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Mechanistic study of novel oxidation of paracetamol by chloramine-T using micro-amount of chloro-complex of Ir(III) as a homogeneous catalyst in acidic medium

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ABSTRACT

The mechanistic study of iridium (III)-catalyzed oxidation of paracetamol has been studied by sodium N-chloro-p-toluenesulfonamide (chloramine-T) in aqueous perchloric acid medium at 308 K. The reaction followed first-order kinetics with respect to [chloramine-T], [paracetamol] and [Cl^-] in their lower concentrations range, tending to zero-order at their higher concentrations. First-order kinetics with respect to [Ir(III)] was observed for the oxidation of paracetamol. The rate of reaction decreased with increasing [H^+] and [p-toluene sulphonamide, PTS] were observed for the oxidation of paracetamol. The variation of the ionic strength of the medium had no significant effect on the rate of the reaction. The first-order rate constant increased with decrease in the dielectric constant of the medium. The values of rate constants observed at five different temperatures were utilized to calculate the activation parameters. The reaction between chloramine-T and paracetamol in acid medium exhibits 1:2 stoichiometry. A plausible mechanism from the results of kinetic studies, reaction stoichiometry and product analysis has been proposed.

1. Introduction

Paracetamol (4-hydroxyacetanilide or acetaminophen or 4-acetamidophenol) is a well-known drug that finds extensive applications in pharmaceutical industries. It is an antipyretic and analgesic compound that has high therapeutic value. It is also used as an intermediate for pharmaceutical (as a precursor in penicillin) and azo dye, stabilizer for hydrogen peroxide, photographic chemical. There are very few reports for the kinetics of oxidation of this drug [1–6]. Chloramine-T (CAT; sodium N-chloro-p-toluenesulfonamide) is the most important member of organic halo-amine family and behaves as an oxidizing agent in both acidic and alkaline media. It is versatile oxidizing agent and has shown a variety of kinetics result due to formation of its various oxidizing species depending upon pH of the medium [7–17].

The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radicals and different oxidizing states of Ir(III). Iridium (III) chloride is the important platinum group metal ion and has been widely used as homogeneous catalyst in various redox reactions [18]. To the best of our knowledge there is no information available on the mechanistic aspects of Ir(III) catalyzed oxidation of paracetamol by chloramine-T. This has encouraged us to investigate the kinetic behavior of the title reaction on the oxidation of paracetamol by chloramine-T in the presence of Ir(III) in the acidic medium. Preliminary experimental results indicate that the reaction of paracetamol (PA) with CAT in the acidic medium without a catalyst were very sluggish, but the reaction becomes facile in the presence of micro-amount of Ir(III) catalyst. Therefore, Ir(III) has been selected as a catalyst in the present investigations. The objectives of the present study are: (i) to ascertain the reactive species of catalyst and oxidant, (ii) find the catalytic efficiency of Ir(III), (iii) to elucidate the plausible reaction mechanism, (iv) to deduce rate law consistent with kinetic results and (v) to calculate the activation parameters.

2. Experimental

Sodium perchlorate, perchloric acid, KCl (E. Merck.) was used without further purification by preparing their solution in double distilled water. Paracetamol (m.p. 169 °C) solution (S.D. fine chem.) was prepared by dissolving appropriate amount in doubly distilled water. The stock solution of chloramine-T (Loba, AR) was prepared in doubled distilled water and standardized idometrically. A solution of iridium (III) chloride was prepared by dissolving a known

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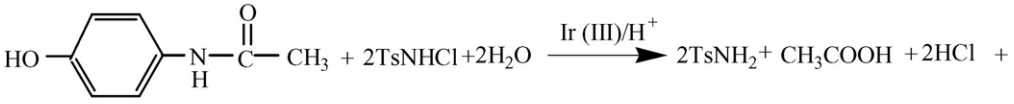
weight of $IrCl_3$ (S.D. fine chem.) in HCl of known strength. The reaction vessels were coated from outside with black paint to avoid any photochemical reactions.

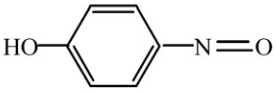
2.1. Kinetic measurements

A thermo-stated water bath was used to maintain the desired temperature within ±0.1 °C. The appropriate strength of the chloramine-T, $HClO_4$, KCl, Ir(III) chloride and water were taken in a reaction vessel which was kept in a thermostatic water bath. After allowing sufficient time to attain the temperature of the experiment, requisite volume of paracetamol solution, also thermo-stated at the same temperature was rapidly pipetted out and poured into the reaction vessel. The total volume of the reaction mixture was 100 ml in each case. 5 ml aliquots of reaction mixture was pipetted out at different intervals of time and quenched with 4% acidified potassium iodide solution. The progress of the reaction was monitored by iodometric estimation of CAT by titration against a standard solution of sodium thiosulphate using starch as an indicator to determine unconsumed chloramine-T at regular time intervals. Each kinetic run was studied for 75% reaction. The initial rate of reaction ($-dc/dt$) was determined by the slope of the tangent drawn at a fixed [CAT] in each kinetic run. The order of reaction in each reactant was calculated with the help of log–log plot of ($-dc/dt$) versus concentration of the reactants.

2.2. Stoichiometry and product analysis

Different sets of the reaction mixture containing paracetamol, Ir(III) chloride, $HClO_4$ and KCl with excess of CAT were kept for 72 h at 308 K. Determination of unconsumed CAT in each set revealed that two moles of CAT were consumed for the oxidation of one mole of paracetamol. Accordingly, the following stoichiometry equation may be formulated:





quinone oxime

The main oxidation product was identified as quinone oxime. The nature of quinone oxime was confirmed by its IR spectrum (1652 cm^{-1} due to C=O stretching, 1615 cm^{-1} due to C=N stretching of oxime, 3332 cm^{-1} due to O–H stretching), It was further confirmed by its melting point 131 °C (reported m.p. 132 °C). Acetic acid was identified by spot test [19].

3. Kinetic results and discussion

The kinetics of Ir(III) catalyzed oxidation of paracetamol by chloramine-T was investigated at several initial concentrations of the reactants in acidic medium at 308 K. The initial rate (i.e. $-dc/dt$) of the reaction in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of chloramine-T. In the variation of the oxidant, the initial rate (i.e. $-dc/dt$) of the reaction was measured from the slope of the tangent drawn at a fixed time of the plot of unconsumed [CAT] versus time (Fig. 1). The first-order rate constant (k_1) was calculated as:

$$k_1 = \frac{-(dc/dt)}{[CAT]^*}$$

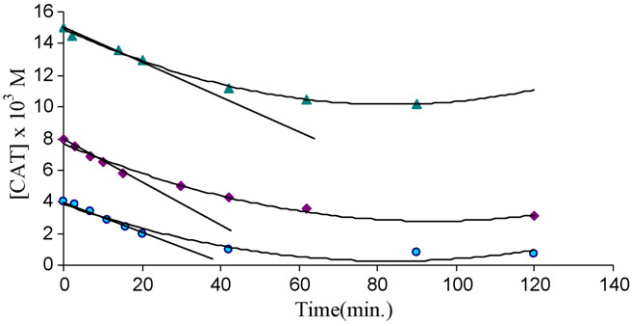


Fig. 1. Sample individual time plots for CAT for its highest and lowest concentration at 303 K. [PA] = 1×10^{-2} M, [Ir(III)] = 6.6×10^{-9} M, [H^+] = 4×10^{-2} M, [KCl] = 5×10^{-5} M.

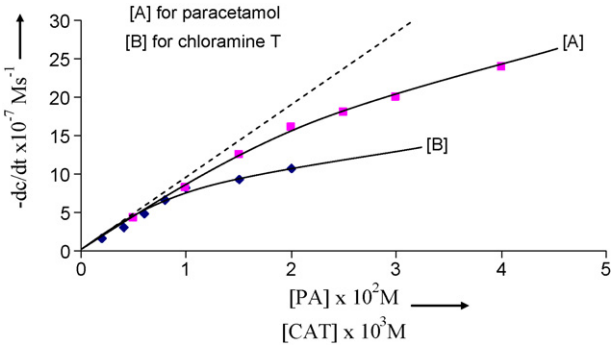


Fig. 2. Effect of variation of [CAT] and [PA] on the reaction rate at 303 K. [Ir(III)] = 6.6×10^{-9} M, [H^+] = 4×10^{-2} M, [KCl] = 5×10^{-5} M.

The first-order dependence of reaction on [CAT], [PA] and [Cl^-] at their lower concentrations and tend to zero-order at their higher concentrations as seen from the plot of ($-dc/dt$) versus [CAT] and [PA] (Table 1, Fig. 2 and Table 2, Fig. 4). The plot of rate of reaction ($-dc/dt$) versus [Ir(III)] was linear passing through the origin, suggesting first-order dependence on the rate of reaction with respect to [Ir(III)]. At the same time, it also shows that the reaction does not proceed with measurable velocity in the absence of [Ir(III)] (Table 1, Fig. 3). Kinetics of catalyzed oxidation of paracetamol indicates that on increasing [H^+], the value of ($-dc/dt$) decreased which is also evident as shown in Fig. 3 (Table 1). This showed the negative effect of [H^+], on the rate of oxidation of paracetamol. Addition of the reduced product of the oxidant, [PTS] from 0.5×10^{-3} mol dm^{-3} to 2×10^{-3} mol dm^{-3} to the reaction mixture decreased the rate of reaction. A plot of log k versus log [PTS] was linear with fractional slope (−0.68) indicating that PTS is involved in a fast pre-equilibrium to the rate determining step (Fig. 4). $NaClO_4$ was used for the study of ionic strength of the medium. Variation of ionic strength of the medium did not bring about any significant change on the rate of reaction under the constant experimental

Table 1
Effect of variation of [CAT], [PA], [Ir(III)], and [H$^+$] on the rate of oxidation of paracetamol at 308 K.

[CAT] × 10^3 mol dm^{-3}	[PA] × 10^2 mol dm^{-3}	[Ir(III)] × 10^9 mol dm^{-3}	[H$^+$] × 10^2 mol dm^{-3}	−dc/dt × 10^7 mol dm^{-3} s^{-1}	k × 10^4 (s^{-1})
0.2	1.0	6.6	4.0	1.64	8.6
0.4	1.0	6.6	4.0	3.10	8.1
0.6	1.0	6.6	4.0	4.80	8.7
0.8	1.0	6.6	4.0	6.60	8.8
1.0	1.0	6.6	4.0	8.30	8.7
1.5	1.0	6.6	4.0	9.20	6.5
2.0	1.0	6.6	4.0	10.70	5.6
1.0	0.5	6.6	4.0	4.20	4.40
1.0	1.0	6.6	4.0	8.30	8.70
1.0	1.5	6.6	4.0	12.50	13.10
1.0	2.0	6.6	4.0	16.00	16.80
1.0	2.5	6.6	4.0	18.00	18.90
1.0	3.0	6.6	4.0	20.00	21.00
1.0	4.0	6.6	4.0	24.00	25.20
1.0	1.0	3.3	4.0	4.20	4.40
1.0	1.0	6.6	4.0	8.30	8.70
1.0	1.0	10.0	4.0	12.00	12.60
1.0	1.0	16.7	4.0	22.00	21.00
1.0	1.0	20.0	4.0	24.00	25.20
1.0	1.0	26.7	4.0	32.00	33.60
1.0	1.0	33.4	4.0	40.00	42.10
1.0	1.0	6.6	1.0	16.00	16.80
1.0	1.0	6.6	2.0	14.40	15.10
1.0	1.0	6.6	3.0	11.40	12.00
1.0	1.0	6.6	4.0	8.30	8.70
1.0	1.0	6.6	5.0	7.40	7.80
1.0	1.0	6.6	6.0	6.20	6.50
1.0	1.0	6.6	8.0	5.80	6.00

Solution conditions: [KCl] = 5 × 10^{-5} mol dm^{-3}.

conditions (Table 2). The rate of reaction increased with decrease in dielectric constant of the medium (by increasing % of acetic acid by volume) (Table 3). It was observed that acetic acid was not oxidized by chloramine-T under the experimental conditions. The reaction was studied at different temperatures (303–323 K) (Table 4). From the linear Arrhenius plot of log k_1 versus 1/T, the activation energy (E_a) was calculated. With the help of the energy of activation, values of the other activation parameters such as enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), Gibbs free energy of activation ($\Delta G^{\#}$) and Arrhenius factor (A), were calculated and these values are given in Table 4.

3.1. Test of free radicals

The intervention of free radicals was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1 h. When the reaction mixture was diluted with methanol, no precipitate resulted, suggesting that there is no participation of free radicals in the reaction.

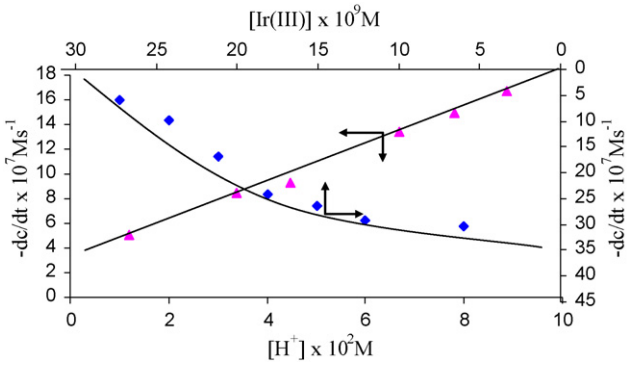


Fig. 3. Effect of variation of [Ir(III)] and [H$^+$] on the reaction rate at 303 K. [CAT] = 1 × 10^{-3} M, [PA] = 1.0 × 10^{-2} M, [KCl] = 5 × 10^{-5} M.

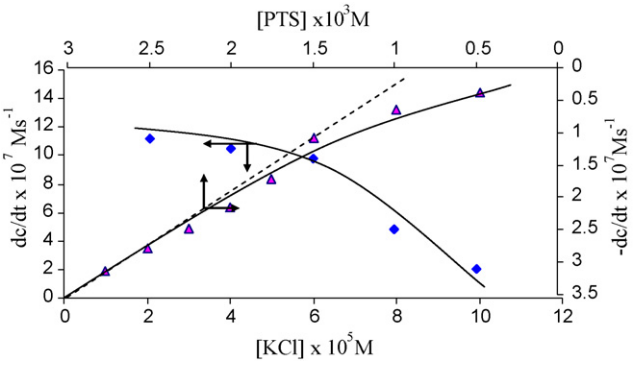


Fig. 4. Effect of variation of [PTS] and [KCl] on the reaction rate at 303 K. [CAT] = 1 × 10^{-3} M, [PA] = 1.0 × 10^{-2} M, [H$^+$] = 4 × 10^{-2} M, [Ir(III)] = 6.6 × 10^{-9} M.

Table 2
Effects of ionic strength and chloride ion on the rate of oxidation of paracetamol at 308 K.

[KCl] × 10^5 mol dm^{-3}	NaClO$_4$ (I)	−dc/dt × 10^7 mol dm^{-3} s^{-1}	k × 10^4 s^{-1}
0.0	–	0.87	0.91
1.0	–	1.85	1.95
2.0	–	3.50	3.60
3.0	–	4.90	5.10
4.0	–	6.40	6.70
5.0	–	8.30	8.70
6.0	–	11.20	11.70
8.0	–	13.20	13.80
10.0	–	14.40	15.10
5.0	0.0	7.40	7.70
5.0	2.0	8.50	8.90
5.0	4.0	8.10	8.50
5.0	6.0	7.70	8.10
5.0	10.0	8.30	8.70
5.0	12.0	7.20	7.50
5.0	16.0	8.00	8.40
5.0	25.0	8.20	8.60

Solution conditions: [CAT] = 1 × 10^{-3} M, [PA] = 1 × 10^{-2} M, [Ir(III)] = 6.6 × 10^{-9} M, and [H$^+$] = 4 × 10^{-2} M, [KCl] = 5 × 10^{-5} M.

Table 3
Effect of solvent on the rate of oxidation of paracetamol at 308 K.

%CH_3COOH (v/v)	D	$-dc/dt \times 10^7$ mol dm^{-3} s^{-1}	$k \times 10^4$ (s^{-1})
0	78.2	8.3	8.7
5	73.2	10.0	10.5
10	70.2	15.0	15.7
20	62.9	20.0	21.0
30	55.1	25.0	26.3
40	48.2	40.0	42.1

Solution conditions: [CAT] = 1×10^{-3} M, [PA] = 1×10^{-2} M, [Ir(III)] = 6.6×10^{-9} M, and [H^+] = 4×10^{-2} M, [KCl] = 5×10^{-5} M.

3.2. Reactive species of CAT

Chloramine-T acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions forming the reduction products, PTS (p-$CH_3C_6H_4SO_2NH_2$ or $TsNH_2$) and sodium chloride. The oxidation potential of CAT–$TsNH_2$ redox couple varies with pH of the medium (E_o is 1.14 V at pH 0.65, 0.778 V at pH 7.0, 0.614 V at pH 9.7 and 0.50 V at pH 12) [20]. Depending on the pH, CAT furnishes different types of reactive species [14,21,22].

$$TsNClNa \rightleftharpoons TsNCl^- + Na^+ \quad (a)$$

(CAT) (where, Ts represents $CH_3C_6H_4SO_2$-group).

The anion ($TsNCl^-$) gets protonated in an acidic solution to give N-chlorotoluene sulphonamide (TsNHCl).

$$TsNCl^- + H^+ \overset{K_a}{\rightleftharpoons} TsNHCl \quad (b)$$

Thus, chloramine-T exists as a free acid (TsNHCl) in acidic media. The dissociation constant of TsNHCl at a pH ca. 4.5 is 2.8×10^{-5} reported by Morris et al. [14]. Further, TsNHCl can undergo disproportionate or hydrolysis according to following reactions [10]:

$$2\,TsNHCl \rightleftharpoons TsNCl_2 + TsNH_2 \quad (c)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \quad (d)$$

It has also been observed that at higher acid concentration (pH < 2.8) TsNHCl is further protonated to form $TsNH_2Cl^+$, which in turn undergoes hydrolysis to give $(H_2OCl)^+$.

$$TsNHCl + H^+ \rightleftharpoons TsNH_2Cl^+ \quad (e)$$

$$TsNH_2Cl^+ + H_2O \rightleftharpoons TsNH_2 + (H_2OCl)^+ \quad (f)$$

Thus, it appears from the equilibrium (a)–(f), that various probable chlorinating/oxidizing species of CAT exists in acidic media such as TsNHCl, $TsNCl_2$ (dichloramine-T), HOCl and $TsNH_2Cl^+$ or $(H_2OCl)^+$. In order to determine the reactive species of CAT in the present investigation, it is necessary to know the effect of [H^+] and [PTS] on the rate of reaction. In the present case, if $TsNCl_2$ was to be the reactive species in the oxidation of PA, then the rate law should predict a second-order dependence on [CAT] and should also show negative effect of $TsNH_2$ according to Eq. (c). However, the predictions [CAT] oxidation is contrary to the observed experimental results. It is clear from equilibrium (e) that with the increase in [H^+] there will be increase in [RNH_2^+Cl] and if there is positive effect of [H^+] on the rate of reaction the species RNH_2^+Cl can be taken as the most reactive species in the reaction. Since in the present study, there is a negative effect of [H^+] on the rate of reaction, the possibility of taken $RNH_2^+Cl^-$ species as the most reactive species is ruled out. Further, It is clear from equilibrium (d) if there is negative effect of [H^+] and [PTS] on the rate of reaction, the species HOCl can safely be taken as the most reactive oxidizing species in the reaction. Under the circumstances the only choice left is to assume HOCl as the most reactive species of CAT in the reaction, which gives a rate law capable of explaining all the kinetic observations and other effects.

Table 4
Activation parameters for the oxidation of paracetamol.

Temperature K	$k \times 10^4$ s^{-1}
303	5.78
308	8.7
313	10.3
318	17.4
323	21.8
E_a (kJ mol^{-1})	54.9
$\Delta H^{\#}$ (kJ mol^{-1})	52.3 ± 1.32
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−129.4 ± 3.68
$\Delta G^{\#}$ (kJ K^{-1} mol^{-1})	92.15 ± 1.93
log A	6.24 ± 0.19

Solution conditions: [CAT] = 1×10^{-3} M, [PA] = 1.0×10^{-2} M, [Ir(III)] = 6.6×10^{-9} M, and [H^+] = 4×10^{-2} M, [KCl] = 5×10^{-5} M.

3.3. Reactive species of iridium (III) chloride in acidic medium

It has been reported that Ir(III) and Ir(I) ions are the stable species of iridium [23]. A spectrophotometric study of the kinetics of hydration of $IrCl_6^{3-}$ and addition of the Cl^- to $[Ir(H_2O)Cl_5]^{2-}$ in 1.0–2.5 M $HClO_4$ (or HCl) at 50 °C was reported [24], where the rate constants and the equilibrium constant (K) for the reversible reaction were given.

$$[IrCl_6]^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ir(H_2O)Cl_5]^{2-} + Cl^- \quad (A)$$

UV–Visible absorption spectra of the new Ir(III) complexes $[Ir(H_2O)_2Cl_4]^-$ and $[Ir(H_2O)_3Cl_3]$, together with the spectra of $[Ir(Cl_6)]^{3-}$ and $[Ir(H_2O)Cl_5]^{2-}$ in 2.5 M $HClO_4$–1.2 M $NaClO_4$, were also reported and found in reasonable agreement with those reported in the literature [24–26]. When Ir(III) chloride dissolved in 0.1 M HCl solution, $IrCl_6^{3-}$ and $[Ir(H_2O)Cl_5]^{2-}$ species were formed. On the basis of the effect of [Cl^-] on the rate of the reaction and also assuming the existence of the above equilibrium in the reaction (A), $IrCl_6^{3-}$ is taken as the reactive species of Ir(III) chloride in the acidic medium.

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 study indicating that change in the oxidation state of iridium may not be possible. According to the reaction Scheme 1, $[IrCl_6]^{3-}$ combines with paracetamol to give complex C_3 which in turn combine with HOCl (reactive species of CAT) to give the complex C_4 with the liberation of H^+. Complex C_4 in the slow and rate determining steps gives rise to the intermediate product, which ultimately converts into final products.

3.4. Mechanism and derivation of rate law

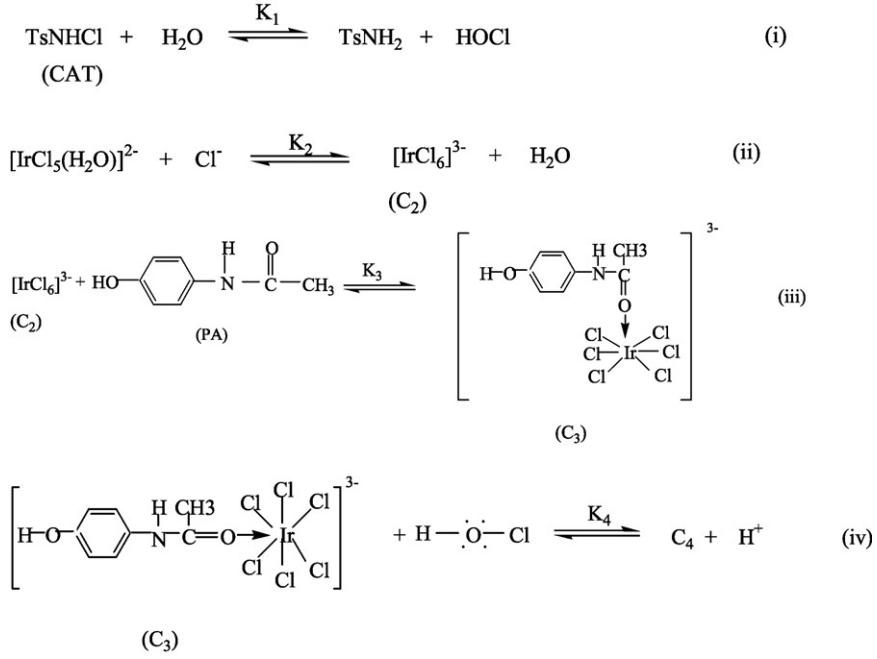
According to the reaction Scheme 1 and considering the fact that 1 mole of paracetamol (PA) is oxidized by 2 mole of CAT, the rate in terms of decrease in the concentration of CAT can be expressed as:

$$\text{rate} = -\frac{d[CAT]}{dt} = 2k[C_4] \quad (1)$$

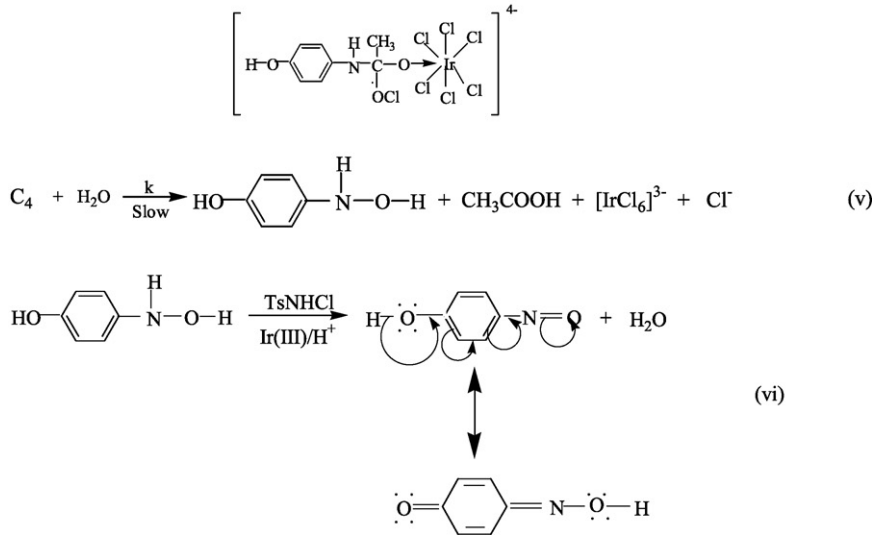
On the basis of equilibrium steps (i)–(v), Eqs. (2)–(5) can be obtained in the following forms and taking TsNHCl as CAT, respectively

$$[HOCl] = \frac{K_1[CAT]}{[TsNH_2]} \quad (2)$$

$$[C_2] = K_2[C_1][Cl^-] \quad (3)$$



The structure of C_4 might be written as



Scheme 1.

$$[C_3] = K_3[C_2][PA] \quad (4)$$

and

$$[C_4] = \frac{K_4[C_3][HOCl]}{[H^+]} \quad (5)$$

With the help of Eqs. (2)–(5), we can write Eq. (6):

$$[C_4] = \frac{K_1K_2K_3K_4[CAT][PA][Cl^-][C_1]}{[TsNH_2][H^+]} \quad (6)$$

with the help of Eqs. (6) and (1), we can write Eq. (7) as:

$$\text{rate} = \frac{2kK_1K_2K_3K_4[CAT][PA][Cl^-][C_1]}{[TsNH_2][H^+]} \quad (7)$$

At any moment in the reaction, the total concentration of Ir(III) i.e. $[Ir(III)]_T$ can be shown as:

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3] + [C_4] \quad (8)$$

On substituting the values of $[C_2]$, $[C_3]$ and $[C_4]$ from Eqs. (3), (4) and (6), respectively, in Eq. (8), we get Eq. (9)

$$[C_1] = \frac{[H^+][TsNH_2][Ir(III)]_T}{[H^+][TsNH_2] + [H^+][TsNH_2]K_2[Cl^-] + K_2K_3[PA][Cl^-][H^+][TsNH_2] + K_1K_2K_3K_4[CAT][Cl^-][PA]} \quad (9)$$

From Eq. (7) and (9), we get Eq. (10)

$$\text{rate} = \frac{2kK_1K_2K_3K_4[CAT][Cl^-]PA][Ir(III)]_T}{[H^+][TsNH_2] + K_2[H^+][TsNH_2][Cl^-] + K_3K_2[PA][Cl^-][H^+][TsNH_2] + K_1K_2K_3K_4[CAT][PA][Cl^-]} \quad (10)$$

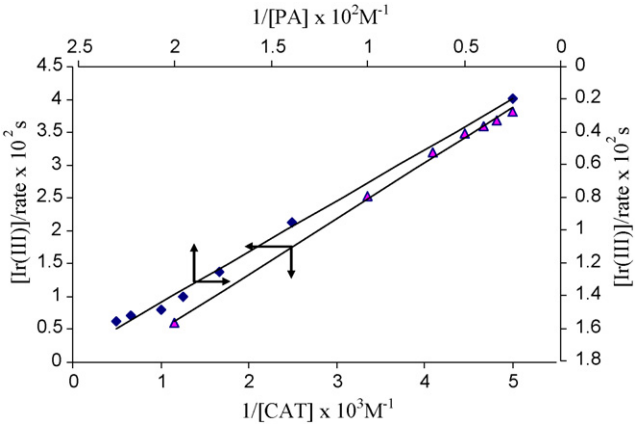


Fig. 5. Varification of rate law for 1/[PA]and 1/[CAT] of Ir(III)-catalyzed oxidation of paracetamol by chloramine-T at 303 K. $[Ir(III)] = 6.6 \times 10^{-9}$ M, $[H^+] = 4 \times 10^{-2}$ M, $[KCl] = 5 \times 10^{-5}$ M.

Eq. (10) is the rate law on the basis of which observed kinetic orders with respect to each reactant of the reaction can very easily be explained.

On reversing Eq. (10), we have Eq. (11)

$$\frac{[Ir(III)]}{rate} = \frac{[TsNH_2][H^+]}{2kK_1K_2K_3K_4[CAT][Cl^-][PA]} + \frac{[TsNH_2][H^+]}{2kK_1K_3K_4[CAT][PA]} + \frac{[TsNH_2][H^+]}{2kK_1K_4[CAT]} + \frac{1}{2k} \quad (11)$$

Eq. (11), indicates that if a plot is made between $[Ir(III)_T]$/rate] and $[TsNH_2]$ or $[H^+]$ or 1/[CAT] or 1/[PA] or $1/[Cl^-]$, a straight line with positive intercept on *y*-axis will be obtained. Straight lines with positive intercept on y-axis were obtained by the plots of $[Ir(III)_T]$/rate] and 1/[CAT] or 1/[PA] (Fig. 5) or [PTS] or $[H^+]$ (Fig. 6), this proves the validity of the rate law (10) and the proposed reaction scheme, on the basis of which the rate law (10) has been derived. For the oxidation of PA the values obtained for k, $K_1K_2K_3K_4$, $K_1K_3K_4$, K_1K_4, K_2K_3, K_2, and K_3 have been calculated and found as 5.00×10^2 s^{-1}, 5.88×10^3 mol l^{-1}, 2.88×10^{-2} mol^{-1} l, 2.90×10^{-4} mol^{-1} l, 2.00×10^7, 2.00×10^5 mol^{-1} l and 1.00×10^2 mol l^{-1}, respectively.

In the present study of the iridium (III)-catalyzed oxidation of paracetamol Scheme 1 has been proposed. In this reaction Scheme 1, the most unstable activated complex is formed by the interaction of C_3 and HOCl, as a result of which the transition state will be more highly charged species. Due to this, more solvent molecules will be required than for the separate ions. This would lead to a decrease in entropy. The observed negative entropy of activation supports the formation of aforesaid activated complex by the interaction of ion–dipole system in step (iv) of Scheme 1.

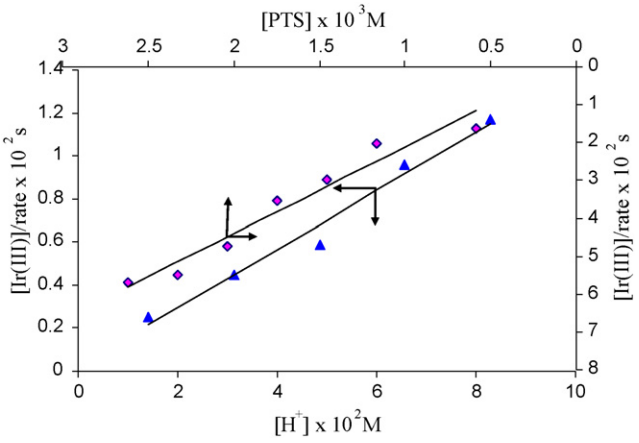


Fig. 6. Varification of rate law for [PTS] and $[H^+]$ of Ir(III)-catalyzed oxidation of paracetamol by chloramine-T at 303 K $[CAT] = 1 \times 10^{-3}$ M, $[PA] = 1.0 \times 10^{-2}$ M, $[Ir(III)] = 6.6 \times 10^{-9}$ M, $[KCl] = 5 \times 10^{-5}$ M.

3.5. Effect of dielectric constant and calculation of the size of the activated complex

The change in dielectric constant of the medium has been made by addition of acetic acid in reaction mixture. Before conducting experiments for the study of the effect of dielectric constant of the medium on the rate of reaction, we performed experiments taking acetic acid as an organic substrate instead of paracetamol in the usual manner and found that acetic acid under the condition of our experiments is not oxidized in the presence of Ir(III). It is clear from Table 3, that $-dc/dt$ and k_1 values are increased with the decrease in dielectric constant (D) of the medium. The dependence of the rate constant on the dielectric constant of the medium is given by the following equation:

$$\log k_1 = \log k_0 - \frac{Z_A Z_B e^2 \tilde{N}}{2.303(4\pi \in_0) d_{AB} RT} \times \frac{1}{D} \quad (B)$$

where k_o is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the charges of reacting ion, d_{AB} refers to the size of activated complex, T is absolute temperature and D is dielectric constant of the medium. This equation shows that if a plot is made between $\log k$ versus $1/D$ straight line having slope equal to $-Z_AZ_B$ and $e^2N/2.303(4\pi\varepsilon_o)d_{AB}RT$ will be obtained. The effect of solvent on the reaction kinetics has been described in detail in the older literature [27–32]. For the limiting case of a zero angle approach between two dipoles or an ion–dipole system. Amis has shown that a plot $\log k_1$ versus $1/D$ gives a straight line with a positive slope for a reaction between a ion and a dipole or two dipoles. The decrease in first-order rate constant with the increase in dielectric constant (D) of the medium was also evident from the plot of $\log k_1$ vs. $1/D$ (Fig. 7). The plot of $\log k_1$ versus $1/D$ was linear, having positive slope. This clearly supports the involvement of an ion–dipole system in the rate limiting step in the proposed mechanism. The value of d_{AB} has been evaluated with the help of slope of straight line and found to be 2.76 Å.

According to the rate determining step in Scheme 1 that involves ion–dipole interaction, negligible effect of variation of ionic strength of the medium on the rate of oxidation of paracetamol is well explained. Entropy of activation plays an important role in the case of reaction between ions or between an ion and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two similarly charged species, the transition state will be a more highly charged ion, and due to this, more solvent

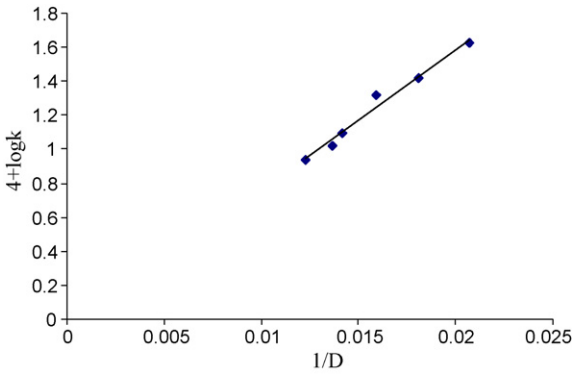


Fig. 7. Plot between $\log k$ vs $1/D$ at 303 K. $[CAT] = 1 \times 10^{-3}$ M, $[PA] = 1.0 \times 10^{-2}$ M, $[H^+] = 4 \times 10^{-2}$ M, $[Ir(III)] = 6.6 \times 10^{-9}$ M, $[KCl] = 5 \times 10^{-5}$ M.

molecules will be required than for the separate ions, leading to a decrease in entropy. On the other hand, when reaction takes place between two ions of opposite charges, their union will results in a lowering of the net charge and due to this some frozen solvent molecules will be released with an increase of entropy. On the basis of this information, observed negative entropy of activation supports the rate limiting step of the proposed Scheme 1. The proposed mechanism is also supported by moderate value of energy of activation and other activation parameters. The high positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate that the transition state is highly solvated.

4. Conclusion

The Ir(III) catalyzed oxidation of paracetamol by chloramines-T was studied in the acidic medium at 35 °C. The oxidation of paracetamol by CAT in perchloric acid become facile in the presence of micro-quantity of Ir(III) (10^{-9} M). Among the various species of Ir(III) in acidic medium, $[IrCl_6]^{3-}$ is considered as the reactive species while HOCl is considered as the reactive species of oxidant. Oxidation products have been identified and activation parameters were evaluated for the catalyzed reaction. A plausible reaction mechanism and related rate law has been worked out. In conclusion, it can be said that Ir(III) is a most efficient catalyst in the oxidation of the paracetamol by CAT in acidic medium.

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