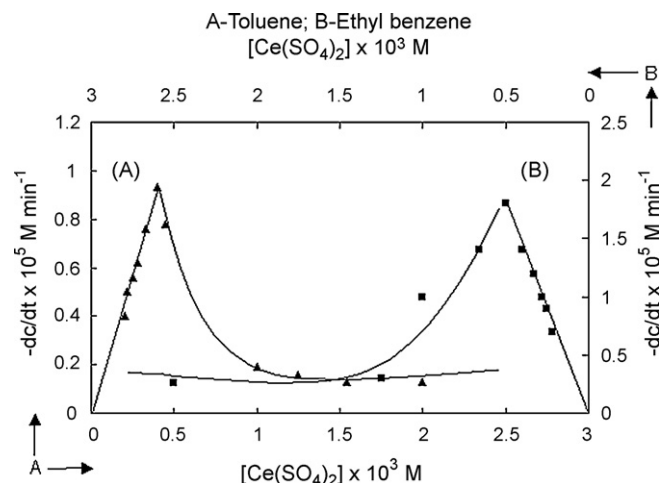


Fig. 1. Effect of variation of [cerium(IV) sulphate] on the rate at 35°C : A – [toluene] = 10.0; B – [ethyl benzene] = 5.0 ($\times 10^{-3}$ M), $[\text{H}_2\text{SO}_4]$ = A and B – 0.60 (M), $[\text{IrCl}_3]$ = A and B – $7.35 (\times 10^{-6}$ M), $[\text{CH}_3\text{COOH}]$ = A – 1.82; B – 1.25 (M).

beginning, reach to a maximum and beyond which further increase in oxidant concentration retards the rate (Fig. 1). These facts indicate that the rate follows direct proportionality with respect to oxidant at low concentrations but at higher concentrations of the oxidant rate decreases with increasing oxidant concentrations. In both the cases, initial increase in organic substrate concentration results in proportionate increase in the rate values in the beginning while at higher concentrations the increase, in $-dc/dt$ values becomes less prominent (Table 1). First order rate constants for molar concentration of organic substrates (k values) show fair constancy in the beginning but at higher concentrations k values start decreasing. On plotting $-dc/dt$ values versus [organic substrate], straight lines passing through the origin are obtained which tend to become parallel to the x -axis at higher concentrations (Fig. 2). These facts confirm that rate of the reaction shows direct proportionality with respect to organic substrate at low concentrations and tend to become independent of concentration at higher concentrations of organic substrate. In both cases study at still lower concentrations of organic substrate could not be performed as the reaction becomes too slow to be measured properly, yet the trend of lines can be seen clearly. On plotting $-dc/dt$ values versus $[\text{IrCl}_3]$, straight lines passing through the origin were obtained (Fig. 3) while slope values of 1.0 and 1.08 were obtained

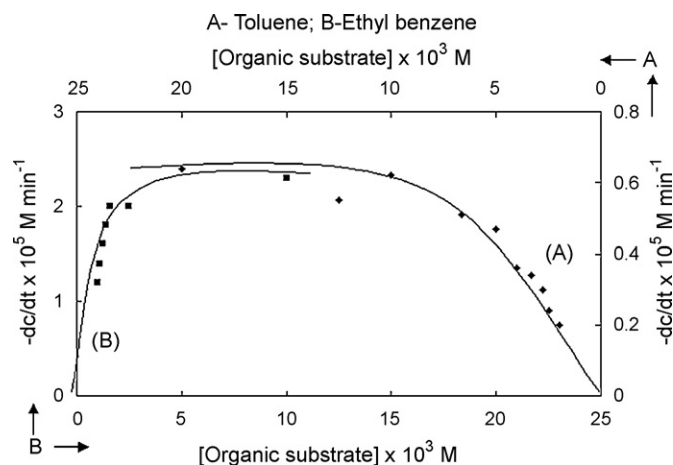


Fig. 2. Effect of variation of [organic substrate] on the rate at 35°C : $[\text{Ce}(\text{SO}_4)_2]$ = A – 0.28; B – 0.66 ($\times 10^{-3}$ M), $[\text{H}_2\text{SO}_4]$ = A and B – 0.60 (M), $[\text{IrCl}_3]$ = A and B – 7.35 ($\times 10^{-6}$ M), $[\text{CH}_3\text{COOH}]$ = A – 1.82; B – 1.25 (M).

Table 1
Effect of variation of [cerium(IV)] and [organic substrate] on the rate at 35 °C.

[Ce ^{IV}] × 10 ³ M	$k_{\text{obs}} = -dc/dt/[Ce^{IV}] \times 10^2 \text{ min}^{-1}$		[Organic substrate] × 10 ³ M	$k^* = k_{\text{obs}}/[\text{organic substrate}] \text{ M}^{-1} \text{ min}^{-1}$	
	(A)	(B)		(A)	(B)
0.20	2.00	–	1.00	–	18.20
0.22	2.20	3.20	1.10	–	19.30
0.25	2.20	3.60	1.25	–	19.40
0.28	2.20	3.60	1.40	–	19.00
0.33	2.30	3.60	1.60	–	–
0.40	2.30	3.50	2.00	3.57	12.10
0.45	1.70	–	2.50	3.42	–
0.50	–	3.60	2.80	3.82	–
0.66	–	2.10	3.33	3.67	–
1.00	0.19	1.00	4.00	3.21	–
1.25	0.13	0.40	5.00	3.35	–
1.54	0.08	–	6.66	2.76	–
2.00	0.06	–	10.00	2.21	3.50
2.50	–	0.10	12.50	1.57	–
–	–	–	20.00	1.14	–

Cerium(IV) variation: A – [toluene] = 10.0; B – [ethyl benzene] = 5.0 (× 10⁻³ M), [H₂SO₄] = A and B – 0.60 (M), [IrCl₃] = A and B – 7.35 (× 10⁻⁶ M), [CH₃COOH] = A – 1.82; B – 1.25 (M).

Organic substrate variation: [Ce(SO₄)₂] = A – 0.28; B – 0.66 (× 10⁻³ M), [H₂SO₄] = A and B – 0.60 (M), [IrCl₃] = A and B – 7.35 (× 10⁻⁶ M), [CH₃COOH] = A – 1.82; B – 1.25 (M).

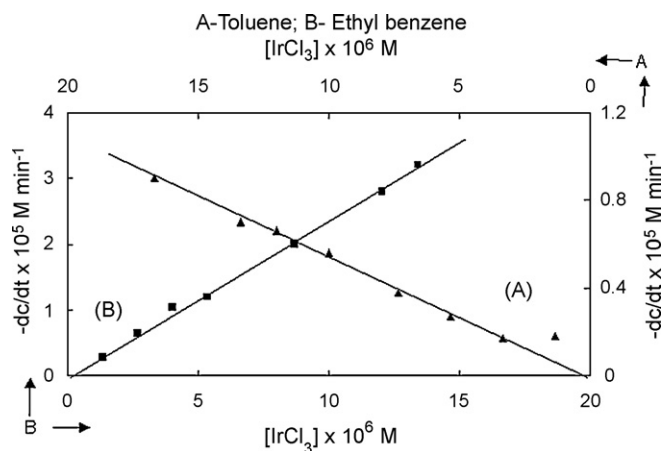


Fig. 3. Effect of variation of [IrCl₃] on the rate at 35 °C. [Ce(SO₄)₂] = A – 0.28; B – 0.66 (× 10⁻³ M), [H₂SO₄] = 0.60 M (A and B), [CH₃COOH] = A – 1.82; B – 1.25 (M), A – [toluene] = 3.30; B – [ethyl benzene] = 5.00 (× 10⁻³ M).

on plotting log $-dc/dt$ and log [IrCl₃]. Constancy in the k values with average deviation of 1.89 ± 0.07 and 3.54 ± 0.22 (Table 1) in case of toluene and ethyl benzene, respectively, indicates that in both the cases reaction follows first order kinetics with respect

to iridium(III) chloride concentrations. The rate values ($-dc/dt$) go on decreasing with increasing concentrations of sulphuric acid (Table 1) and externally added Ce₂(SO₄)₃ (Table 2) in the reaction mixture, which indicates that in both the cases these ions have a retarding effect on the reaction velocity. 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, change in ionic strength of the medium with the help of a standard KCl solution does not affect the reaction velocity in both the cases and rate values in case of toluene remain constant at $0.98 (\pm 0.09) \times 10^{-5} \text{ M min}^{-1}$ when [KCl] was changed from 0.10 to 0.75 M (under the conditions [IrCl₃] = $7.35 \times 10^{-6} \text{ M}$, [Ce(SO₄)₂] = $0.28 \times 10^{-3} \text{ M}$, [toluene] = $3.30 \times 10^{-3} \text{ M}$, [H₂SO₄] = 0.60 M and [acetic acid] = 1.82 M). In case of ethyl benzene, the rate values remain constant at $2.43 (\pm 0.5) \times 10^{-5} \text{ M min}^{-1}$ (under the conditions [IrCl₃] = $7.35 \times 10^{-6} \text{ M}$, [Ce(SO₄)₂] = $0.66 \times 10^{-3} \text{ M}$, [ethyl benzene] = $5.00 \times 10^{-3} \text{ M}$, [H₂SO₄] = 0.60 M and [acetic acid] = 1.25 M) on changing the concentration of potassium chloride from 0.10 to 0.70 M. Effect of change of HSO₄⁻ ion concentration on the rate was studied by adding KHSO₄ externally in the reaction mixture and it was found that change in [KHSO₄] (from 0.05 to 0.50 M) does not affect the reaction velocity in both the cases. Rate values in case of toluene remain constant at $1.64 (\pm 0.08) \times 10^{-5} \text{ M min}^{-1}$ (under

Table 2
Effect of variation of [iridium(III)], [H⁺] and [Ce(III)] on the rate at 35 °C.

[Ir ^{III}] × 10 ⁶ M	$k^* = k_{\text{obs}}/[IrCl_3] \text{ M}^{-1} \text{ min}^{-1}$		[Ce ^{III}] × 10 ³ M	$-dc/dt \times 10^5 \text{ M min}^{-1}$		[H ⁺] M	$-dc/dt \times 10^5 \text{ M min}^{-1}$	
	(A)	(B)		(A)	(B)		(A)	(B)
1.34	4.99	3.16	0.25	1.60	2.00	0.30	1.30	1.60
2.67	–	3.63	0.28	1.40	2.80	0.50	–	1.30
3.34	1.82	–	0.40	–	2.50	0.90	–	1.00
4.00	–	3.93	0.50	1.46	–	1.00	1.00	–
5.34	1.81	3.40	0.66	–	2.00	1.30	–	0.80
7.34	1.85	–	1.00	1.20	1.50	1.50	–	0.80
8.68	–	3.49	1.25	1.10	–	1.60	0.27	–
10.02	1.99	–	–	–	–	1.70	–	0.73
12.02	1.96	3.52	–	–	–	2.00	0.22	–
13.40	1.86	3.62	–	–	–	3.00	0.20	0.66
16.70	1.92	–	–	–	–	–	–	–

Catalyst variation: [Ce(SO₄)₂] = A – 0.28; B – 0.66 (× 10⁻³ M), [H₂SO₄] = 0.60 M (A and B), A – [toluene] = 3.30; B – [ethyl benzene] = 5.00 (× 10⁻³ M), [CH₃COOH] = A – 1.82; B – 1.25 (M).

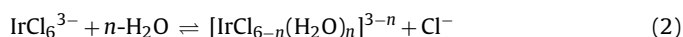
Hydrogen ion variation: [Ce(SO₄)₂] = A – 0.28; B – 0.66 (× 10⁻³ M), [CH₃COOH] = A – 1.82; B – 1.25 (M), A – [toluene] = 3.30; B – [ethyl benzene] = 5.00 (× 10⁻³ M), [IrCl₃] = $7.35 \times 10^{-6} \text{ M}$ (A and B).

Cerium(III) variation: [Ce(SO₄)₂] = A – 0.28; B – 0.66 (× 10⁻³ M), [CH₃COOH] = A – 1.82; B – 1.25 (M), A – [toluene] = 3.30; B – [ethyl benzene] = 5.00 (× 10⁻³ M), [IrCl₃] = $7.35 \times 10^{-6} \text{ M}$ (A and B), [H₂SO₄] = 0.60 M (A and B).

the conditions $[\text{IrCl}_3] = 7.35 \times 10^{-6} \text{ M}$, $[\text{Ce}(\text{SO}_4)_2] = 0.28 \times 10^{-3} \text{ M}$, $[\text{toluene}] = 3.30 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.60 \text{ M}$, $[\text{acetic acid}] = 1.82 \text{ M}$. In the case of ethyl benzene the rate values remain constant at $1.33 (\pm 0.25) \times 10^{-5} \text{ M min}^{-1}$ (under the conditions $[\text{IrCl}_3] = 7.35 \times 10^{-6} \text{ M}$, $[\text{Ce}(\text{SO}_4)_2] = 0.66 \times 10^{-3} \text{ M}$, $[\text{ethyl benzene}] = 5.00 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.60 \text{ M}$, $[\text{acetic acid}] = 1.25 \text{ M}$). All these observations show that change in the ionic strength of the medium, concentrations of chloride ions and potassium hydrogen sulphate 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. 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 8.80 and 7.04 (kJ mol^{-1}), -45.54 and -45.79 ($\text{J K}^{-1} \text{ mol}^{-1}$), 14.03 and 14.11 (kJ mol^{-1}) for toluene and ethyl benzene, respectively.

3.2. Reactive species of iridium(III) chloride

It is known that IrCl_3 in hydrochloric acid gives IrCl_6^{3-} species [16]. It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium [17]. 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 [18–20]. This equilibrium may be shown by the general Eq. (2)



Considering our experimental results and no effect of chloride ions on the rate, IrCl_6^{3-} has been considered to be the reactive species of iridium(III) chloride in the present study, which has been considered by other workers also [9,10,21].

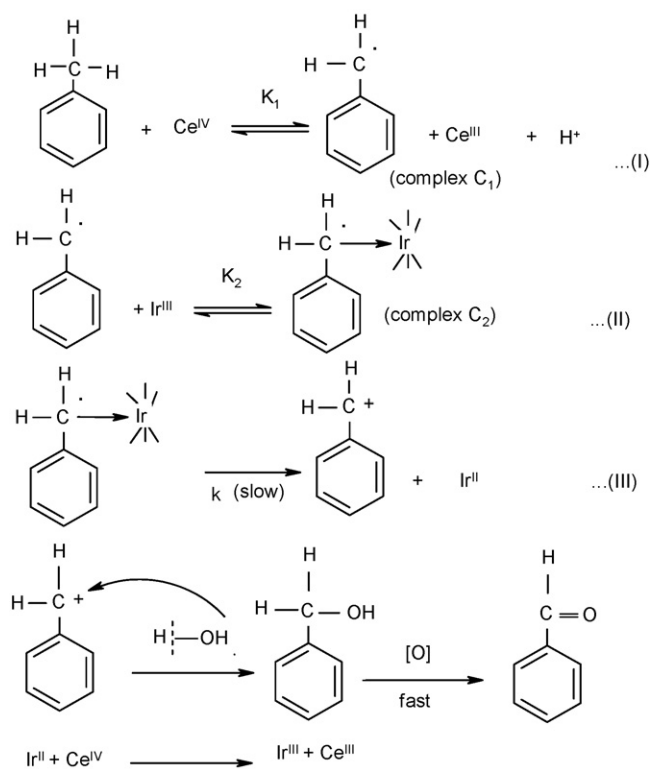
3.3. Reactive species of cerium(IV) sulphate

The nature of cerium(IV) complexes in H_2SO_4 has been widely investigated. Various species of cerium(IV) sulphate have been suggested by previous workers which exist in sulphuric acid medium, but these species can not be considered to be the active species in the present study because these studies [22–24] were conducted at low concentration of H_2SO_4 and ionic strength of the medium was not kept constant. In the present study rate decreases with the increase in $[\text{H}^+]$ while the rate remains independent of $[\text{HSO}_4^-]$ at constant H^+ . Thus, we presume that the species $\text{HCe}(\text{SO}_4)_3^-$ and $\text{Ce}(\text{SO}_4)_3^{2-}$ are in a state of equilibrium as shown in Eq. (3) and $\text{HCe}(\text{SO}_4)_3^-$ is the reactive species in the present study. Although there is no information available about the value of equilibrium constant for the equilibrium step (3) but considering the fact that sulphatoceric acid, $\text{H}_2\text{Ce}(\text{SO}_4)_3$, is partly or completely dissociated [24] in aqueous medium and the first dissociation constant of sulphatoceric acid is closed to or slightly greater than the dissociation constant of sulphuric acid [25]. Thus, $\text{HCe}(\text{SO}_4)_3^-$ has been considered as the reactive species in the present study, which has been considered by other workers [26,27] also.



3.4. Discussion

Shifting of the spectral peak of Ce(IV) and that of the mixture of Ce(IV) and toluene from 222.4 to 228.0, under the experimental conditions supports the formation of complex between Ce(IV) and organic substrate. Moreover, oxidation of toluene by ceric ammonium nitrate in aqueous sulphuric acid medium giving rise to benzaldehyde has already been reported [28]. Complex formation between cerium(IV) and alcohols [29] and ketones [30] with the elimination of cerium(III) and hydrogen ions is very



well documented. Complex formation between cerium(IV) [31] with alcohols to give complexes of the composition $[\text{ROH}\cdot\text{Ce}(\text{IV})]^{4+}$ and Michaelis–Menten type of kinetics [32–34] along with similar results obtained in the case of aromatic aldehydes [35–37], ketones [38–39] and cyclic alcohols [40–41] is also well documented. Strong retarding effect of $\text{Ce}(\text{III})$ and H^+ ions on the rate clearly suggests their elimination before the rate-determining step while first order kinetics tending towards zero order with respect to organic substrate indicates the complex formation in the present study.

3.5. Mechanism

According to Scheme 1, cerium(IV) oxidizes the organic substrate and in the process itself gets reduced to Ce(III) along with the elimination of one hydrogen ion. Subsequently the organic substrate with a single unpaired electron combines with Ir^{3+} to give a complex C_2 , which in turn gives rise to benzyl alcohol as the intermediate product. In the subsequent fast steps intermediate product and Ir^{2+} species by taking more of cerium(IV) ions give rise to the final product and the original Ir^{3+} species is obtained. It has been reported that benzyl alcohol is oxidized very rapidly to benzaldehyde [42] under the similar reaction conditions. In the study of these oxidations from synthetic point of view we also have reported benzaldehyde and acetophenone as the final oxidation products [13].

3.6. Derivation of rate law

Considering the equilibrium concentrations of complexes C_1 and C_2 in steps (I) and (II) of Scheme 1 and putting concentration of C_1 from step (I) into the concentration of $[\text{Ir}^{III}]$ obtained from step (II), concentration of complex C_2 in terms of total concentration of catalyst may be given as

$$[\text{C}_2] = \frac{K_1 K_2 [\text{Ce}^{IV}] [\text{S}] [\text{Ir}^{III}]_T}{[\text{Ce}^{III}] [\text{H}^+] + K_1 K_2 [\text{Ce}^{IV}] [\text{S}]} \quad (4)$$

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

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = \frac{kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_T}{[\text{Ce}^{\text{III}}][\text{H}^+] + K_1K_2[\text{Ce}^{\text{IV}}][\text{S}]} \quad (5)$$

This Eq. (5) explains first order kinetics tending towards zero order with respect to organic substrate and the retarding nature shown by $[\text{Ce}^{\text{III}}]$ and $[\text{H}^+]$. At low concentrations of oxidant and organic substrate the inequality $[\text{Ce}^{\text{III}}][\text{H}^+] \gg K_1K_2[\text{Ce}^{\text{IV}}][\text{S}]$ may hold and the Eq. (5) reduces to (6) which, explains the nature shown by various reactants at low concentrations.

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = \frac{kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_T}{[\text{Ce}^{\text{III}}][\text{H}^+]} \quad (6)$$

At higher concentrations of oxidant and substrate the reverse inequality $[\text{Ce}^{\text{III}}][\text{H}^+] \ll K_1K_2[\text{Ce}^{\text{IV}}][\text{S}]$ holds good and the Eq. (5) becomes

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

This equation shows that at higher concentrations of cerium(IV) and organic substrates, the rate should become independent of [organic substrate], $[\text{Ce}^{\text{III}}]$ and $[\text{H}^+]$ ions concentrations which has been actually observed. However, according to Eq. (5), the rate should become independent with respect to $[\text{Ce}^{\text{IV}}]$ at higher concentrations, while our experimental results show that at higher concentration, instead of giving zero order kinetics, the rate starts decreasing. Falling off the reaction velocity at higher oxidant concentrations may be due to the formation of some dimeric species of Ce(IV) in the reaction mixture. Formation of dimeric species of Ce(IV) has been reported by a number of workers in sulphuric acid [43,44], perchloric acid [45–47] and nitric acid [48,49], while existence of trimeric cerium has been reported in acetic acid medium [50]. In a number of studies it has been reported that the first order velocity constant k_1 values decrease with increasing Ce(IV) concentrations due to the formation of dimeric species. Conversion of reactive cerium(IV) into the un-reactive dimer may be the cause of retardation in reaction rate at higher oxidant concentrations. Retardation in the rate at higher cerium(IV) concentrations may also be due to the formation of some un-reactive complex in the reaction mixture. Under the experimental conditions, complex formation may take place between cerium(IV) and intermediate product or with final oxidation products and this may be the reason of decrease in the reaction velocity. Further verification of the rate law may be given by rewriting the Eq. (5) as

$$\frac{1}{-d[\text{Ce}^{\text{IV}}]/dt} = \frac{[\text{Ce}^{\text{III}}][\text{H}^+]}{kK_1K_2[\text{Ce}^{\text{IV}}][\text{S}][\text{Ir}^{\text{III}}]_T} + \frac{1}{k[\text{Ir}^{\text{III}}]_T} \quad (8)$$

From this equation if we plot graphs between $1/\text{rate}$ versus $1/[\text{Ce}^{\text{IV}}]$, $1/[\text{substrate}]$ and $[\text{H}^+]$, we should get straight lines with positive intercepts at y -axes, which has actually been observed. From the slopes of these lines kK_1K_2 values were calculated. These values come out to be 4.67 and 8.16 ($\times 10^5$) from $1/\text{rate}$ versus $1/[\text{Ce}^{\text{IV}}]$, 4.26 and 14.7 ($\times 10^5$) from $1/\text{rate}$ versus $1/[\text{substrate}]$, and 6.51 and 6.65 ($\times 10^5$) from $1/\text{rate}$ versus $[\text{H}^+]$ for toluene and ethyl benzene, respectively. Fair constancy in the kK_1K_2 values calculated from three different graphs further indicates the validity of the Scheme 1 and the rate law (5). Absence of any reaction between the organic substrate and iridium(III) rules out the possibility of interaction between these two giving rise to the complex C_1 in first step of Scheme 1. 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.

4. 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 hydrocarbons in acidic medium when used in conjunction with cerium(IV) sulphate. It is also observed that in the oxidation of ethyl benzene oxidation is selective at the secondary carbon atom instead of the primary one. The present iridium(III)–cerium(IV) system is highly useful to oxidize aliphatic and aromatic organic compounds both from the kinetic as well as from the synthetic point of views.

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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.2009.01.035.

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