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Mechanistic Investigation on Pd (II) Catalyzed Oxidation of Paracetamol by Potassium Bromate ($KBrO_3$) in Presence of $HClO_4$ Acid Medium: A Kinetic Model

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Abstract: The present paper deals with the kinetic and mechanistic investigation of pd(II) catalyzed oxidation of paracetamol by potassium bromate ($KBrO_3$) in presence of perchloric acid medium at 303 K. The experimental result shows a first order kinetics with respect to [Palladium] and [bromate]. The reaction showed negative effect for $[H^+]$. Paracetamol positively influenced the rate of reaction. Negligible effect of $[HgOAc)_2]$ and ionic strength of the medium was observed. Variation of $[Cl^-]$ does not show any significant change on the rate of reaction. The values of rate constants observed at different temperatures (30 to 45^0C) were utilized to calculate the activation parameters. Quinoneoxime and acetic acid have been identified as main oxidation products of the reactions. Feasible mechanism has been proposed conforming with the kinetics, stochiometry and product of the reaction. The rate law has been derived from obtained kinetic data.

Keywords: Kinetics, Pd(II) chloride, oxidation, Paracetamol, Potassium bromate, Acidic medium.

1. INTRODUCTION

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.[1-9]. 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[10-11]. It is also used as an intermediate for pharmeceutical (as a precursor in penicillin) and azo dye [112-15]. Oxidation reactions are important in the synthesis of organic compounds, create new functional groups or modify existing functional groups in a molecule[16-17]. Various advanced oxidation processes such as electrochemical[18-20] ozonation and H_2O_2 / UV oxidation[21-24] have been employed to remove aqueous paracetamol.

The oxidation kinetics of Paracetamol drug by oxidant like organic haloamines, metal ion oxidants, metal complex, use of catalyst, variation of media, product effect, is of importance to understand the mechanism of metabolic conversion of paracetamol in biological systems and also identify the reactive species of the oxidant in aqueous acid/ base. Till date the action of paracetamol at a molecular level is not completely understood but could be related to production of reactive metabolites by the peroxidase function of COX-2, which could deplete glutathione, a cofactor of enzymes such as PGE synthase[25]. which has high therapeutic value. The results of various studies are interpreted and consolidated. In recent years have been metal platinum group metal ion including Ru(III), Os(VIII), Ir(III), Rh(III), and Pd(II) widely used as catalyst due to their strong catalytic influence in various reactions. Palladium (II) chloride is the most important salt in the catalytic chemistry of palladium. Several authors have performed studies using Pd(II) because of the commercial importance of reactions catalyzed by Pd(II). The kinetics for the oxidation of ethylene by aqueous Pd (II) is an example[26-27]. In this study the effect of chloride ion on the reaction rate was studied in order to establish the active species of the catalyst. Generally the mechanism of catalysis depends on the nature of the substrate, the oxidant, and other experimental conditions [28-29]. In most of the catalytic studies for organic transformations, the nature of active form of Pd(II) remain obscure. The kinetic methods of analysis are highly sensitive, selective, simple, accurate, and less expensive. In recent years, several kinetic catalytic techniques have been reported for the detection of biomolecules[30-32]. The present study examines, in detail the kinetic and mechanistic aspects of the Pd(II) catalyzed oxidation of paracetamol by $KBrO_3$ in acidic media with the following objective.

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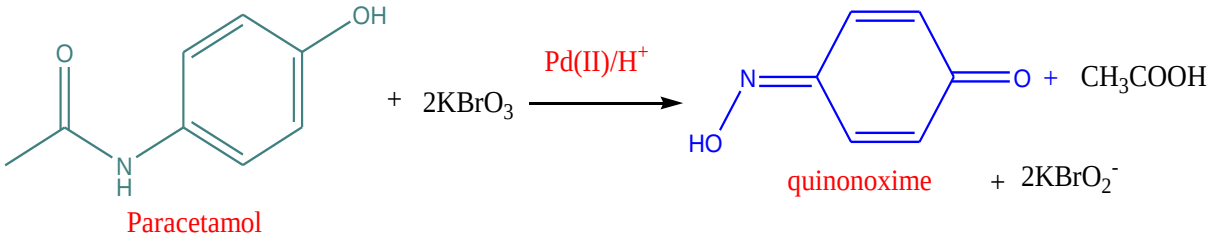
i. To ascertain the reactive species of the catalyst and the oxidant.
ii. To deduce the rate law consistent with the kinetic results.
iii. Identify the oxidation products.
iv. To estimate activation parameters.
v. To elucidate the plausible reaction mechanism based on the observed reacion rate law and stoichiometry.

2. MATERIAL AND PROCEDURE

2.1. 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. Palladium (II) 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.

2.2: Kinetic Procedure: A thermostated 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, Pd (II) 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-log plot of (-dc/dt) versus concentration of the reactants.

2.3. Determination of stoichiometry and product analysis: Different sets of the reaction mixture containing Paracetamol, Pd(II) 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 quinone oxime 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.

3. RESULT AND DISCUSSION

The kinetic results were collected at several initial concentrations of reactants (Table-1). 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). The first order kinetics with respect to $KBrO_3$ was also confermed by least square method (fig-2). Insignificant effect on the rate was observed on increasing the concentration of chloride ion, indicating zero order (Table-1). Kinetic result obtained on varying concentrations of [PA] indicates fractional positive order of substrate i.e. Paracetamol, which implies that rate of

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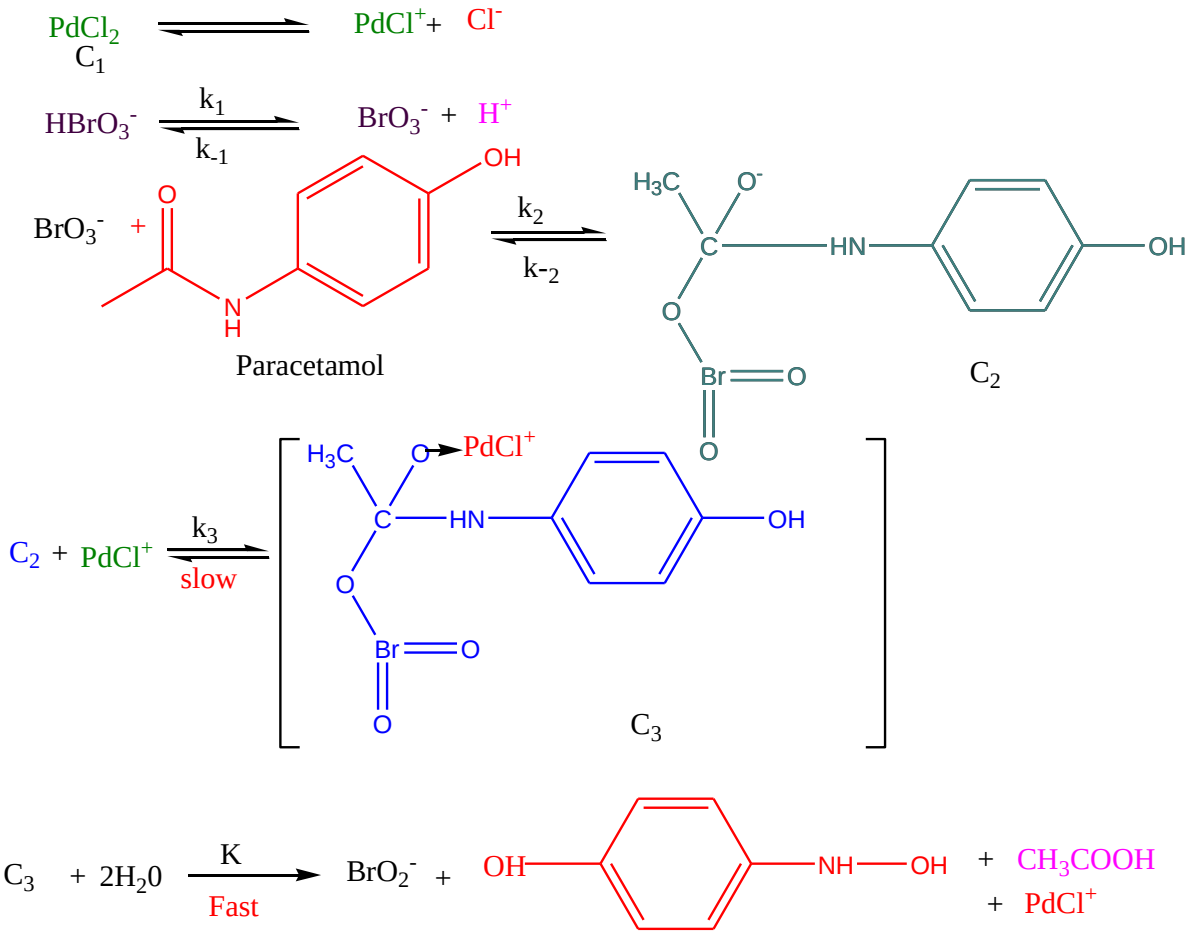
reaction increases when the concentration of [PA] is increased (Table-1) (fig-3).The rate of reaction increases as the concentration of palladium (II) chloride is increased, It was observed that values of (-dc/dt) were doubled when the concentration of palladium(II) was made two times, showing first order dependence on $PdCl_2$ indicating first order of catalyst i.e. Pd(II) chloride (Table-1) (fig-4). 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-5). 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-6). 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 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 [33]. 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[34]. The activation parameters evaluated for the catalyzed and uncatalyzed reaction explain the catalytic effect on the reaction. 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.

4. MECHANISM AND DERIVATION OF RATE LAW

In alkaline and acidic medium, potassium bromate is ionised:

$$KBrO_3 \longrightarrow K^+ + BrO_3^-$$

The BrO_3^- species has been reported to act as an oxidising agent in acidic as well as in alkaline medium. 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.



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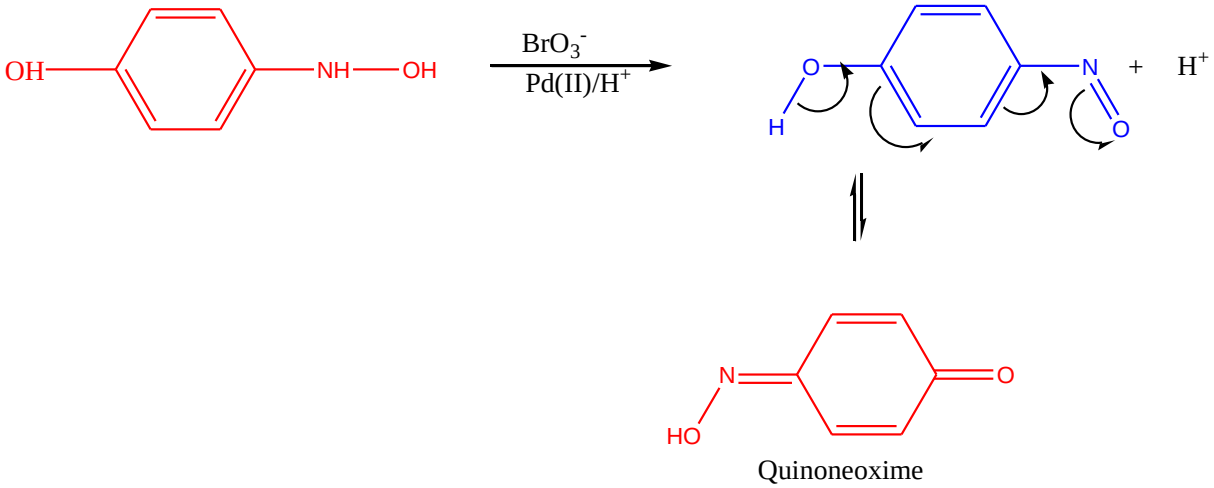

Quinoneoxime

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.

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

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

$$\text{R} = \frac{2\text{k}\,\text{K}_1\text{K}_2\,\text{K}_3\,[\text{Pd(II)}][\text{PA}][\text{HBrO}_3]}{[\text{H}]^+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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

$$[\text{HBrO}_3]_\text{T} = [\text{HBrO}_3] + [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

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

$$[\text{HBrO}_3] = \frac{[\text{HBrO}_3]_\text{T}}{[\text{H}]^+ + \text{K}_1 + \text{K}_1\text{K}_2[\text{PA}] + \text{K}_1\text{K}_2\,\text{K}_3\,[\text{Pd(II)}][\text{PA}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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

$$\text{R} = \frac{2\text{k}\,\text{K}_1\text{K}_2\,\text{K}_3\,[\text{Pd(II)}][\text{PA}][\text{HBrO}_3]_\text{T}}{[2\text{H}]^+ + \text{K}_1 + \text{K}_1\text{K}_2[\text{PA}] + \text{K}_1\text{K}_2\,\text{K}_3\,[\text{Pd(II)}][\text{PA}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

5. CONCLUSION

Oxidation of paracetamol by $KBrO_3$ does not proceed in the absence of catalyst, but it becomes facile in the presence of Pd(II) 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 Pd(II) acts as an efficient catalyst for the oxidation of paracetamol. In the present study A kinetic and Mechanistic investigation on Pd(II) catalyzed oxidation of paracetamol by potassium bromate ($KBrO_3$) in presence of $HClO_4$ acid medium : A kinetic model has been performed and following conclusions drawn:

- $[PdCl]^+$ is considered as the reactive species of Pd(II) in acidic medium.
- $HBrO_3$ 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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Table-1 : Effect of variation of oxidant, substrate, catalyst at 35^0C

Oxidant x 10^3M (Potassium bromate)	[Substrate]x 10^2M (Paracetamol)	Pd(II) x 10^5M	(-dc/dt)x10^7ML^{-1}s^{-1}
0.83	1.00	11.2	1.92
1.00	1.00	11.2	2.60
1.25	1.00	11.2	2.82
1.67	1.00	11.2	3.81
2.50	1.00	11.2	5.32

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5.00	1.00	11.2	10.60
1.00	0.40	11.2	1.32
1.00	0.50	11.2	1.60
1.00	0.66	11.2	2.10
1.00	1.00	11.2	2.60
1.00	2.00	11.2	4.25
1.00	4.00	11.2	6.20
1.00	1.00	5.60	1.33
1.00	1.00	11.2	2.60
1.00	1.00	16.8	4.60
1.00	1.00	22.4	5.18
1.00	1.00	33.6	8.35
1.00	1.00	44.8	10.21

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 Perchloric acid, Potassium chloride, Mercuric acetate at 35^0C

$HClO_4$ x 10^3 M	KCl x 10^3 M	$Hg(OAc)_2$ x 10^3 M	(-dc/dt)x10^7 $ML^{-1}s^{-1}$
0.83	1.00	1.25	3.12
1.00	1.00	1.25	2.60
1.25	1.00	1.25	2.41
1.67	1.00	1.25	2.00
2.50	1.00	1.25	1.22
5.00	1.00	1.25	0.82
1.00	0.83	1.25	2.23
1.00	1.00	1.25	2.60
1.00	1.25	1.25	2.00
1.00	1.67	1.25	2.81
1.00	2.50	1.25	2.52
1.00	5.00	1.00	2.42
1.00	1.00	0.83	2.21
1.00	1.00	1.00	2.60
1.00	1.00	1.25	2.60
1.00	1.00	1.67	3.00
1.00	1.00	2.50	2.42
1.00	1.00	5.00	2.51

Solution Condition: [Oxidant ($KBrO_3$)] = 1.00 X 10^{-3} M, [Paracetamol (PA)] = 1.00 X 10^{-2} M,
[Pd (II) Chloride] = 11.2 X 10^{-5} M

Table-3: Activation parameters for Pd(II) chloride catalyzed oxidation of Paracetamol by $KBrO_3$ at 35^0C

Parameter	Temperature(T^0C)	Paracetamol(-dc/dt) x 10^7
k_1 x $10^4 s^{-1}$	30^0	1.55
k_1 x $10^4 s^{-1}$	35^0	2.60
k_1 x $10^4 s^{-1}$	40^0	3.18
k_1 x $10^4 s^{-1}$	45^0	5.18
log A	...	10.80
Ea* (k J mol^{-1})	35^0	60.98
Δ G* (k J mol^{-1})	35^0	74.63
Δ H * (k J mol^{-1})	35^0	71.45
Δ S* ($JK^{-1}mol^{-1}$)	35^0	-10.03

Solution Condition: [Pd(II)] = 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

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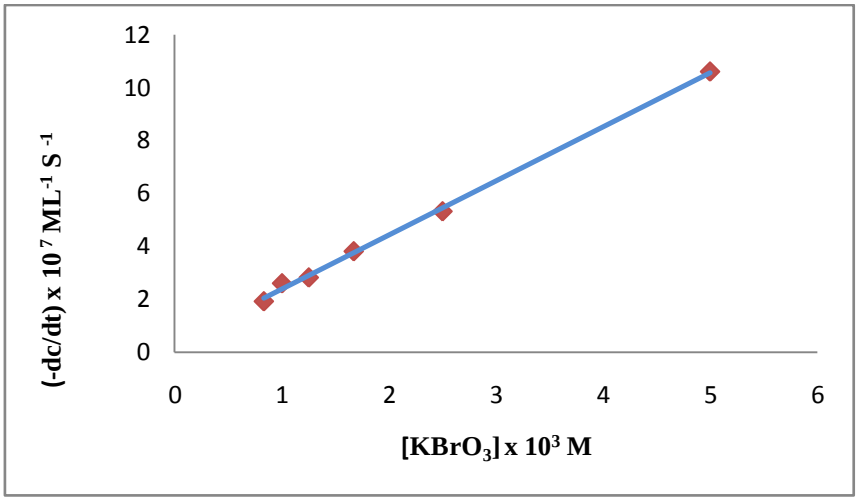

Figure1. Plot between rate of reaction (-dc/dt) vs [$KBrO_3$] for the oxidation of paracetamol at 35^{0}C. [$HClO_4$] = 1.00 x 10 ^{3}M, [KCl] = 1.00 x 10 ^{3} M, [$Hg(OAc)_2$] = 1.25 x 10 ^{3} M, Paracetamol [PAM] = 1.00 x 10^2 M, Pd(II) Chloride = 11.2 x 10^5 M

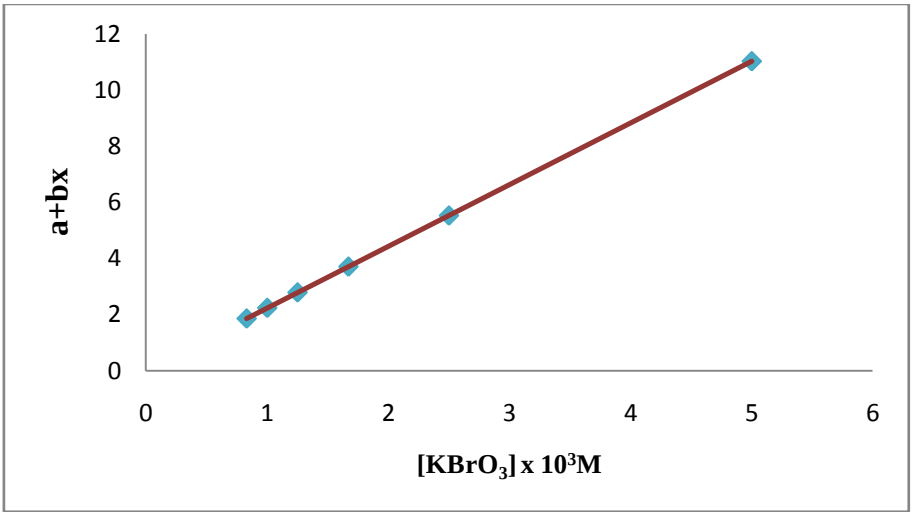

Figure 2. Plot between rate of reaction (a+bx) vs [$KBrO_3$] for the oxidation of paracetamol at 35^{0}C. [$HClO_4$] = 1.00 X 10 ^{3} M, [KCl] = 1.00 X 10 ^{3} M, [$Hg(OAc)_2$] = 1.25 X 10 ^{3}M, Paracetamol [PA] = 1.00 x 10 ^{2} M, Pd(II) = 11.2 x 10 ^{5} M

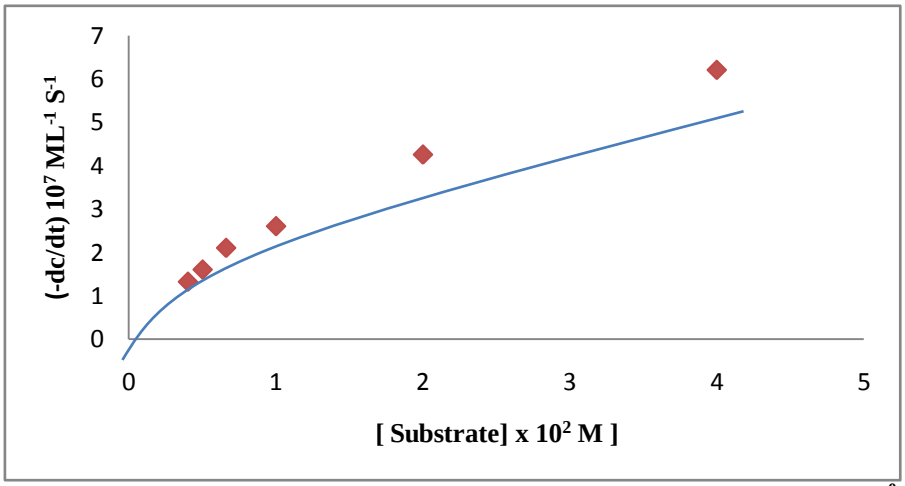

Figure3. Plot between rate of reaction (-dc/dt) vs [PA] on the reaction rate at 35^{0}C. [$HClO_4$] = 1.00 X 10 ^{3}M, [KCl] = 1.00 X 10 ^{3} M, [$Hg(OAc)_2$] = 1.25 X 10 ^{3} M, [$KBrO_3$)] = 1.00 X 10^3 M, [Pd(II)] = 11.2 X 10^5 M

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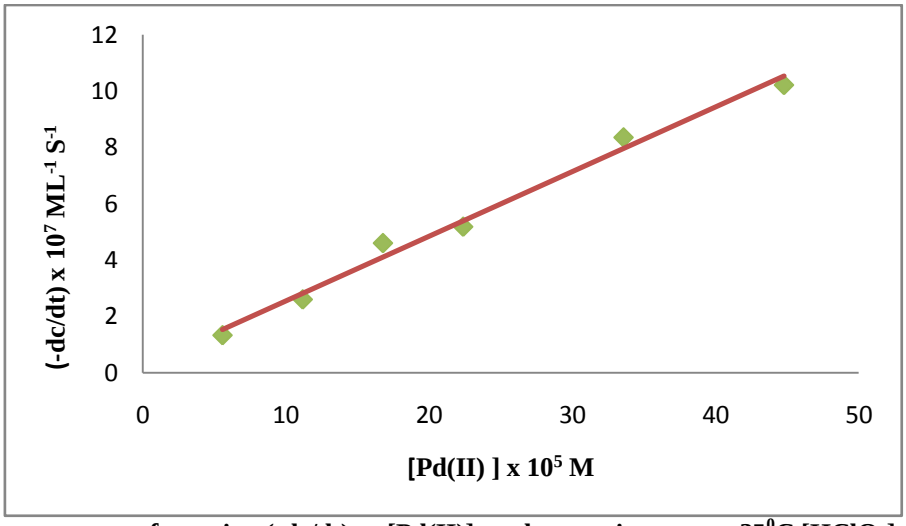

Figure4. Plot between rate of reaction (-dc/dt) vs [Pd(II)] on the reaction rate at 35^0C.[$HClO_4$] = 1.00 X 10^{-3}M, [KCl] = 1.00 X 10^{-3} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3} M , [$KBrO_3$] = 1.00 X 10^{-3} M , [Substrate(PA)] = 1.00 X 10^{-2} M

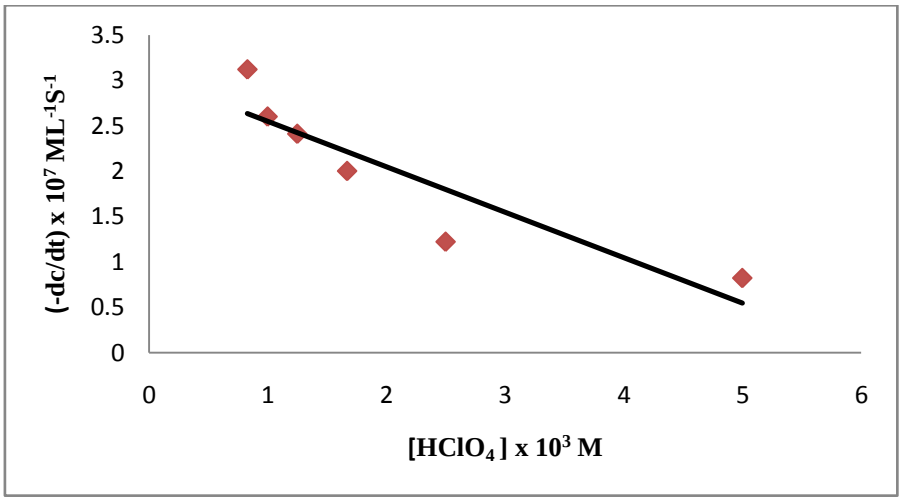

Figure5. Plot between rate of reaction (-dc/dt) vs [$HClO_4$] for the oxidation of paracetamol at 35^0C. [Pd (II) Chloride] = 11.2 X 10^{-5} M, [KCl] = 1.00 X 10^{-3} M, [Hg $(OAc)_2$] = 1.25 X 10^{-3} M, [Oxidant ($KBrO_3$)] = 1.00 X 10^{-3} M, [Substrate(PA)] = 1.00 X 10^{-2} M

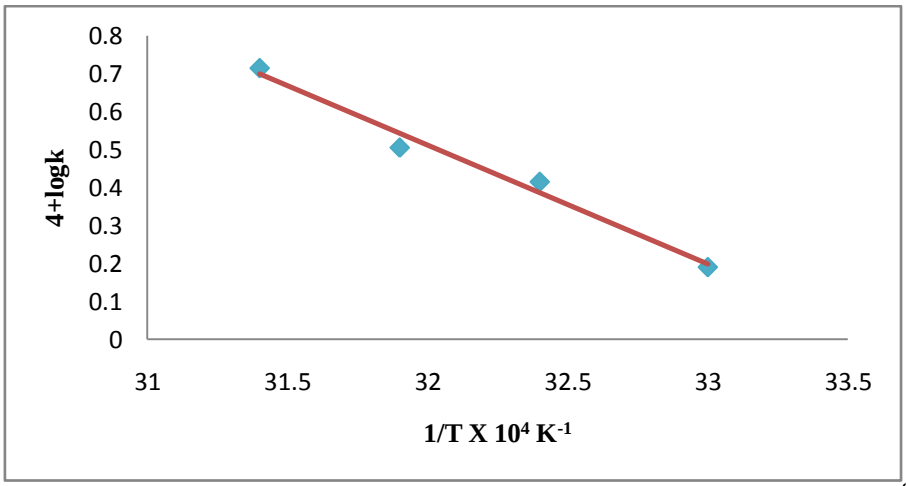

Figure6. Arrhenius plot of the oxidation of paracetamol on the reaction rate at 35^0C [Pd(II) Chloride] = 11.2 x 10^{-5} M, [KCl] = 1.00 x 10^{-3} M, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M [Oxidant ($KBrO_3$)] = 1.00 x 10^{-3} M, [Substrate(PA)] = 1.00 X 10^{-2} M, [$HClO_4$] = 1.00 X 10^{-3} M

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