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Thermodynamic properties and Mechanism of Aquachloro iridium (III) Catalyzed Oxidation of Pharmaceutical drug (Paracetamol) by Acidic solution of Potassium Bromate ($KBrO_3$): A kinetic study

Reena Patel[1], Shailesh kumar[2], Abhishek Verma[3], Sheila Srivastava[4]
[1, 3] *Ph. D student, Department of Applied Chemistry B.B.A.U. Lucknow, UP, India*
[2]*Assistant Professor, Department of Applied Chemistry B.B.A.U. Lucknow, UP, India*
[4]*Associate Professor, Department of Chemistry Feroze Gandhi College, Raebareli, UP, India*

Abstract: ***The thermodynamic properties and mechanism of a quachloroiridium(III) Catalyzed oxidation of pharmaceutical drug(Paracetamol) by acidic solution of potassium bromated(KBrO3) at 350C. The reaction followed first order kinetics with respect to Ir (III) and potassium bromated (KBrO3). 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+] was observed for the oxidation of paracetamol. Negligible effect of [Hg(OAC)2] and ionic strength of the mediumwas observed at different temp.(300 C to 450 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 to the kinetics, stochiometry and product of the reaction. The rate law has been derived from obtained kinetic data.***

Key words: Kinetics, oxidation, Paracetamol, Potassium bromate, Ir (III) chloride, Acidic medium.

I. INTRODUCTION

Cataysis by transition metal ions, 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^{0}[1-2] or from the tetrahydroxideIr $(OH)_4$ by the action of chlorine at 600^{0}, Or hydrogen chloride at 310^{0}[2]. It has a large range of stability. It is formed from its elements at a temperature below 100^{0}, and it does not decompose until 760^{0}. The rate of chlorination of metal is greater in presence of sunlight or ultraviolate light; the addition of a trace of carbon monoxide diminishes the rate of reaction in the dark, but increases it in ultraviolate light.[2] The kinetics of redox reactions incorporating certain transition metal ions like osmium(VIII), ruthenium(VIII), ruthenium(III), and palladious ions as homogeneous catalyst has been extremely investigated.[3-8] These are non toxic and homogeneous catalyst reported by several workers.[9-10] Scant attention has been paid on catalytic role of ruthenium(III) chloride with potassium bromated 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 bromated ($KBrO_3$) which has been reported to be a powerful oxidant with redox potential of 1.44 volt in acidic media. $KBrO_3$ hasbeen widely used in oxidation of alcohols[16], ketones[17], aniline[18], phenols, aldehydes[[19], tartaric acid[20], some labile substrate[21], nitrites[22], pyrogallic acid[23], amino acids[24], diols[25], unsaturated corboxlylic 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] Uncatalyzed reactions of aldoses and aldosamines[30], carbohydrates[31] compound oxidation by potassium bromate has also been reported. Ir(III) catalyzed cyclicalcohols[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 (PAM) 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 acetmidophenol) is a well known drug that is having extensive appliction in pharmaceutical industries. It is antipyretic and analgesic compound of high therapeutic value.[43-44] It is also used as an intermediate for pharmeceutical (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 H2O2 / 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 $KBrO_3$ in acidic media with the following objective.

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 reacion rate law and stoichiometry.

II. MATERIAL AND PROCEDURE

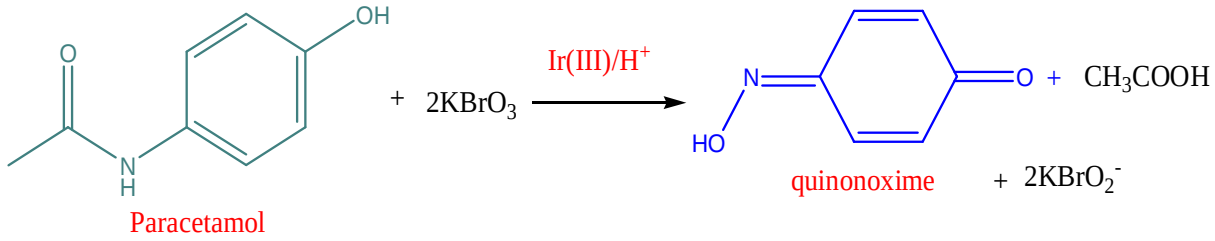
A. Materials

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.

B. Kinetic Procedure

A the rmostated water bath was used to maintain the desired temperature within ± 0.1 °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 (5mL) 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 (-dc/dt) was determined from the slope of the tangent drawn at a fixed $[BrO_3^-]$ in each kinetic run. The order of reaction in each reactant was measured with the help of log plot of (-dc/dt) versus concentration of the reactants.

C. Determination Of Stoichiometry And Product Analysis



Different sets of the reaction mixture containing Paracetamol, Ir(III) chloride, and $HClO_4$ with excess $KBrO_3$ were equilibrated for 72 h at 303 K. Estimation of unconsumed $KBrO_3$ in each set revealed that for the oxidation of 1 mol of Paracetamol, 2 mols of $KBrO_3$ 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 quinine oxime were identified as oxidation products of Paracetamol and $2KBrO_2$ was the reduction product of $KBrO_3$. The quinoneoxime was identified by its IR spectrum (1652 cm-1, C=O stretching; 1615 cm-1, C=N

stretching of oxime; 3332 cm^{-1}, O-H stretching). Identification was further confirmed by its melting point of 131^0C (literature mp 132^0C). Quinone oxime was also analyzed via GC- MS (JEOL- JMS, Mate-MS system, Japan. GC - MS results were analyzed by extraction of the reaction mixture with diethyl ether and by concentrating the ether layer by a slow evaporation procedure. Acetic acid was identified by the spot test.

III. 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 (-dc/dt) in each kinetic run was calculated by the slope of tangent drawn at fixed time for the variation of [$KBrO_3$] while in the variation of other [reactants], tangents drawn at fixed [$KBrO_3$] which was written as [$KBrO_3^*$] (fig-1). The first order rate constant K_1 was calculated as

$$K_1 = \frac{-(dc/dt)}{[KBrO_3^*]}$$

Each kinetic run was studied for two half lives of the reaction. The observed rates of reaction were reproducible with in ± 5% in replicate kinetic run. The order of reaction in each reactant was determined with the help of log-log plot of (-dc/dt) vs. Concentration of reactant. First order rate constant k_1 i.e. (-dc/dt/$KBrO_3^*$) were calculated from the plots of unconsumed potassium bromate vs. time. The plots of log(-dc/dt) versus log (oxidant) were linear indicating first order dependence on $KBrO_3$ (Fig-1).Insignificant effect on the rate was observed on increasing the concentration of [Cl^-] indicating zero order 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 $IrCl_3$ indicating first order of catalyst i.e. Ir(III) chloride(fig-2). With increasing the concentration of [H^+], the value of reaction rate decreases (Table-2). This showed negative effect of [H^+] on the rate of oxidation of paracetamol (fig-3).Negligible effect of [$HgOAc)_2$] and ionic strength of the medium was observed. Kinetic result obtained on varying concentrations of substrat indicates fractional positive order, which implies that rate of reaction increases when the concentration of [PA] is increased (table-1),(fig-4). The rate measurements were taken at 30^0-45^0C and specific rate constants were used to draw a plot of log k vs. 1/T which was linear (Fig-5).

A. Role of entropy of Activation And Other Activation Parameters

The value of energy of Activation (ΔE*) Arrhenius factor (A), entropy of activation (ΔS*) and free energy of activation (ΔG*) were calculated from rate measurement at 30^0, 35^0, 40^0, 45^0C and these values have been recorded in Table-3. Moderate ΔH* and ΔS* values are favourable for electron transfer reaction. The value of ΔH* was due to energy of solution changes in the transition state. The high positive values of change in free energy of activation (ΔG*) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation(ΔS*) 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 [21]. The high positive values of change in free energy of activation (ΔG*) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation(ΔS*) suggest the formation of an activated complex with reduction in the degree of freedom of molecule [57]. 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 and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two ions of opposite charges, their union will results in a lowering of net charge, and due to this some frozen solvent molecules will 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 seprate the ions, leading to decrease the entropy.

IV. 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 [Br^-] ion formed in the reaction. It helps to eliminate the parallel oxidation by Br_2 which would have been formed as a result of interaction between Br^- and bromate ion. Potassium bromate has been used as an oxidant for a variety of compounds in acidic media (Srivastava, S., (1999). sometimes in the presence of a catalyst. In alkaline and acidic medium, potassium bromate is ionised:

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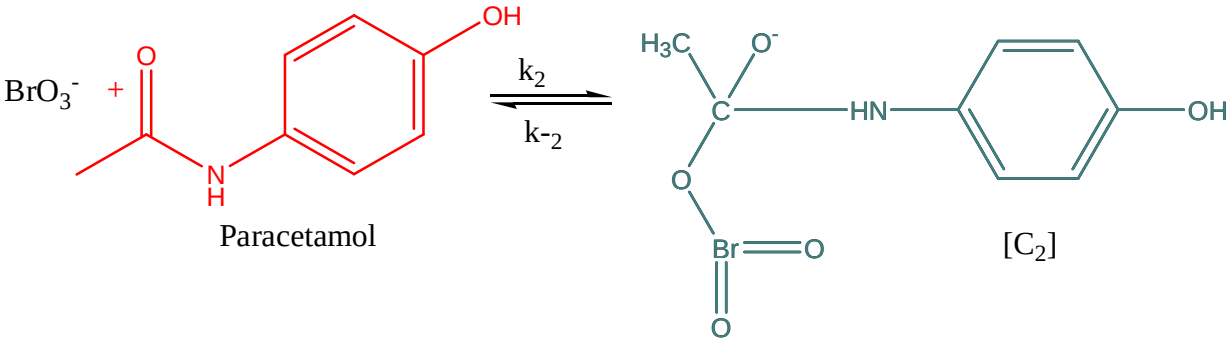
$$KBrO_3 \rightarrow \quad K^+ + BrO_3^-$$

The BrO_3^- species has been reported to act as an oxidising agent in acidic as well as in alkaline medium (Singh and Srivastava, 1991). Pd(II) 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.

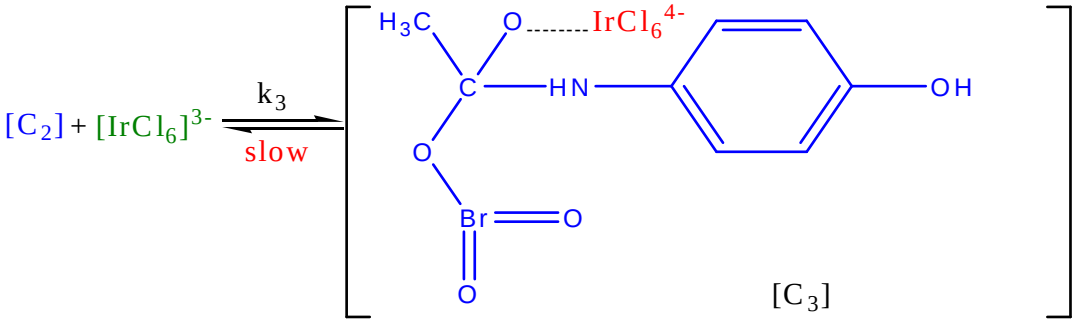
$$[IrCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [IrCl_6]^{3-} + H_2O$$

$[C_1]$

$$HBrO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BrO_3^- + H^+$$

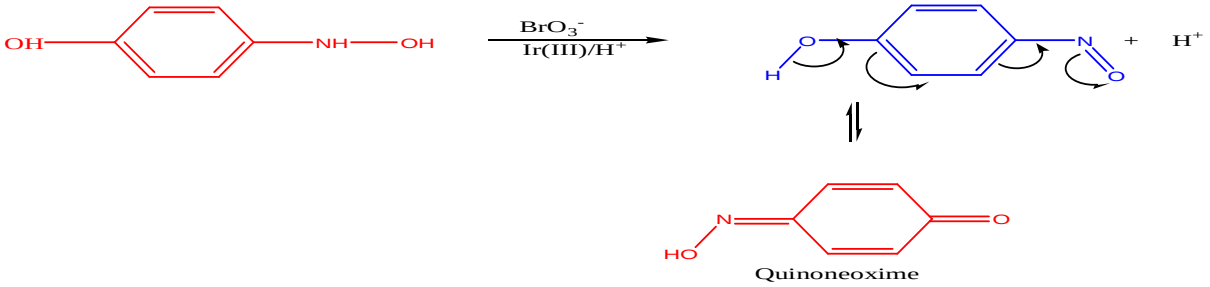


Paracetamol $[C_2]$



$[C_3]$

$$C_3 + 2H_2O \xrightarrow[\text{Fast}]{K} BrO_2^- + \text{OH-C}_6\text{H}_4\text{-NH-OH} + CH_3COOH + [IrCl6]^{3-} + H+$$



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

$$\text{rate(R)} = \frac{-\text{d}\,[BrO_3]^-}{dt} = 2\text{k}[C_3] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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

$$R = \frac{2k\,K_1K_2K_3[Ir(III)][PA][HBrO_3]}{[H]^+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

At any time in the reaction the total concentration of $HBrO_3$ that is $[HBrO_3]_T$ can be expressed as-

$$[HBrO_3]_T = [HBrO_3] + [C_1] + [C_2] + [C_3] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Substitution of the variable of $[C_1]$ $[C_2]$ and $[C_3]$ in equation [3]. Equation [4] is obtained.

$$[HBrO_3] = \frac{[HBrO_3]_T}{[H]^+ + \text{K}_1 + \text{K}_1\text{K}_2[\text{PA}] + K_1K_2K_3[Ir(III)][PA]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Substituting the value of $[HBrO_3]$ in equation [2] we obtained the expression equation [5].

$$R = \frac{2k\,K_1K_2K_3[Ir(III)][PA][HBrO_3]_T}{[2H]^+ + \text{K}_1 + \text{K}_1\text{K}_2[\text{PA}] + K_1K_2K_3[Ir(III)][PA]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

V. CONCLUSION

Oxidation of paracetamol by $KBrO_3$ does not proceed in the absence of catalyst, but it becomes facile in the presence of 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 Ir(III) acts as an efficient catalyst for the oxidation of paracetamol. In the present study"Thermodynamic properties and Mechanism of Aquachloroiridium(III) Catalyzed Oxidation Of Pharmaceutical drug(Paracetamol) by Acidic solution of Potassium Bromate ($KBrO_3$) : A kinetic study" has been performed and following conclusions drawn:

1) $[IrCl_6]^{3-}$ is considered as the reactive species of Ir(III) in acidic medium.
2) $HBrO_3$ is the reactive species of potassium bromate in acidic medium.
3) The stoichiometry of the reaction was found to be 2:1 and the oxidation products of Paracetamol were identified .
4) Activation parameters were computed from the Arrhenius plot.
5) The observed results have been explained by a plausible mechanism and the related rate law has been derived.

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Table-1
Effect of variation of oxidant ($KBrO_3$), substrate(Paracetamol), catalyst [Ir(III)] chloride at 35^0C

Oxidant x 10^3M (Potassium bromate)	[Substrate]x 10^2M (Paracetamol)	[Ir(III)] x 10^5M Iridium chloride	(-dc/dt)x10^7ML^{-1}s^{-1}
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: $[HClO_4]$ = 1.00 X 10^{-3} M, [KCl] = 1.00 X 10^{-3}M , $[Hg(OAC)_2]$ = 1.25 X 10^{-3} M

Table-2
Effect of variation of reactant $[HClO_4]$, [KCl], $[Hg(OAc)_2]$ at 35^0C

$[HClO_4]$ x 10^3M	[KCl] x 10^3M	$[Hg(OAc)_2]$x 10^3M	(-dc/dt)x10^7ML^{-1}s^{-1}
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 ($KBrO_3$)] = 1.00 X 10^{-3}M, [Paracetamol(PA)] = 1.00 X 10^{-2} M, [Ir (III) Chloride] = X 10^{-5} M

Table-3
Activation parameters for Ir(III) chloride catalyzed oxidation of paracetamolby $KBrO_3$ at 35^0C

Parameter	Temperature(T^0C)	Paracetamol(-dc/dt)x 10^7
k_1 x 10^4s^{-1}	30^0	3.70
k_1 x 10^4s^{-1}	35^0	5.20
k_1 x 10^4s^{-1}	40^0	7.35
k_1 x 10^4s^{-1}	45^0	10.12
log A	...	9.51
ΔE_a* (k J mol^{-1})	35^0	55.25
Δ G* (k J mol^{-1})	35^0	76.12
Δ H * (k J mol^{-1})	35^0	55.52
Δ S* ($JK^{-1}mol^{-1}$)	35^0	-66.82

Solution Condition: [Ir(III)] = 11.2 x 10^{-5} M, [$KBrO_3$] = 1.00 x 10^{-3}M,Paracetamol = 1.00 x 10^{-2} M, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M,[$HClO_4$] = 1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M

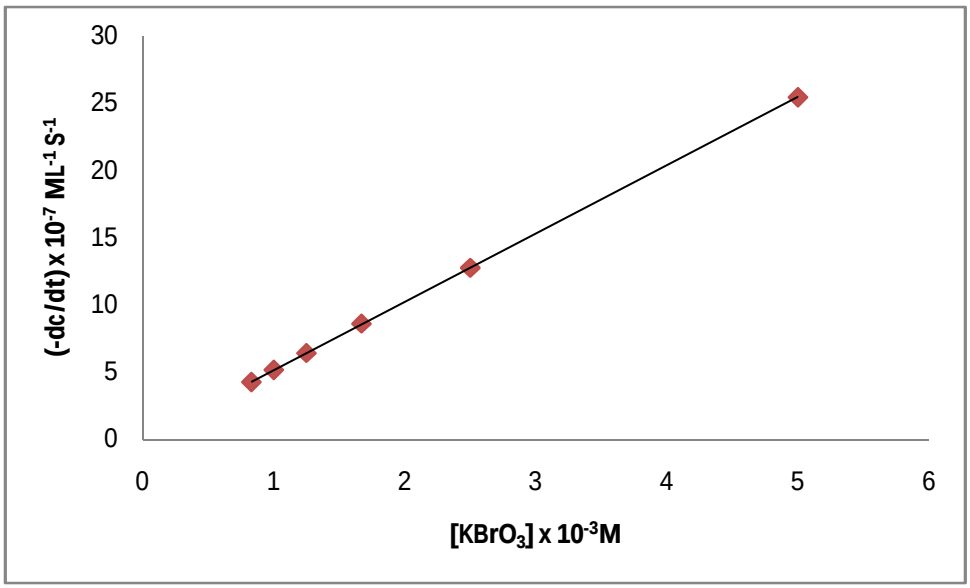


Figure 1. Plot between rate of reaction (dc/dt) vs [$KBrO_3$] for the oxidation of paracetamol at 35^0C. [$HClO_4$] = 1.00 X 10^{-3} M, [KCl] = 1.00 X 10^{-3} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3}M, Paracetamol [PA] = 1.00 x 10^{-2} M, [Ir(III)CI_3] = 11.2 x 10^{-5} M

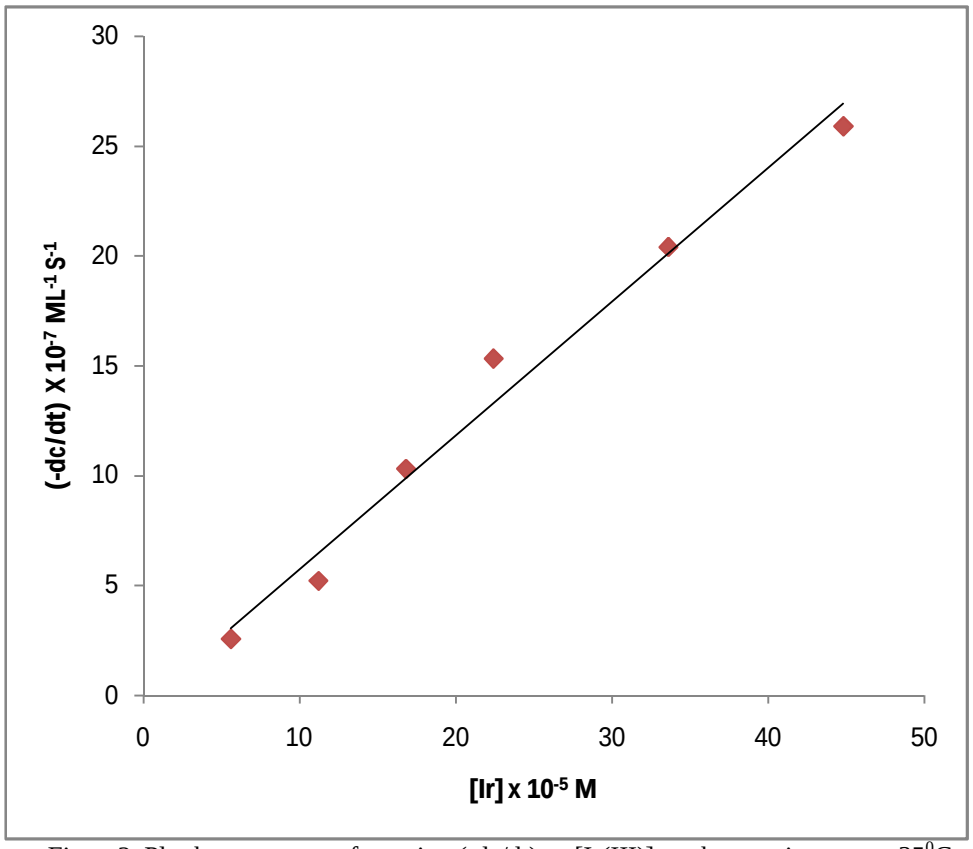


Figure2. Plot between rate of reaction (-dc/dt) vs [Ir(III)] on the reaction rate at 35^0C.

$[HClO_4]$ = 1.00 X 10^{3}M, [KCl] = 1.00 X 10^{3} M, $[Hg(OAc)_2]$ = 1.25 X 10^{3} M , $[KBrO_3]$ = 1.00 X 10^{3} M , [Paracetamol)] = 1.00 X 10^{2} M

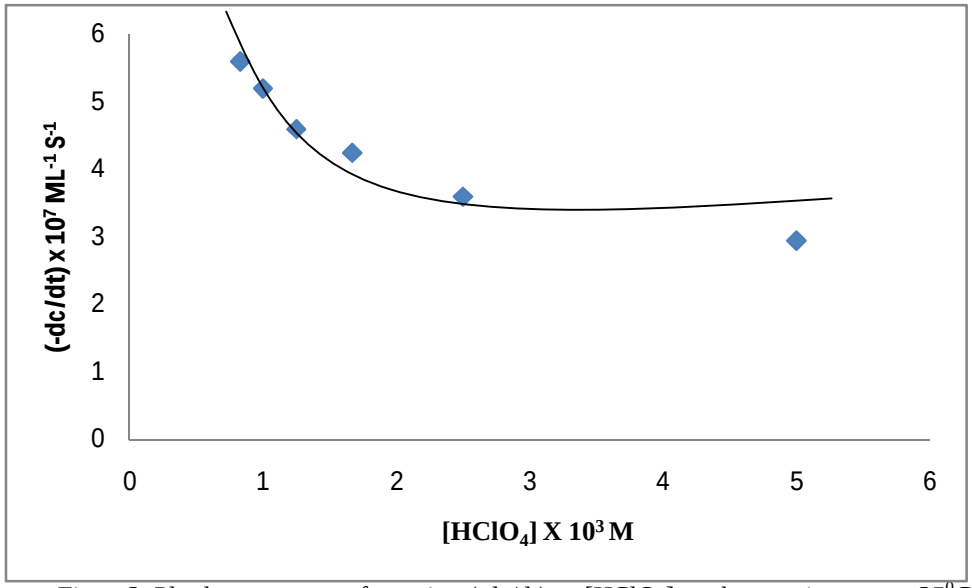


Figure3. Plot between rate of reaction (-dc/dt) vs $[HClO_4]$ on the reaction rate at 35^0C.

[Ir(III)] = 11.20 X 10^{5}M, [KCl] = 1.00 X 10^{3} M, $[Hg(OAc)_2]$ = 1.25 X 10^{3} M , $[KBrO_3]$ = 1.00 X 10^{3} M , [Paracetamol)] = 1.00 X 10^{2}

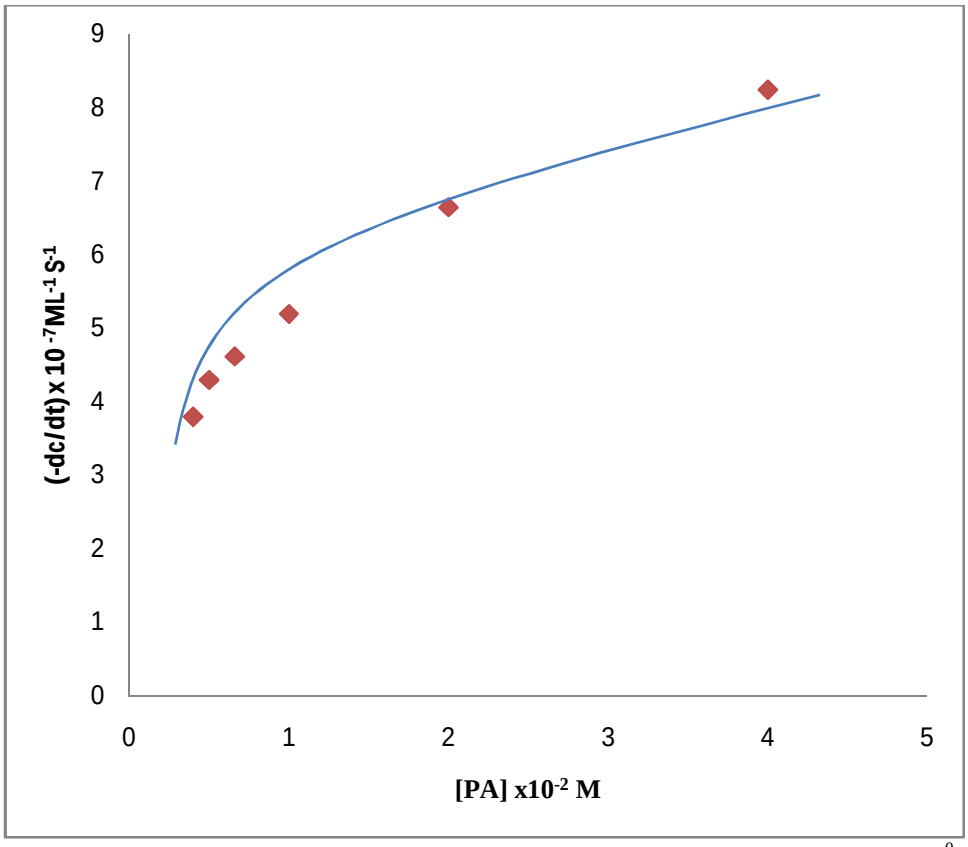


Figure 4. Plot between rate of reaction (-dc/dt) vs [Paracetamol] on the reaction rate at 35^0C.

$[HClO_4]$ = 1.00 X 10^{3}M, [KCl] = 1.00 X 10^{3} M, $[Hg(OAc)_2]$ = 1.25 X 10^{3} M , $[KBrO_3]$ = 1.00 X 10^{3} M , [Ir(III)] = 11.20 X 10^{5} M

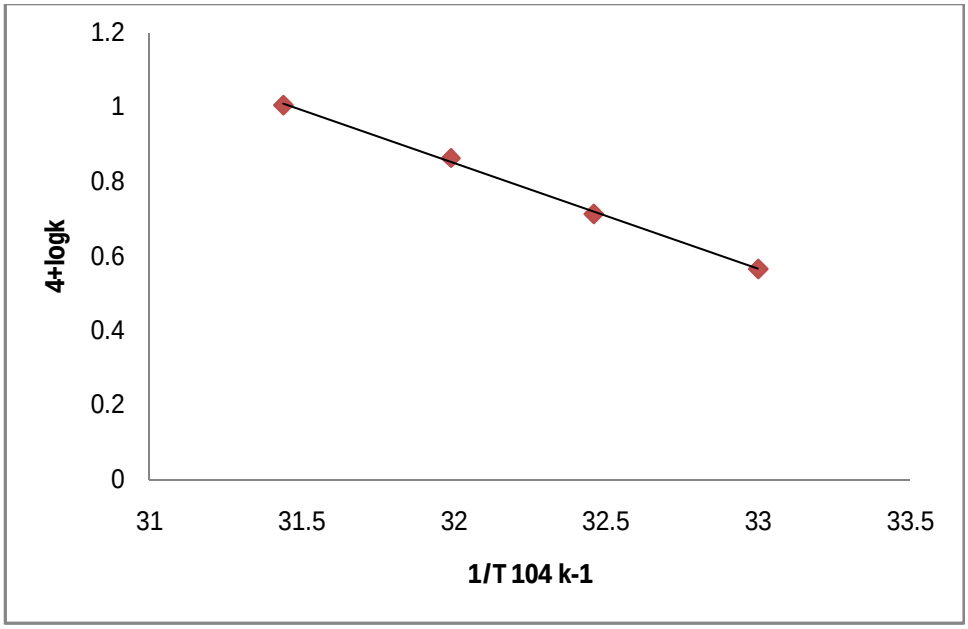
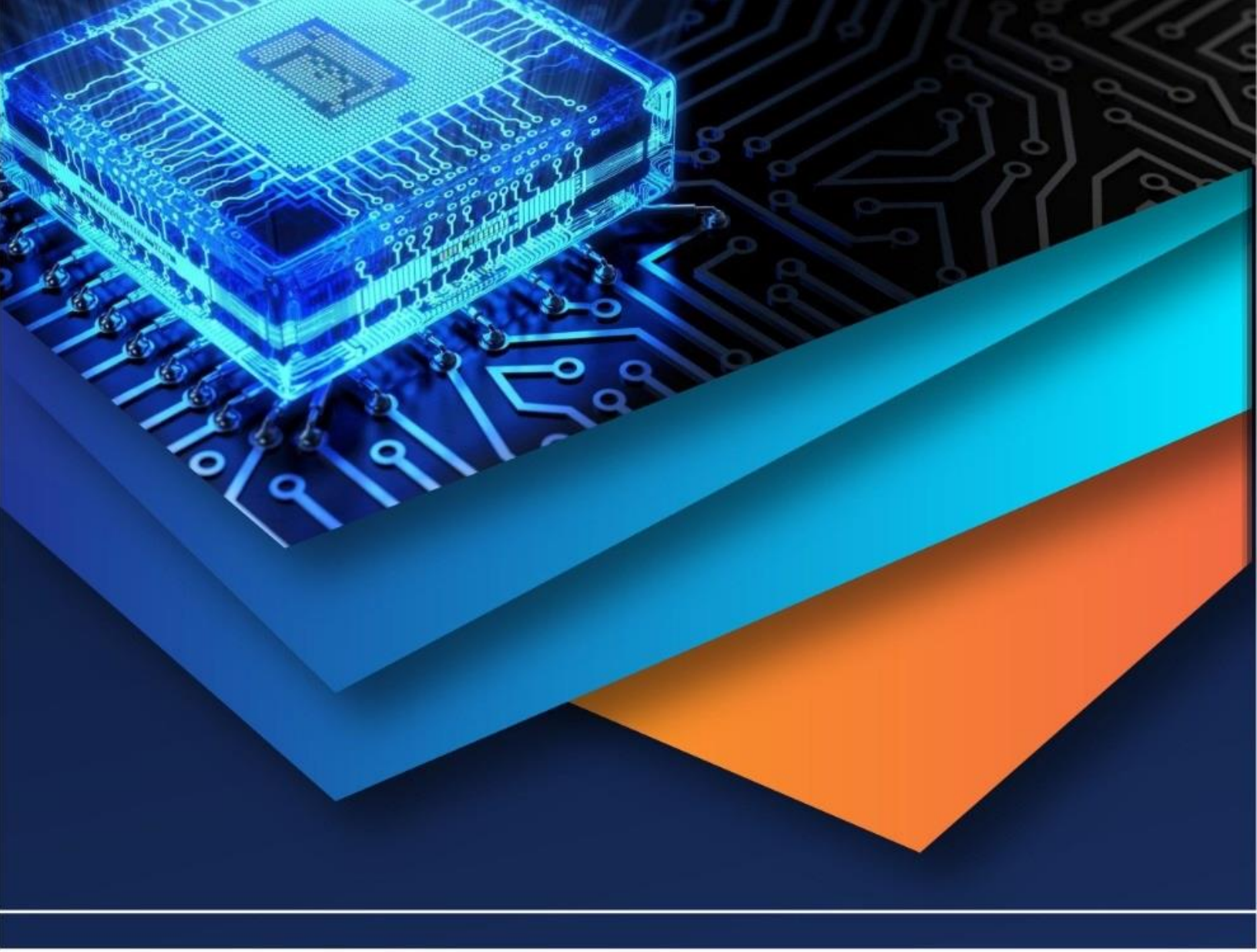


Figure5. Arrhenius plot of the oxidation of paracetamol on the reaction rate at 35^0C.[Ir(III) Chloride] = 11.2 x 10^{5} M, [KCl] = 1.00 x 10^{3} M, $[Hg(OAc)_2]$ = 1.25 x 10^{3} M[Oxidant ($KBrO_3$)] = 1.00 x 10^{3} M, [Paracetamol] = 1.00 X 10^{2} M, $[HClO_4]$ = 1.00 X 10^{3} M



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