Comparative Kinetic Investigation of Oxidation of 3-Methylindole by Peroxomonosulphate and Peroxodisulpahte Using Ethanol Medium

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ABSTRACT

The kinetic studies of oxidation of 3-methylindole (3-MI) by Peroxomonsulphate (PMS) and Peroxoxdisulphate (PDS) have been carried out in ethanol medium. A total second order, first order first order each with respect to [3-MI] and [Oxidant] has been observed. The reaction was unaffected by increase of [H^+]. Increase of percentage of ethanol decreases the rate. Variation of ionic strength had no influence on the rate. Activation and thermodynamic parameters have been calculated from kinetic values. A suitable mechanism scheme based on these observations is proposed. The reactivity of Peroxodisulphate toward 3-methhylindole was found to be lower than that with Peroxomonsulpahte.

Keywords: Kinetics, Mechanism, Oxidation, 3-methylindole (3-MI), Peroxomonosulphate (PMS), Peroxodisulphate (PDS)

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INTRODUCTION

Oxidation of indoles has received much attention due to the involvement of their resulting products in significant biological processes [1]. The oxidation of 2,3-dimethylindole by peroxodisulphate anions (PDS) to give 3-methylindole-3-carbaldehyde have been already reported in the literature [2]. The oxidation of indole into isatin using PMS [3] and oxidation of indole-3-acetic acid (IAA) into 2-hydroxy indole-3-methanol [4] has been reported in the literature. In view of this, the present work is significant as it involves the reaction of a peroxo linkage containing oxidant namely PMS and PDS with 3-MI. The lack of kinetic and mechanistic investigation on the oxidation of 3-MI by this oxidants investigated us to carry out this work and is presented as a first report in this study.

EXPERIMENTAL

Materials

3-Methylindole and Peroxomonosulphate (PMS) under the other name Oxone[R] from Sigma alrdich and Peroxodisulphate(PDS) under the other name potassium persulphate from Qualigens of highest purity grade was used as such. Solutions of this salt were assayed iodometrically and by cerimetry [5]. Other chemicals and reagents such as sulphuric acid, ethanol, sodium sulphate, and KI used were of analytical grade from Qualigens. All reagents and solutions were prepared using this doubly distilled water. All the reactions were carried out in a thermostat and the temperature was controlled to $\pm 0.1^0$C.Various kinds of experiment were carried out varying the concentration of the substrate [3-MI] by keeping constant concentrations of Oxidants, Solvent, [H+], μ and vice-versa.

Kinetic Measurements

PMS

Kinetic studies were carried out in 50% (v/v) aqueous ethanol medium under pseudo first-order conditions with a large excess of 3-MI over PMS in the temperature range of 283–293 K. The reaction was followed by estimating the unreacted PMS as a function of time by using the iodometric method. The liberated iodine was titrated against standard sodium thiosulphate solution by using starch as indicator. From the titre values, plots of log [PMS] vs time were made and from the slope of such plots, the pseudofirst order rate constants, k (s^{-1}) were obtained. It was checked that the results were reproducible within ±5% error.

PDS

Kinetic studies were carried out in 50% (v/v) aqueous ethanol medium under pseudo first-order conditions with a large excess of 3-MI over PDS in the temperature range of 303-323 K. The reaction was followed by estimating the unreacted PDS as a function of time by using the iodometric method. The liberated iodine was titrated against standard sodium thiosulphate solution by using starch as indicator.

$$S_2O_8^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \rightarrow 2SO_4^{2-}{}_{(aq)} + I_{2(aq)}$$
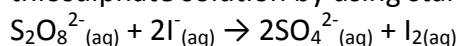
From the titre values, plots of log [PDS] vs time were made and from the slope of such plots, the pseudofirst order rate constants, k (s^{-1}) were obtained. It was checked that the results were reproducible within ±5% error.

RESULTS AND DISCUSSION

Factors influencing the rate of oxidation of [3-MI] by oxidants such as effects of (i) [3-MI], (ii) [Oxidant], (iii) ionic strength (μ), (iv) [H$^+$], and (v) dielectric constant have been studied. Rate and activation parameters were evaluated.

Effect of [3-MI]

[3-MI] vs PMS

Kinetic runs were carried out with various initial concentrations of [3-MI] at 293K by fixing constant [PMS], [H$^+$], μ, and percentage of ethanol, which yielded [3-MI] dependent rate constants. The values of pseudofirst-order rate constants k'(s^{-1}) thus obtained were found to increase with [3-MI] (Table 1 & Fig. 1) over a range of [3-MI] used ($2.0 \times 10^{-2} - 4.0 \times 10^{-2}$ mol dm^{-3}). This shows that the reaction obeys first order with respect to [3-MI]. This was confirmed by the linear plots of k'(s^{-1}) vs [3-MI] passing through origin (r = 0.999) (Fig. 2). Such a kinetic behaviour indicates the absence of any self-decomposition of PMS [6]. The experiments were carried out at various temperatures 288 K and 283 K and the rate constant values of K' and K2 were tabulated (Table 2). The value of k_2 (mol^{-1} dm^3 s^{-1}) was evaluated from the slope of k'(s^{-1}) vs [3-MI] plots. The k_2 (mol^{-1} dm^3 s^{-1}) values were calculated from the values of k' using the formula k' (s^{-1})/[3-MI].

Table 1: Variation of [3-MI] @ 293 K against [PMS]

Time (min)	[3-MI] x 10^2 mol dm^{-3}				
	4 + Log [PMS]				
	2.0	2.5	3.0	3.5	4.0
1	1.1808	1.1808	1.1808	1.1760	1.1760
4	1.1303	1.1947	1.0851	1.0479	1.0280
9	1.0669	1.0413	1.0000	0.9378	0.8846
14	0.9852	0.9461	0.8939	0.8129	0.7403
19	0.8846	0.8346	0.7659	0.6842	0.5835
24	0.8346	0.7132	0.6690	0.5642	0.4522
29	0.7533	0.669	0.5228	0.3979	0.3010
k' x 10^4, (s^{-1})	5.8899	7.3204	8.7026	10.1595	11.6398
k_2 x10^2(mol^{-1}dm^{3}s$^{-1)}$	2.9449	2.9281	2.9008	2.9027	2.9099

[PMS] = 2 x 10^{-3} mol dm^{-3}; [H+] = 0.02 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Ethanol = 50 % (v/v);

Table 2: Calculation of k' and k_2 for 3-MI – PMS system

[3-MI]x10^2, mol dm^{-3}	283 K		288 K		293 K	
	k' x10^4, s^{-1}	k_2x10^{2}mol^{-1}dm^3 s^{-1}	k'x10^4, s^{-1}	k_2x10^{2}mol^{-1}dm^3 s^{-1}	k'x10^4, s^{-1}	k_2x10^{2}mol^{-1}dm^3 s^{-1}
2.0	5.8899	2.9449	5.3120	2.6560	4.5229	2.2614
2.5	7.3204	2.9281	6.5008	2.6003	5.5183	2.2073
3.0	8.7026	2.9008	7.6851	2.5617	6.5323	2.1774
3.5	10.1595	2.9027	9.2574	2.6449	7.3803	2.1086
4.0	11.6398	2.9099	10.2839	2.5708	8.8484	2.2121
	Overall k_2 @283 K	2.9173	Overall k_2 @288 K	2.6067	Overall k_2 @293 K	2.1934

[PMS] = 2 x 10 mol dm^{-3}; [H+] = 0.02 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Ethanol = 50 % (v/v);

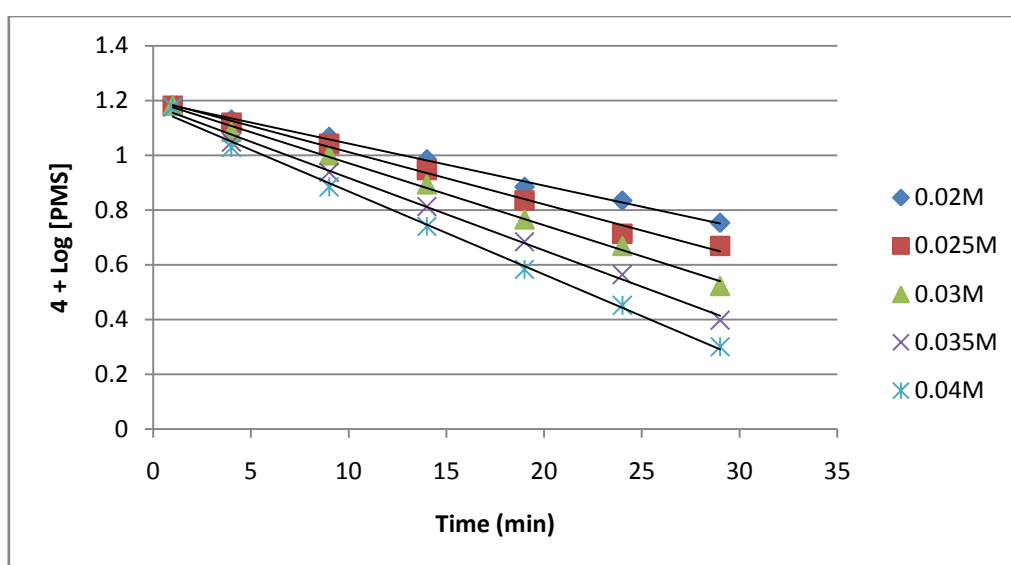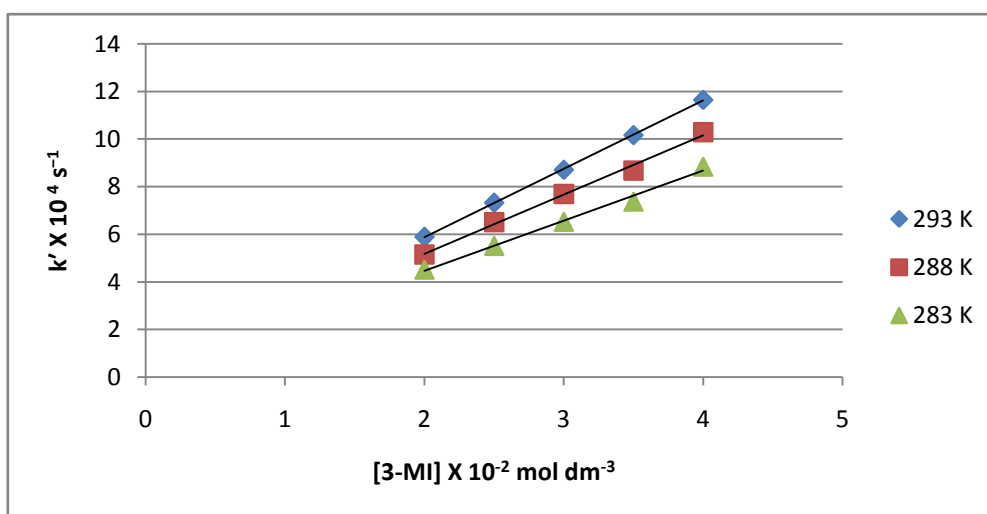**Figure 1: Variation of [3-MI] @ 293 K against [PMS]**

Figure 2; Evaluation of k_2 for 3-MI – PMS system

[3-MI] Vs [PDS]

Kinetic runs were carried out with various initial concentrations of [3-MI] at 303K by fixing constant [PDS], [H$^+$], μ, and percentage of ethanol, which yielded [3-MI] dependent rate constants. The values of pseudofirst-order rate constants k'(s^{-1}) thus obtained were found to increase with [3-MI] (Table 3& Fig. 3) over a range of [3-MI] used (2.0 × 10^{-2} – 4.0 × 10^{-2}mol dm^{-3}). This shows that the reaction obeys first order with respect to [3-MI]. This was confirmed by the linear plots of k'(s^{-1}) vs [3-MI] passing through origin (r = 0.999) (Fig. 4). Such a kinetic behaviour indicates the absence of any self-decomposition of oxidant [6]. The experiments were carried out at various temperatures 313 K and 323 K and the rate constant values of k' and k_2 were tabulated (Table 4). The value of k_2 (mol^{-1} dm^3 s^{-1}) was evaluated from the slope of k'(s^{-1}) vs [3-MI] plots. The k_2 (mol^{-1} dm^3 s^{-1}) values were calculated from the values of k' using the formula k' (s^{-1})/[3-MI].

Table 3: Variation of [3-MI] @ 303 K against [PDS]

[3-MI] x 10^{-2}mol dm^{-3}									
2.0		2.5		3.0		3.5		4.0	
Tim (min)	4+log [PDS]	Tim(min)	4+log [PDS]	Tim (min)	4+log [PDS]	Tim (min)	4+log [PDS]	Tim (min)	4+log [PDS]
1	1.7841	1	1.7841	1	1.7841	1	1.7829	1	1.7817
10	1.7805	10	1.7757	10	1.7708	10	1.7403	10	1.6857
20	1.6989	20	1.6812	20	1.6674	20	1.6384	20	1.5740
30	1.6266	30	1.5965	30	1.5603	30	1.5378	30	1.4286
60	1.4795	60	1.4259	60	1.3921	60	1.1949	60	1.1461
90	1.3256	90	1.2430	90	1.1249	90	0.8346	90	0.8346
180	0.8450	180	0.6020	180	0.3679	180	0.1760	150	0.1760
k'x10^4,s^{-1}	2.0472		2.5595		3.0717		3.5797		4.1048
k_2x10^{2}mol dm^{-3}	1.0236		1.0238		1.0239		1.0235		1.0262

[PDS] = 2 x 10^{-2}mol dm^{-3}; [H$^+$] = 0.02 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Ethanol = 50% (v/v);
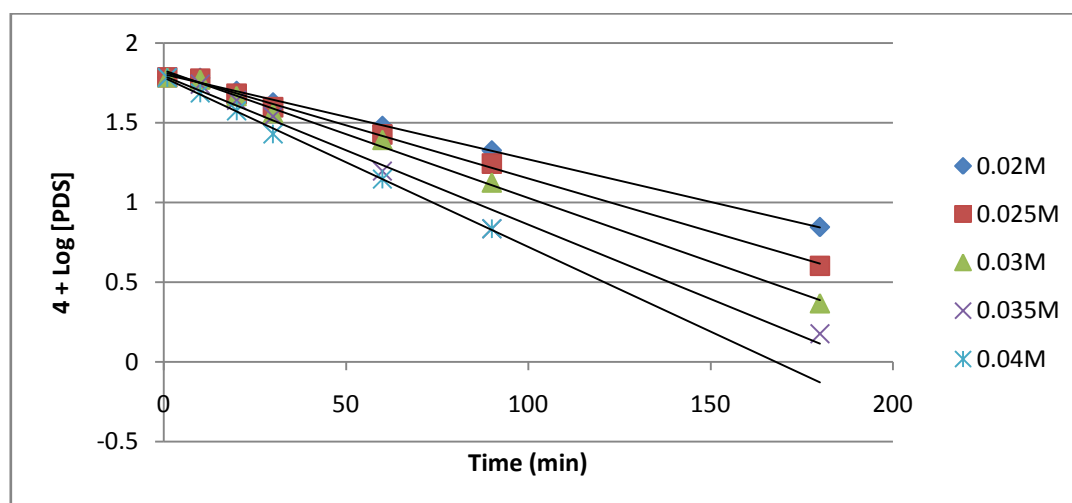
Figure 3: Variation of [3-MI] @ 303 K against PDS

Table 4: Calculation of k' and k_2 for 3-MI – PDS system

[3-MI]x10⁻², mol dm⁻³	303 K		313 K		323 K	
	k' x10⁴,s⁻¹	k_2x10²mol⁻¹dm³ s⁻¹	k'x10⁴, s⁻¹	k_2x10²mol⁻¹dm³ s⁻¹	k'x10⁴, s⁻¹	k_2x10²mol⁻¹dm³ s⁻¹
2.0	2.0472	1.0236	2.9805	1.4902	4.2013	2.1006
2.5	2.5595	1.0238	3.7260	1.4904	5.2547	2.1018
3.0	3.0717	1.0239	4.4726	1.4908	6.3092	2.1030
3.5	3.5822	1.0227	5.2173	1.4906	7.3525	2.1007
4.0	4.1048	1.0262	5.9636	1.4909	8.4022	2.1005
	Overall k_2 @303 K	1.0240	Overall k_2 @313 K	1.4906	Overall k_2 @323 K	2.1013

[PDS] = 2 x 10⁻²mol dm⁻³; [H+] = 0.02 mol dm⁻³; μ = 0.3 mol dm⁻³; Ethanol = 50 % (v/v);

Figure 4: Evaluation of k_2 for 3-MI – PDS system
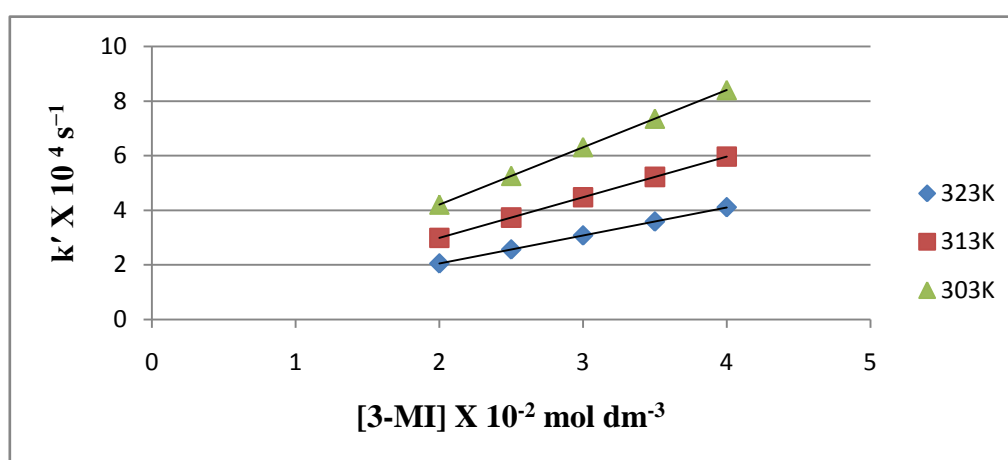
Effect of Oxidants

It is observed that the reaction rate was unaffected as evident from the constant slopes of log [Oxidants] Vs time plots for various [Oxidants] at fixed [3-MI], [H⁺], μ, and percentage of ethanol (Table 5). This observation confirms the first-order dependence of rate on [Oxidants].

Table 5: Effect of Oxidants

[PMS] (10⁻³mol dm⁻³)[a]	k' (10⁴ s⁻¹)		[PDS] (10⁻²mol dm⁻³)[b]	k' (10⁴ s⁻¹)
1.0	8.6991		1.0	3.0766
1.5	8.6745		1.5	3.0709
2.0	8.7026		2.0	3.0717
2.5	8.6960		2.5	3.07522
3.0	8.7057		3.0	3.07194

[a][3-MI] = 3 x 10⁻²mol dm⁻³; μ = 0.3 mol dm⁻³ ; [H+] = 0.02 mol dm⁻³; Ethanol = 50 % (v/v); Temp = 293 K
[b][3-MI] = 3 x 10⁻²mol dm⁻³; μ = 0.3 mol dm⁻³ ; [H+] = 0.02 mol dm⁻³; Ethanol = 50 % (v/v);

Effect of μ

The influence of ionic strength (μ) maintained by the addition of sodium sulphate on the reaction rate was found to be negligible for both PMS and PDS system. This shows that the reaction occurs between a neutral species namely the 3-methylindole molecule and the negative ion (for PMS mononegative ion HSO_5^- and for PDS dinegative ion $S_2O_8^{2-}$), the active species of the oxidants.

Effect of [H⁺]

The reaction rates measured at constant [3-MI], [Oxidants], μ, and percentage of ethanol but with various [H⁺] (5×10^{-3}–3×10^{-2} mol dm^{-3}) were found to be the same. Such a kinetic behaviour indicates the nonexistence of any protonation equilibrium with respect to both Oxidants and 3-methyindole under the present experimental conditions employed.

Effect of Dielectric Constant

So as to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of 3-MI by oxidants (PMS and PDS) was studied in aqueous ethanol mixtures of various compositions. The data clearly reveals that the rate increases with decrease in the percentage of ethanol, i.e. with increasing dielectric constant or polarity of the medium, and lead to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants [7], a neutral molecule (3-MI), and oxidants a mononegative ion (HSO_5^-) for PMS and a dinegative ion ($S_2O_8^{2-}$) for PDS suggesting a polar (ionic) mechanism.

Stochiometry

Solutions of 3-MI containing an excess of Oxidants (PMS and PDS) were kept overnight at room temperature. Titrimetric estimation of the concentration of Oxidant consumed and assuming that all the 3-MI taken had reacted, the stoichiometry of 3-MI: Oxidant was found to be 1:2.

Test for Free Radical Intermediates

The observed total second-order dependence of rate, beside first-order dependence each on both [3-MI] and [Oxidant], shows that the reaction involves a nonradical pathway. Moreover no polymer formation was observed when a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

Rate Law

In accordance with the above observations, the rate law for the disappearance of Oxidant is given as follows:

$$-d[\text{Oxidant}]/dt = k_2\,[\text{Oxidant}][\text{3-MI}]$$

$$\text{rate} / [\text{Oxidant}] = k'(s^{-1}) = k_2[3\text{-MI}]$$
$$(i : e :) \, k^{-1} = k_2 \, [3\text{-MI}]$$

where k' = pseudo-first order rate constant and k_2 = second order rate constant.

Product Analysis

A reaction mixture containing slight excess of Oxidants and 3-MI dissolved in ethanol was kept aside at room temperature for a day, so that the substrate was completely converted into product. The mixture was extracted with ether. A resinuous mass was obtained in the ether layer and it could not be identified. The aqueous layer was treated with acetone and then with methanol. The final product obtained from the both oxidants were characterised by using IR spectra. The above product was identified as 3-methyloxoindole from IR frequencies at 1714 cm^{-1} for C=O (str), at 3434cm^{-1} for N-H (str).

Mechanism

PMS – 3-MI

Based on the foregoing observations such as first-order dependence of rate each on [3-MI], [PMS], zero-order dependence on [H^{+}], negligible effect of [μ], and the stoichiometry, the following mechanism is suggested (Fig.5):

### Figure 5: Mechanism for 3-MI – PMS System
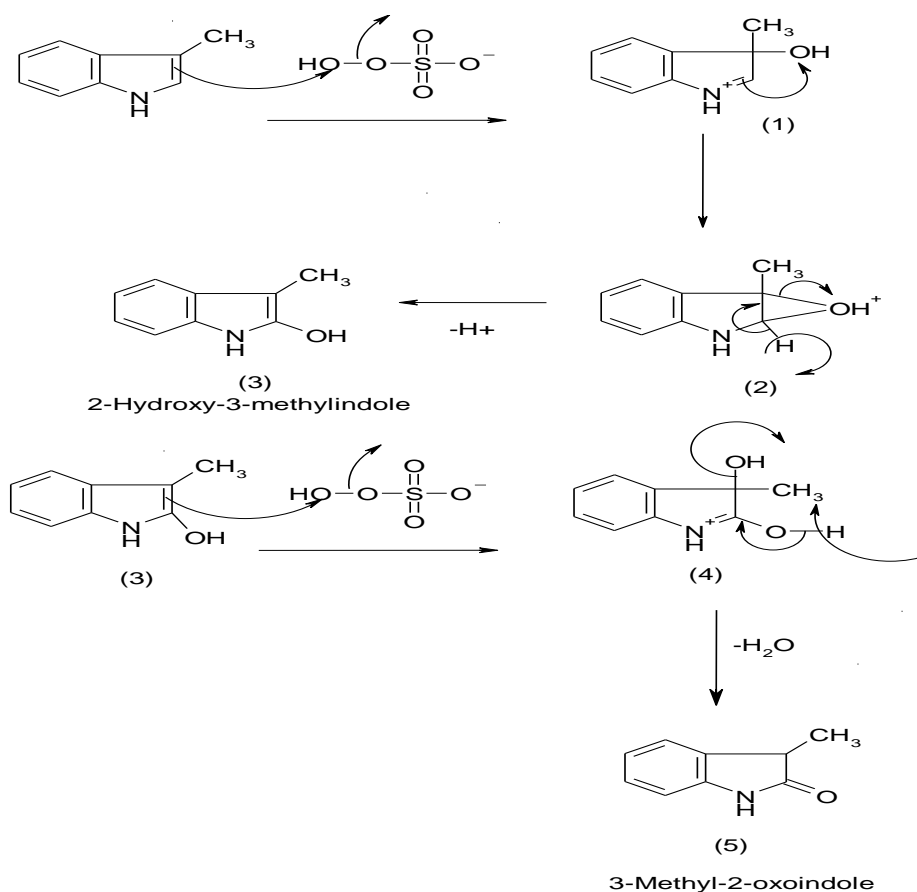
PMS exists as HSO_5^- ion in solution and the ion is weak nucelophile. It is suggested that the reaction proceeds through an electrophilic attack of the oxidant (PMS) [8] at the nucleophilic site C3 of 3-MI by a mechanism involving displacement of sulphate ion to 3-hydroxy-3-methylindole (1) as the rate determining step. Compound (1) undergoes intramolecular rearrangement [9] to give 2-hydroxy-3-methylindole (3) through a cyclic intermediate (2). The second attack of PMS ion on compound (3) gives 2,3-dihydroxy-3-methylindole (4) which finally loses H_2O to give 3-methyl-2-oxoindole (5) as the product.

PDS – 3-MI

Based on the foregoing observations such as first-order dependence of rate each on [3-MI], [PDS], zero-order dependence on [H^+], negligible effect of [μ], and the stoichiometry, the following mechanism is suggested (Fig.6):

Our result suggest that the reaction proceeds through an electrophilic attack of the oxidant (PDS) exists as $S_2O_8^{-2}$ ion in solution at the nucleophilic site C3 of 3-MI by a mechanism involving displacement of sulphate ion to form compound (1) as the rate determining step. Compound (1) undergoes intramolecular rearrangement [9] to give 2-hydroxy-3-methylindole (4) through a cyclic intermediate (2). The second attack of PDS ion on compound (4) gives Compound (5) which finally loses HSO_4^- to give 3-methyl-2-oxoindole as the product.

Fig-6 Mechanism for 3-MI – PDS System
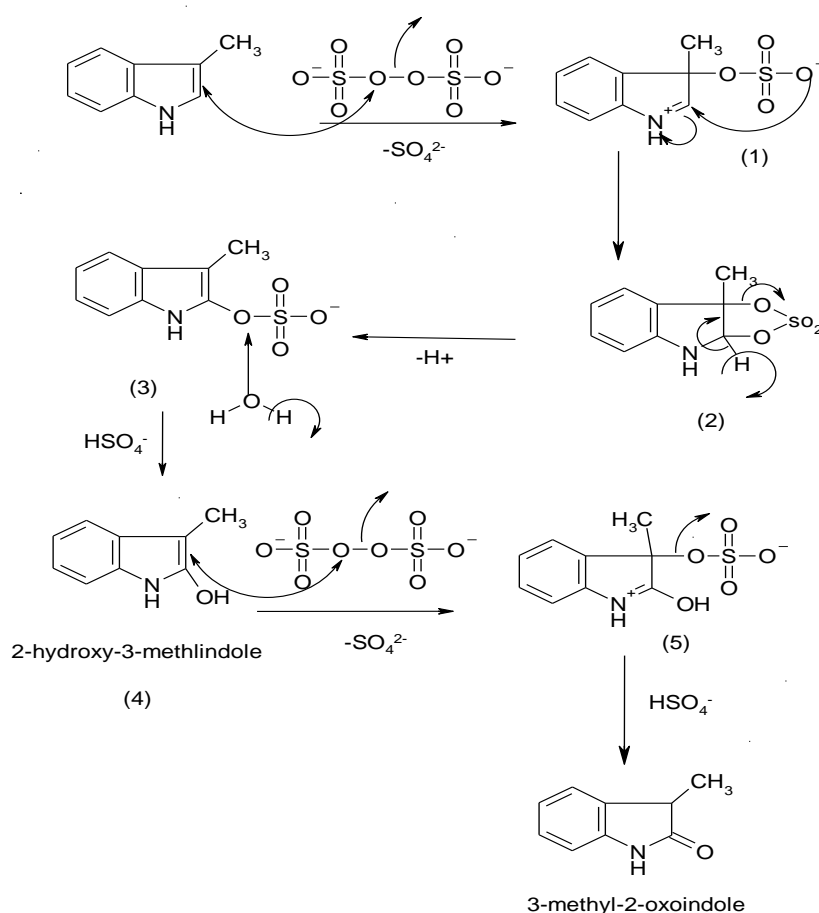
Rate and Activation Parameters

The effect of temperature on k' (s^{-1}) was studied in the range of 283–293 K for PMS and in the range of 303 – 023 K for PDS and the results are shown in Table 2and Table 4 respectively. The Arrhenius plot of log k_2 vs $1/T$ was linear. From the above plot, the values of energy of activation (E_a) was calculated (Fig.7& Fig. 8). The value of $\Delta S^{\#}$ was computed from Eyring equation. The large negative value of entropy of activation ($\Delta S^{\#}$) obtained is attributed to the severe restriction of solvent molecules around the transition state [10]. All the thermodynamic parameters were tabulated in Table 6

Table 6: Thermodynamic Parameters

Thermodynamic parameters of Oxidation of 3-MI		PMS	PDS
Energy of Activation (Ea)	kJmol^{-1}	20.088	29.302
Enthalpy ($\Delta H^{\#}$)	kJ mol^{-1}	17.652	26.782
Entropy ($\Delta S^{\#}$)	J K^{-1} mol^{-1}	-271.05	-278.57
Free Energy ($\Delta G^{\#}$)	kJ mol^{-1}	97.070	111.19

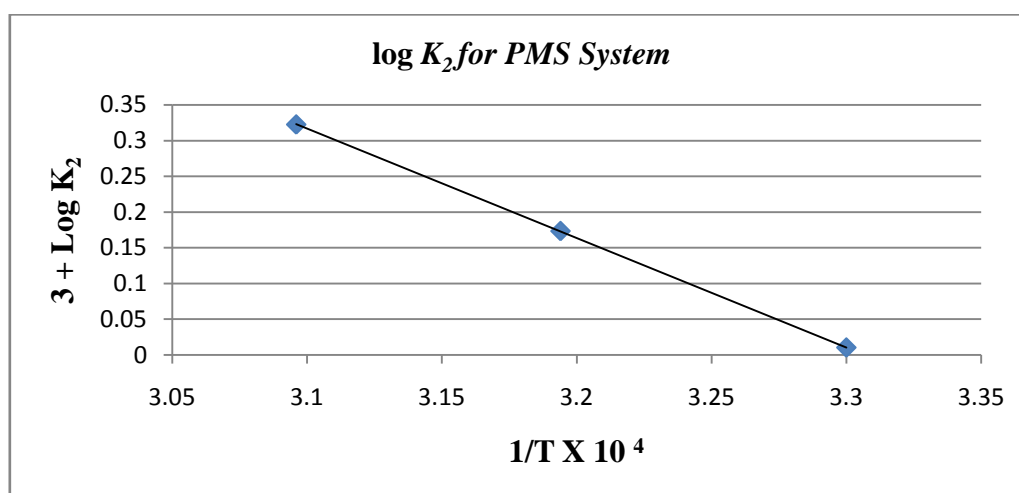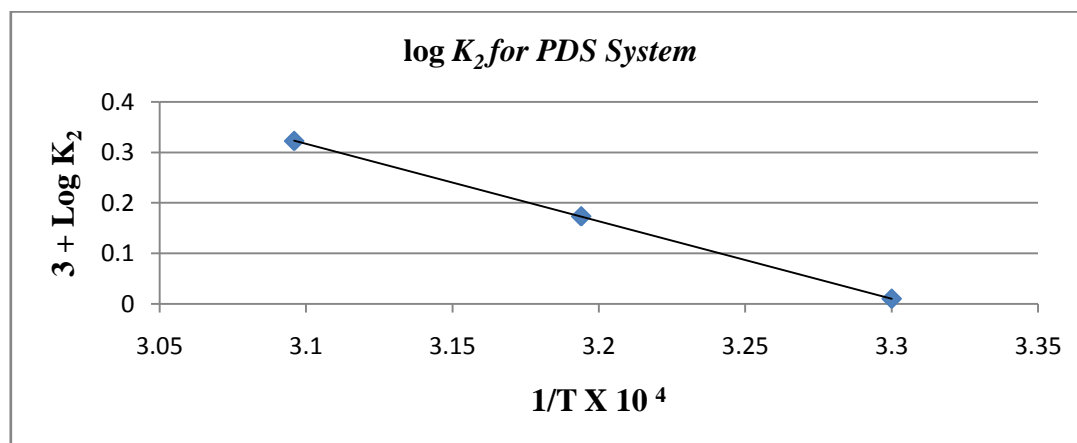**Figure 7: Evaluation of Ea for PMS System**

Figure 8: Evaluation of Ea for PDS System

CONCLUSION

On comparing the results, it is clear that peroxodisulphate (PDS) reacts slowly even though the redox potential of PDS (E^0 = 2.01 V) [11] is higher than that of Peroxomonsulphate (PMS) (E^0 = 1.82 V) [12]. This could possibly be due to steric hindrance caused by the presence of two SO_3 groups on both sides of the O-O linkage [13] in $S_2O_8^{2-}$.

ACKNOWLEDGEMENT

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