



## Mechanistic and Thermodynamic study of Iridium (III) Catalyzed Oxidation of Paracetamol Drug by Acidic Solution of Potassium Bromate (KBrO<sub>3</sub>): A Kinetic Study

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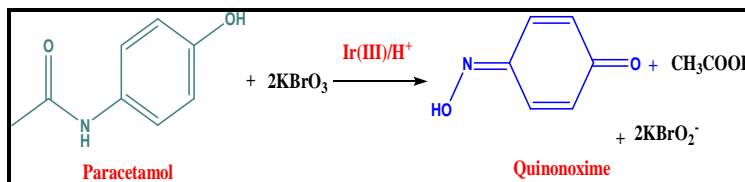
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### ABSTRACT

Mechanistic and thermodynamic study of Iridium(III) Catalyzed Oxidation Of Paracetamol drug by Acidic solution of Potassium Bromate (KBrO<sub>3</sub>) at 35°C. The reaction followed first order kinetics with respect to Ir(III) and potassium bromate (KBrO<sub>3</sub>). Rate of reaction exhibits zero order and fractional positive order kinetics with respect to [KCl] and [PA] respectively. The rate of reaction decreased with increasing [H<sup>+</sup>] was observed for the oxidation of paracetamol. Negligible effect of [Hg(OAc)<sub>2</sub>] and ionic strength of the medium was observed at different temperature (30°C to 45°C) were utilized to calculate the activation parameters. The reaction between potassium bromate and paracetamol in acid medium exhibits 1:2 stoichiometry. Quinoneoxime and acetic acid have been identified as main oxidation products of the reactions. Feasible mechanism has been proposed conforming with the kinetics, stoichiometry and product of the reaction. The rate law has been derived from obtained kinetic data.

### Graphical abstract



**Keywords:** Kinetics, oxidation, Potassium bromate, Ir(III) chloride, Acidic medium.

## INTRODUCTION

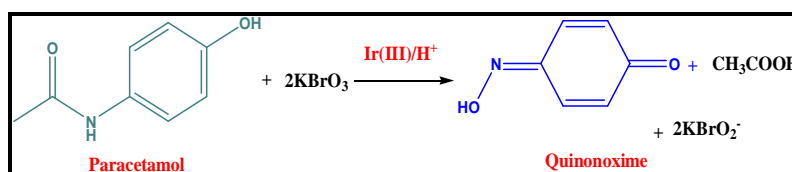
Catalysis by transition metal ion plays an important role in understanding the mechanistic aspects of a particular redox reaction. Ir(III) chloride is a strong catalyst and is more conveniently prepared either by the action of chlorine on iridium powder at 600-620°C [1-2] or from the tetrahydroxide Ir(OH)<sub>4</sub> by the action of chlorine at 600°C, Or hydrogen chloride at 310°C [2]. It has a large range of stability. It is formed from its elements at a temperature below 100°, and it does not decompose until 760°C. The rate of chlorination of metal is greater in presence of sunlight or ultraviolet light, the addition of a trace of carbon monoxide diminishes the rate of reaction in the dark, but increases it in ultraviolet light [2]. The kinetics of redox reactions incorporating certain transition metal ions like osmium(VIII), ruthenium(VIII), ruthenium(III), and palladium ions as homogeneous catalyst has been extremely investigated [3-8]. These are nontoxic and homogeneous catalyst reported by several workers [9-10]. Scant attention has been paid on catalytic role of ruthenium(III) chloride with potassium bromate as oxidant. [11-12]. Ir(III) chloride is seen to be a good catalyst in recent years. It has been investigated very little as a homogeneous catalyst with N-bromosuccinimide [13]. Iridium(III) chloride has also been used as catalyst in N-bromoacetamide oxidation [14] of some organic compounds. Kinetics of Ir(III) catalysis have also been reported [15]. Oxidant chosen for the present work is potassium bromate (KBrO<sub>3</sub>) which has been reported to be a powerful oxidant with redox potential of 1.44 volt in acidic media. KBrO<sub>3</sub> has been widely used in oxidation of alcohols [16], ketones [17], aniline [18], phenols, aldehydes [19], tartaric acid [20], some labile substrate [21], nitrites [22], pyrogallol acid [23], amino acids [24], diols [25], unsaturated carboxylic acids [26] and n-substituted phenyl methyl sulphides [27] with ruthenium (III) chloride as catalyst. Potassium bromate is used for oxidation of uncatalyzed reactions by several workers [28-29]. An uncatalyzed reaction of aldoses and aldosamines [30], carbohydrates [31] compound oxidation by potassium bromate has also been reported. Ir(III) catalyzed cyclic alcohols [32], cyclic ketones [33] oxidation by potassium bromate has also been reported. Comparatively Ir(III) catalyzed oxidation has been dealt than other catalyst and scant attention has been paid with potassium bromate as an oxidant. The kinetics of paracetamol oxidation has been studied both spectrophotometrically and iodometrically. Spectrophotometric determination of paracetamol in drug formulation has been a subject of several investigators [34-42]. In this paper it has been tried to consolidate the various work done on the well-known drug that finds extensive application in pharmaceutical industries in the last few decades. Paracetamol (4-hydroxyacetanilide or acetamidophenol) is a well-known drug that is having extensive application in pharmaceutical industries. It is antipyretic and analgesic compound of high therapeutic value [43, 44]. It is also used as an intermediate for pharmaceutical (as a precursor in penicillin) and azo dye [45-47]. Oxidation reactions are important in the synthesis of organic compounds, create new functional groups or modify existing functional groups in a molecule [48, 49]. Various advanced oxidation processes such as electrochemical [50-52] ozonation and H<sub>2</sub>O<sub>2</sub>/UV oxidation [53-56] have been employed to remove aqueous paracetamol. The present study examines, in detail the kinetic and mechanistic aspects of the Ir(III) catalyzed oxidation of paracetamol by KBrO<sub>3</sub> in acidic media with the following objectives. To ascertain the reactive species of the catalyst and the oxidant, to deduce the rate law consistent with the kinetic results. Identify the oxidation products. To estimate activation parameters, to elucidate the plausible reaction mechanism based on the observed reaction rate law and stoichiometry.

## MATERIALS AND METHODS

**Materials:** Aqueous solution of Paracetamol (CDH), potassium bromate (S.D. Fine A.R.) and mercuric acetate (E. Merck) were prepared by dissolving the weighed amount of sample in triple distilled water. Perchloric acid (60% E. Merck) was used as a source of hydrogen ions. Iridium(III) chloride (Johnson Matthey) was prepared by dissolving the sample in hydrochloric acid of known strength. All other reagents of analytical grade were available. Sodium perchlorate (E. Merck) was used to maintain the ionic strength of the medium. The reaction stills were blackened from outside to prevent photochemical effect.

**Kinetic Procedure:** A thermo stated water bath was used to maintain the desired temperature within  $\pm 0.1^\circ\text{C}$ . Calculated amount of the reactants i.e. paracetamol, perchloric acid, mercuric acetate, Ir(III) chloride, KCl and water, except potassium bromate 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 amount of potassium bromate solution, also thermostated at the same temperature was rapidly pipetted out and run into the reaction vessel. The total volume of reaction mixture was 50 mL in each case. Aliquots (5 mL) of the reaction mixture were pipetted out at regular intervals of time and poured in to a conical flask containing 5 mL of 4 % KI solution and 5 mL of dilute sulfuric acid. The liberated bromine equivalent to consumed oxidant was estimated with standard sodium thiosulphate solution using starch as an indicator. The rate of reaction ( $-\text{dc dt}^{-1}$ ) was determined from the slope of the tangent drawn at a fixed  $[\text{BrO}_3^-]$  in each kinetic run. The order of reaction in each reactant was measured with the help of log plot of ( $-\text{dc dt}^{-1}$ ) versus concentration of the reactants.

**Determination of stoichiometry and product analysis:** Different sets of the reaction mixture containing Paracetamol, Ir(III) chloride, and  $\text{HClO}_4$  with excess  $\text{KBrO}_3$  were equilibrated for 72 h at 303 K. Estimation of unconsumed  $\text{KBrO}_3$  in each set revealed that for the oxidation of 1 mole of Paracetamol, 2 moles of  $\text{KBrO}_3$  were consumed. Accordingly, the stoichiometry equation may be expressed as the reaction products were extracted with ether after completion of the reaction (monitored by TLC). Evaporation of the ether layer was followed by column chromatography on silica gel using a gradient elution (from dichloromethane to chloroform). After the initial separation, the products were further purified by recrystallization. Acetic acid and quinone oxime were identified as oxidation products of Paracetamol and  $2\text{KBrO}_2$  was the reduction product of  $\text{KBrO}_3$ . The quinone oxime was identified by its IR spectrum ( $1652\text{ cm}^{-1}$ , C=O stretching;  $1615\text{ cm}^{-1}$ , C=N stretching of oxime;  $3332\text{ cm}^{-1}$ , O-H stretching). Identification was further confirmed by its melting point of  $131^\circ\text{C}$  (literature mp  $132^\circ\text{C}$ ).



## RESULT AND DISCUSSION

It is necessary to study the effect of variation in concentration of different reactants on the rate of reaction. The kinetic results were collected at several initial concentrations of reactants (Table 1). The initial rate ( $-\text{dc dt}^{-1}$ ) in each kinetic run was calculated by the slope of tangent drawn at fixed time for the variation of  $[\text{KBrO}_3]$  while in the variation of other [reactants], tangents drawn at fixed  $[\text{KBrO}_3]$  which was written as  $[\text{KBrO}_3^*]$  (figure 1). The first order rate constant  $K_1$  was calculated as

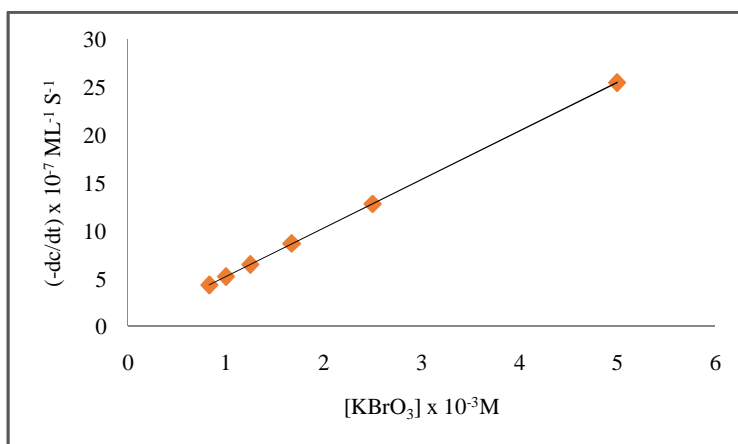
$$K_1 = \frac{-\text{(dc/dt)}}{[\text{KBrO}_3^*]}$$

Each kinetic run was studied for two half lives of the reaction. The observed rates of reaction were reproducible with in  $\pm 5\%$  in replicate kinetic run. The order of reaction in each reactant was determined with the help of log-log plot of ( $-\text{dc dt}^{-1}$ ) vs. Concentration of reactant. First order rate constant  $k_1$  i.e. ( $-\text{dc/dt}/\text{KBrO}_3^*$ ) were calculated from the plots of unconsumed potassium bromate vs. time. The plots of  $\log(-\text{dc/dt})$  versus  $\log(\text{oxidant})$  were linear indicating first order dependence on  $\text{KBrO}_3$  (Figure 1). Insignificant effect on the rate was observed on increasing the concentration of  $[\text{Cl}^-]$  indicating zero

**Table 1.** Effect of variation of oxidant (KBrO<sub>3</sub>), substrate (Paracetamol), catalyst [Ir(III)] chloride at 35°C

Oxidant x 10 <sup>-3</sup> M (Potassium bromate)	[Substrate]x 10 <sup>-2</sup> M (Paracetamol)	[Ir(III)] x 10 <sup>-5</sup> M Iridium chloride	(-dc/dt)x10 <sup>-7</sup> ML <sup>-1</sup> S <sup>-1</sup>
0.80	1.00	11.2	4.30
1.00	1.00	11.2	5.20
1.25	1.00	11.2	6.45
1.69	1.00	11.2	8.65
2.50	1.00	11.2	12.80
5.00	1.00	11.2	25.50
1.00	0.40	11.2	3.80
1.00	0.50	11.2	4.30
1.00	0.66	11.2	4.62
1.00	1.00	11.2	5.20
1.00	2.00	11.2	6.65
1.00	4.00	11.2	8.25
1.00	1.00	5.60	2.56
1.00	1.00	11.2	5.20
1.00	1.00	16.8	10.30
1.00	1.00	22.4	15.32
1.00	1.00	33.6	20.40
1.00	1.00	44.8	25.90

Solution Condition: [HClO<sub>4</sub>] = 1.00 X 10<sup>-3</sup> M, [KCl] = 1.00 X 10<sup>-3</sup> M,  
[Hg(OAc)<sub>2</sub>] = 1.25 X 10<sup>-3</sup> M

**Figure 1.** Plot between rate of reaction (dc/dt) vs [KBrO<sub>3</sub>] for the oxidation of paracetamol at 35°C. [HClO<sub>4</sub>] = 1.00 X 10<sup>-3</sup> M, [KCl] = 1.00 X 10<sup>-3</sup> M, [Hg(OAc)<sub>2</sub>] = 1.25 X 10<sup>-3</sup> M, Paracetamol [PA] = 1.00 x 10<sup>-2</sup> M, [Ir(III)Cl<sub>3</sub>] = 11.2 x 10<sup>-5</sup> M.

in [KCl], i.e. potassium chloride (Table 2). The rate of reaction increases as the concentration of Iridium (III) chloride is increased (Table 1). It was observed that values of  $(-dc/dt)$  were doubled when the concentration of Ir(III) was made two times, showing first order dependence on IrCl<sub>3</sub> indicating first order of catalyst i.e. Ir(III) chloride. With increasing the concentration of [H<sup>+</sup>], the value of reaction rate decreases (Table 2). This showed negative effect of [H<sup>+</sup>] on the rate of oxidation of paracetamol. Negligible effect of [Hg(OAc)<sub>2</sub>] and ionic strength of the medium was observed. Kinetic result obtained on varying concentrations of substrate indicates fractional positive order, which implies that rate of reaction increases when the concentration of [PA] is increased (Table 1). The rate measurements were taken at 30°-45°C and specific rate constants were used to draw a plot of log k vs. 1/T which was linear (Figure 2-5).

**Table-2.** Effect of variation of reactant [HClO<sub>4</sub>], [KCl], [Hg(OAc)<sub>2</sub>] at 35°C

[HClO <sub>4</sub> ] x 10 <sup>-3</sup> M	[KCl] x 10 <sup>-3</sup> M	[Hg(OAc) <sub>2</sub> ] x 10 <sup>-3</sup> M	Paracetamol (-dc/dt)x10 <sup>7</sup> ML <sup>-1</sup> S <sup>-1</sup>
0.80	1.00	1.00	5.60
1.00	1.00	1.00	5.20
1.25	1.00	1.00	4.60
1.67	1.00	1.00	4.25
2.50	1.00	1.00	3.60
5.00	1.00	1.00	2.95
1.00	0.80	1.00	4.90
1.00	1.00	1.00	5.20
1.00	1.25	1.00	4.52
1.00	1.69	1.00	5.45
1.00	2.50	1.00	5.12
1.00	5.00	1.00	4.72
1.00	1.00	0.80	4.52
1.00	1.00	1.00	4.93
1.00	1.00	1.25	5.20
1.00	1.00	1.67	4.62
1.00	1.00	2.50	5.55
1.00	1.00	5.00	5.32

Solution Condition: [Oxidant (KBrO<sub>3</sub>)] = 1.00 X 10<sup>-3</sup>M,  
[Paracetamol(PA)] = 1.00 X 10<sup>-2</sup> M, [Ir (III) Chloride] = X 10<sup>-5</sup> M

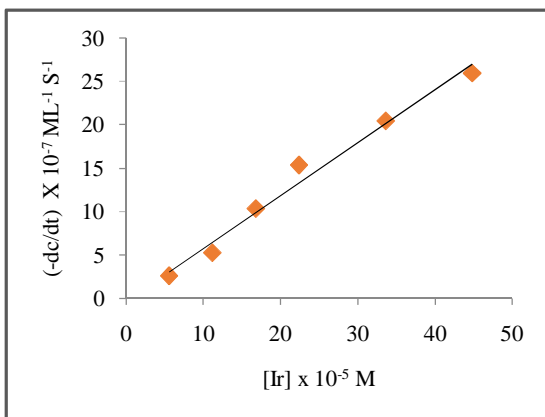
**Role of Entropy of activation and other activation parameters:** The value of energy of Activation ( $\Delta E^*$ ) Arrhenius factor (A), entropy of activation ( $\Delta S^*$ ) and free energy of activation ( $\Delta G^*$ ) were calculated from rate measurement at 30°, 35°, 40°, 45°C and these values have been recorded in table 3. Moderate  $\Delta H^*$  and  $\Delta S^*$  values are favourable for electron transfer reaction. The value of  $\Delta H^*$  was due to energy of solution changes in the transition state. The high positive values of change in free energy of activation ( $\Delta G^*$ ) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation ( $\Delta S^*$ ) suggest the formation of an activated complex with reduction in the degree of freedom of molecule. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [57]. The high positive values of change in free energy of activation ( $\Delta G^*$ ) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation ( $\Delta S^*$ ) suggest the formation of an activated complex with reduction in the degree of freedom of molecule [58]. The activation parameters evaluated for the catalyzed and uncatalyzed reaction explain the catalytic effect on the reaction. Entropy of activation plays an important role in the case of reaction between ions or between an ion

**Table 3.** Activation parameters for Ir(III) chloride catalyzed oxidation of paracetamol by KBrO<sub>3</sub> at 35°C

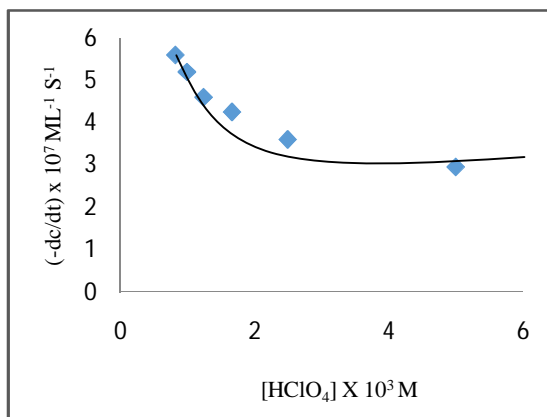
Parameter	Temperature(T°C)	Paracetamol(-dc/dt)x 10 <sup>7</sup>
k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>	30°	3.70
k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>	35°	5.20
k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>	40°	7.35
k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>	45°	10.12
log A	...	9.51
$\Delta E_a^*$ (kJ mol <sup>-1</sup> )	35°	55.25
$\Delta G^*$ (kJ mol <sup>-1</sup> )	35°	76.12
$\Delta H^*$ (kJ mol <sup>-1</sup> )	35°	55.52
$\Delta S^*$ (JK <sup>-1</sup> mol <sup>-1</sup> )	35°	-66.82

Solution Condition: [Ir(III)] = 11.2 x 10<sup>-3</sup> M, [KBrO<sub>3</sub>] = 1.00 x 10<sup>-3</sup> M,  
Paracetamol = 1.00 x 10<sup>-2</sup> M, [Hg(OAc)<sub>2</sub>] = 1.25 x 10<sup>-3</sup> M, [HClO<sub>4</sub>] =  
1.00 x 10<sup>-3</sup> M, [KCl] = 1.00 x 10<sup>-3</sup> M

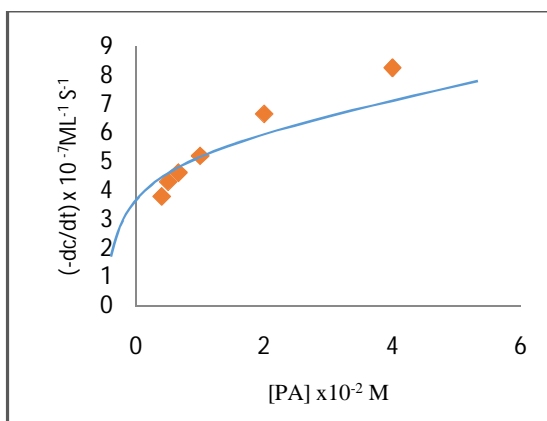
and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two ions of opposite charges, their union will result in a lowering of net charge, and due to this some frozen solvent molecules will be released with increase of entropy but on the other hand when reaction takes place between two similarly charged species, the transition state will be more highly charged ion and due to this, more solvent molecules will be required for separate the ions, leading to decrease the entropy.



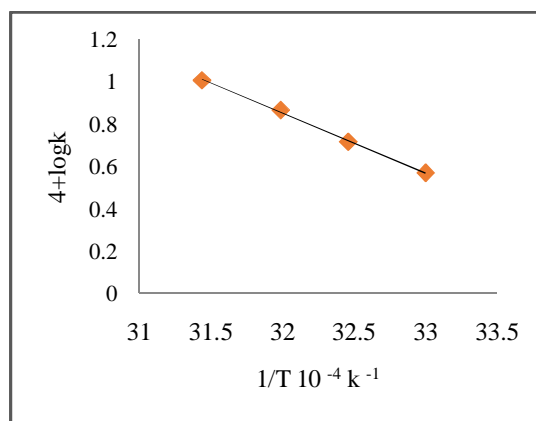
**Figure 2.** Plot between rate of reaction  $(-dc/dt)$  vs  $[\text{Ir(III)}]$  on the reaction rate at  $35^\circ\text{C}$ .  $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$ ,  $[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Paracetamol}] = 1.00 \times 10^{-2} \text{ M}$ .



**Figure 3.** Plot between rate of reaction  $(-dc/dt)$  vs  $[\text{HClO}_4]$  on the reaction rate at  $35^\circ\text{C}$ .  $[\text{Ir(III)}] = 11.20 \times 10^{-5} \text{ M}$ ,  $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$ ,  $[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Paracetamol}] = 1.00 \times 10^{-2}$ .

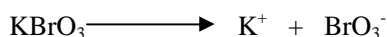


**Figure 4.** Plot between rate of reaction  $(-dc/dt)$  vs  $[\text{Paracetamol}]$  on the reaction rate at  $35^\circ\text{C}$ .  $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$ ,  $[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Ir(III)}] = 11.20 \times 10^{-5} \text{ M}$ .

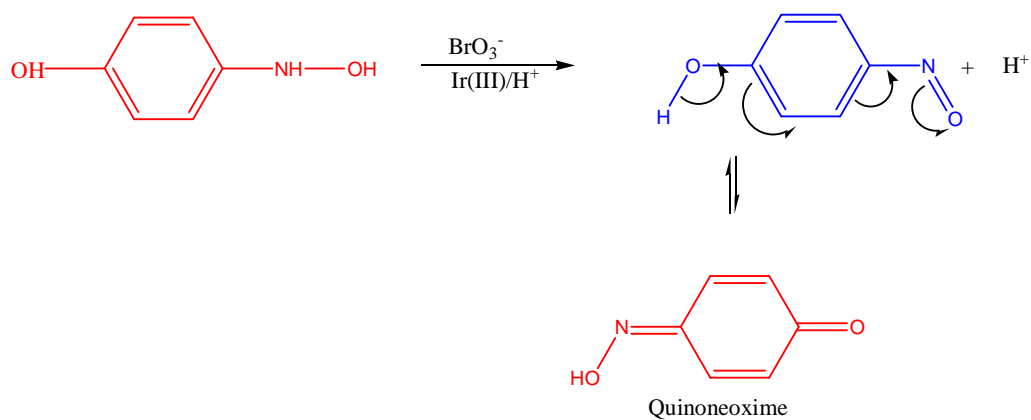
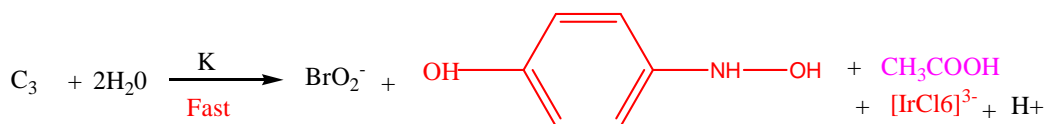
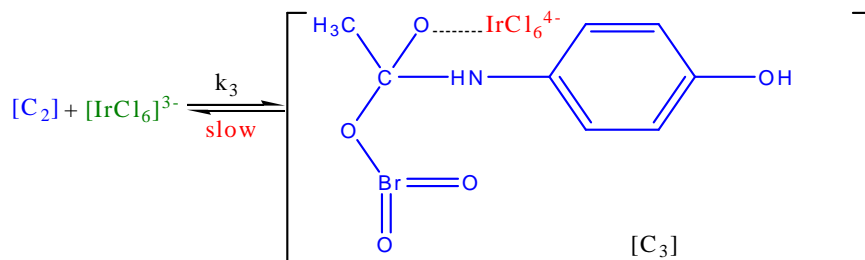
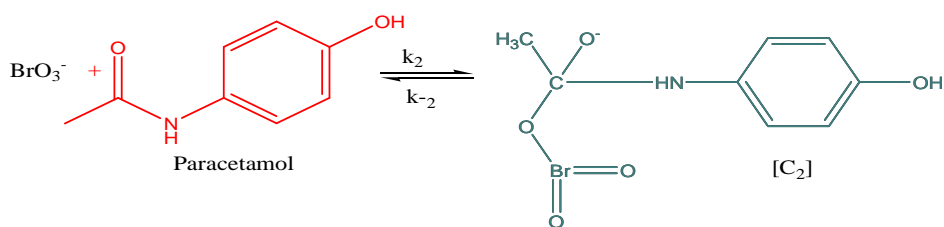
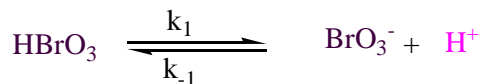
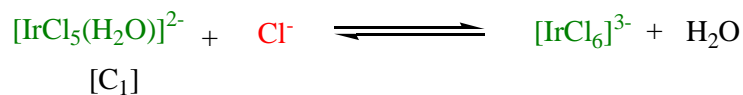


**Figure 5.** Arrhenius plot of the oxidation of paracetamol on the reaction rate at  $35^\circ\text{C}$ .  $[\text{Ir(III) Chloride}] = 11.2 \times 10^{-5} \text{ M}$ ,  $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$ ,  $[\text{Oxidant (KBrO}_3)] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Paracetamol}] = 1.00 \times 10^{-2} \text{ M}$ ,  $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$ .

**Mechanism and Derivation of Rate Law:** Negligible effect of mercuric acetate excludes the possibility of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without potassium bromate. Hence the function of mercuric acetate is to act as a scavenger for any  $[\text{Br}^-]$  ion formed in the reaction. It helps to eliminate the parallel oxidation by  $\text{Br}_2$  which would have been formed as a result of interaction between  $\text{Br}^-$  and bromate ion. Potassium bromate has been used as an oxidant for a variety of compounds in acidic media (S. Srivastava, 1999). sometimes in the presence of a catalyst. In alkaline and acidic medium, potassium bromate is ionised:



The  $\text{BrO}_3^-$  species has been reported to act as an oxidizing agent in acidic as well as in alkaline medium (Singh and Srivastava, 1991). Ir(III) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. The kinetic results have been reported in tables 1, 2 and 3.



Considering the fact that 1 mole of paracetamol is oxidized by 2 moles of bromate and applying the steady state treatment, with reasonable approximation, the rate law may be written as equation.

$$\text{rate}(R) = \frac{-d [\text{BrO}_3]^-}{dt} = 2k[\text{C}_3] \quad \dots (1)$$

On the basis of scheme above step (1) to (4) equation 2-5 can be obtained in the following forms respectively as-

$$R = \frac{2k K_1 K_2 K_3 [\text{Ir(III)}][\text{PA}][\text{HBrO}_3]}{[\text{H}]^+} \quad \dots (2)$$

At any time in the reaction the total concentration of  $\text{HBrO}_3$  that is  $[\text{HBrO}_3]_T$  can be expressed as-

$$[\text{HBrO}_3]_T = [\text{HBrO}_3] + [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \quad \dots (3)$$

Substitution of the variable of  $[\text{C}_1]$   $[\text{C}_2]$  and  $[\text{C}_3]$  in equation [3]. Equation [4] is obtained.

$$[\text{HBrO}_3] = \frac{[\text{HBrO}_3]_T}{[\text{H}]^+ + K_1 + K_1 K_2 [\text{PA}] + K_1 K_2 K_3 [\text{Ir(III)}][\text{PA}]} \quad \dots (4)$$

Substituting the value of  $[\text{HBrO}_3]$  in equation [2] we obtained the expression equation [5].

$$R = \frac{2k K_1 K_2 K_3 [\text{Ir(III)}][\text{PA}][\text{HBrO}_3]_T}{[\text{H}]^+ + K_1 + K_1 K_2 [\text{PA}] + K_1 K_2 K_3 [\text{Ir(III)}][\text{PA}]} \quad \dots (5)$$

## APPLICATION

Although a number of spectrophotometric methods are available for the determination of drugs, these are generally associated with some or the other demerits. The use of iridium (III) for the determination of paracetamol has been suggested. The results from this study show that oxidation of paracetamol by iridium(III) is enhanced in presence of  $\text{KBrO}_3$ . The reactive species of oxidant and catalyst has been identified. Oxidation products were identified and activation parameters were evaluated.  $\text{KBrO}_3$  was most effective as only 5-10 min is required for the completion of the reaction. This is very significant for any industrial preparation of quinoneoxime. This method is simple, accurate, rapid, economical, and precise.

## CONCLUSION

Oxidation of paracetamol by  $\text{KBrO}_3$  does not proceed in the absence of catalyst, but it becomes facile in the presence of  $\text{Ir(III)}$  catalyst. The reactive species of oxidant and catalyst have been identified. Oxidation products were identified and activation parameters were evaluated. The observed results have been explained by a plausible mechanism and the related law has been deduced. Therefore, it can be concluded that  $\text{Ir(III)}$  acts as an efficient catalyst for the oxidation of paracetamol. In the present study the following conclusions drawn:

- $[\text{IrCl}_6]^{3-}$  is considered as the reactive species of  $\text{Ir(III)}$  in acidic medium.
- $\text{HBrO}_3$  is the reactive species of potassium bromate in acidic medium.
- The stoichiometry of the reaction was found to be 2:1 and the oxidation products of Paracetamol were identified.
- Activation parameters were computed from the Arrhenius plot.
- The observed results have been explained by a plausible mechanism and the related rate law has been derived.



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