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Kinetics Of 3-Methylindole Oxidation : A Comparative Study Of Potassium Bromate And Peroxomonosuphate

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Abstract
The kinetic studies of oxidation of 3-Methylindole (3-MI) by peroxomonsulphate (PMS) and potassium bromate ($KBrO_3$) have been carried out in ethanol medium. A total second order, first order each with respect to [3-MI] and [Oxidant] has been observed. The rate of the reaction was not affected by added [H^+]. Variation of ionic strength (μ) had no influence on the rate. Increase of percentage of solvents decreased the rate. Absence of any polymerization indicated a no radical pathway. Activation and thermodynamic parameters have been computed. A suitable kinetic mechanism based on these observations is proposed. The product was confirmed from the IR and NMR spectral analysis. The reactivity of Potassium bromate toward 3-methylindole was found to be lower than that with Peroxomonsulpahte.
Keywords: *Kinetics, Mechanism, Oxidation, 3-Methylindole, Potassium bromate, Peroxomonsulphate, Ethanol, Comparative study.*

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. These compounds have also attracted considerable attention in pharmacology, mainly because of their ability to develop antifungal and antibacterial agents. They also act as candidates for direct oxidation/reduction of biomolecules, and other biological activities [4-5]. Because of the very potent and diverse biological activity exhibited by various indole derivatives, this heterocyclic system has attracted considerable attention in chemistry, biology and medicine[6-7]. Among the various substituted indoles, Skatole or 3-Methylindole [3-MI] is taken for investigation. 3-Methylindole is also known as Skatole, a microbial fermentation product of tryptophan in the rumen cattle[8,9].The oxidation of 3-Methylindole into 3-Methyloxindole was carried out by peracetic acid [10].The oxidation of skatole by brominating agent gave bromo substituted 3-Methyloxindole [11]. Oxidation of 3-Methylindole to indole-3-carboxaldehyde via indole-3-methanol was carried out using an enzyme called Pseudomonas [12]. Oxidation of Indole-3-acetic acid (IAA) by PMS into 2-hydroxy indole-3-Methanol in aqueous acetonitrile medium was carried out by Chandramohan et al [13]. Muniyappan et al., investigated the kinetic study of oxidation of indole by PMS using various solvent medium like ethanol [14].acetonitrile [15] and acetone [16]. Periyasami et al., investigated the oxidation of 3-Methylindole by potassium bromate in acetic acid medium[17].The comparative kinetic and mechanistic investigation on the oxidation of 3-Methylindole by Peroxomonsulphate and potassium bromated in ethanol solvent investigated us to carry out this work and is presented as a first report in this study.

EXPERIMENTAL

Materials and methods

3-Methylindole or Skatole (Sigma Alrdich) of highest purity grade was used as such. The sample potassium bromate (E. Merck. AR. Grade) was used as received and it has an assay value of at least 99.9%. Other chemicals and reagents such as sulphuric acid, Sodium perchlorate, potassium iodide, starch, sodiumthiosulphate, Ethanol, Mercuric acetate (E. Merck) and used were of analytical grade with 99.9% purity.

An aqueous solution of potassium bromate (Merck), $NaClO_4$ were prepared by dissolving the weighted samples in double distilled water. Sodium perchlorate was used to maintain the ionic strength ofthe medium.Water distilled from Kilburn Manesty still was again distilled over alkaline permanganate in an all-glass Pyrex vessel. 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 283–298 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 pseudo first order rate constants, k (s^{-1}) were obtained. It was checked that the results were reproducible within ±5% error.

$KBrO_3$

The requisite volume of all reagents, including substrate, was thermostated at 283-298 K to attain equilibrium. A measured volume of $KBrO_3$ solution, maintained separately at the same temperature, was poured rapidly into the reaction vessel and the progress of the reaction was followed by assaying, aliquots of the reaction mixture of $KBrO_3$ iodometrically, using starch as an indicator after suitable time intervals. The unused bromate reacts with KI in acid solution in accordance with the equation.

$$BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O\ (l)$$

All the reactions were carried out under the condition of using tenfold excess of (3-MI) over [bromate]. The pseudo first orderrate constants (s^{-1}) were computed from linear plots of log[bromate] against time (r^2- 0.998) up to 80% completion of reaction.

RESULTS AND DISCUSSION

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

Effect of [3-Methylindole]$_0$

Kinetic runs were carried out with various initial concentrations of [3-MI] at 293 K by fixing constant of oxidants concentration ($KBrO_3$ and PMS), [H^+], μ, and percentage solvents, which yielded [3-MI] dependent rate constants. The values of pseudo first-order rate constants k'(s^{-1}) thus obtained were found to increase with [3-MI] (Table 2 & 3, Fig.3 & 4) 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 = 0.998) (Fig.3 & 4). Such a kinetic behaviour indicates the absence of any self-decomposition $KBrO_3$. The experiments were carried out at various temperatures 283 K to 298 K and the rate constant values of k and k_2 were calculated. The value of k_2 (mol^{-1} dm^3 s^{-1}) was evaluated from the slope of k'(s^{-1}) vs [3-MI] plots (Fig.3 & 4). Thek_2 (mol^{-1} dm^3s^{-1}) values were calculated from the values of k' using the formula k' (s^{-1}) / [3-MI].

Effect of [Oxidants]

It is observed that the reaction rate was unaffected as evident from the constant slopes of log [$KBrO_3$] or log[PMS] Vs time plots for various [Oxidants] (1×10^{-2} – 5×10^{-2} mol dm^{-3}) at fixed [3-MI], [H^+], μ, and percentage of solvent. This observation confirms the first-order dependence of rate on [Oxidants] (Table 2 & 3).

Effect of μ

The influence of ionic strength (μ) maintained by the addition of sodium perchlorate (1×10^{-1} – 5×10^{-1} mol dm^{-3}) on the reaction rate was found to be negligible for both PMS and $KBrO_3$ system (Table 2 & 3). 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 $KBrO_3$ mononegative ion BrO_3^-), 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}– 9×10^{-2} mol dm^{-3}) were found to be the same (Table 2 & 3). Such a kinetic behaviour indicates the non existence 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 $KBrO_3$) was studied in aqueous ethanol mixtures of various compositions (Table 2 & 3). 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 [18], a neutral molecule (3-MI), and oxidants a mononegative ion (HSO_5^-) for PMS and also mononegative ion for (BrO_3^-) suggesting a polar (ionic) mechanism.

Stoichiometry

Solutions of 3-Methylindole containing an excess of oxidants (PMS and $KBrO_3$) were kept overnight at room temperature. Titrimetric estimation of the concentration of oxidant consumed and assuming that all the 3-Methylindole 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 [Oxidants], 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 [19].

Rate Law

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

$-d[Br(V)] / dt = k_2 [Br(V)][3\text{-MI}]$

$rate / [Br(V)] = k' (s^{-1}) = k_2[3\text{-MI}]$

$k' = k_2 [3\text{-MI}]$

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

Product Analysis

Separate reaction mixture containing a slight excess of Oxidant (0.125 mol dm^{-3} of $KBrO_3$) over the substrate (0.06 mol dm^{-3} of 3-MI) with other additives maintained as in the regular kinetic runs using ethanol as solvent were kept aside at room temperature for about 48 hours, for completion of the reaction. This was confirmed by TLC analysis of the reaction mixture. Then the remaining of the reaction mixture was poured into doubly distilled water. A residual solid thus obtained from both reaction mixtures were filtered, washed and dried.

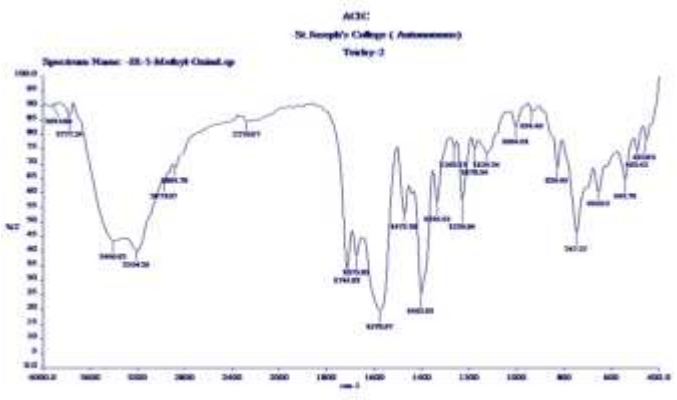


Fig. 1. FT-IR spectrum of product

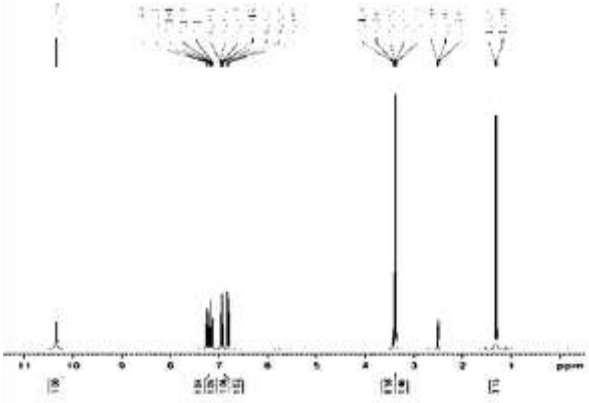


Fig. 2. NMR- spectrum of product

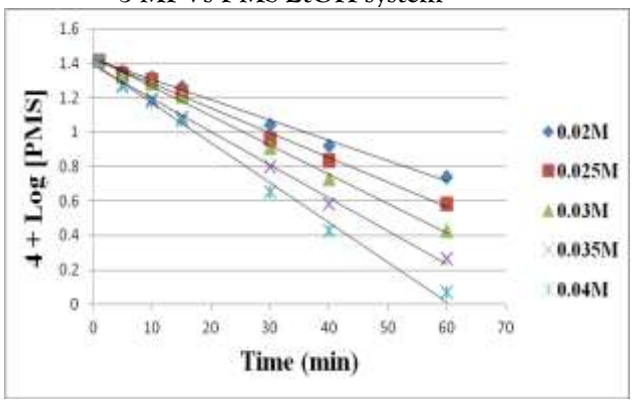
The identity of the product was further confirmed from its FT-IR spectra (Fig .1) and HMNR (Fig .2). FT-IR (KBr) 3406, 1714 and 1675 cm-1, HNMR (DMSO) ppm = 6.0-8.0 (m, 5H, ArH, NH), 3.3 (S, 3H, C-H).

Rate and Activation Parameters

The effect of temperature on k' (s^{-1}) was studied in the range of 283–298 K for $KBrO_3$ and PMS in ethanol solvent system. The results are shown in table 2 and table 3 respectively. The Arrhenius plot of log k_2 vs $1/T$ was linear (Fig.5). From the above plot, the values of energy of activation (E_a) were calculated (Table 4 Fig. 5). 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. All the thermodynamic parameters were tabulated in table 4.

Fig.3.Variation of [3-MI] @ 293 K

3-MI Vs PMS-EtOH system



3-MI Vs $KBrO_3$-EtOH system

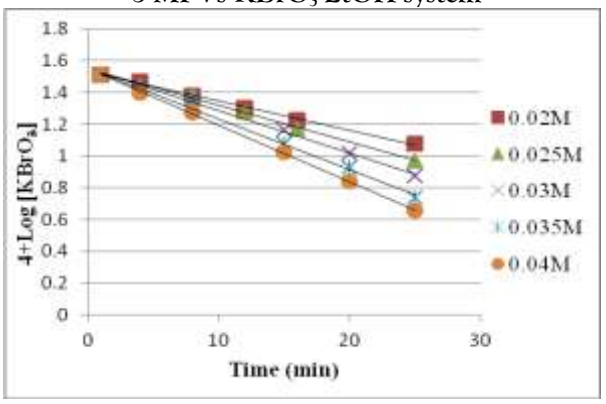
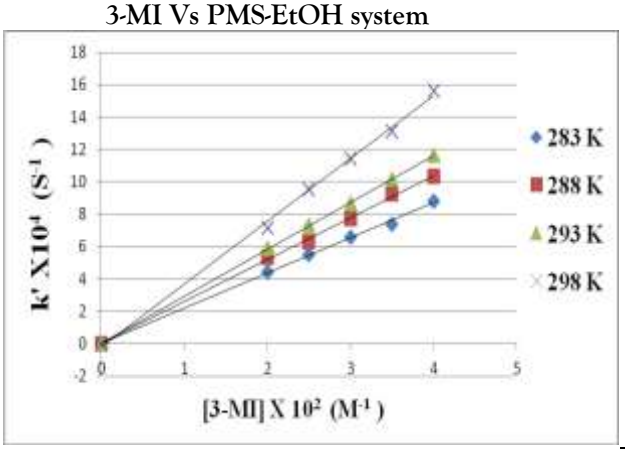


Fig. 4. Evaluation of k_2

3-MI Vs PMS-EtOH system



3-MI Vs $KBrO_3$-EtOH system

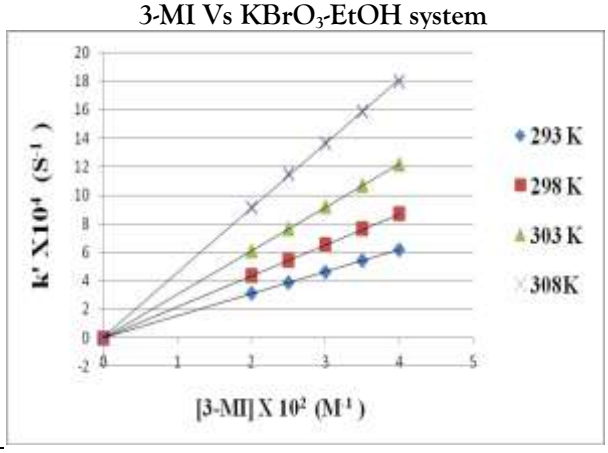


Table 1. Effect of temperature on the reaction rate

Temp (K)	k_2 (10^3 , s^{-1})	
	PMS	$KBrO_3$
283	2.2123	1.0812
288	2.6314	1.5446
293	2.9341	2.1697
298	3.5213	3.0538

Fig. 5. Evaluation of E_a for PMS and Bromate System

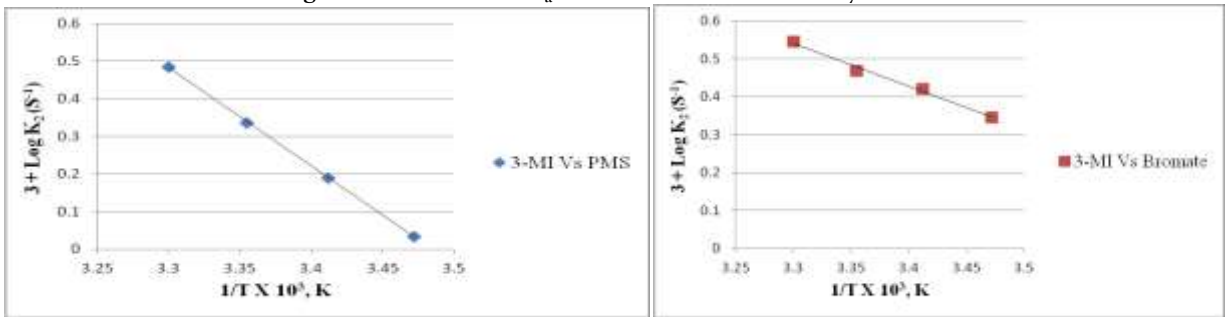


Table 4. Thermodynamic parameters

Thermodynamic parameters of Oxidation of 3-MI	Activation Parameters	
	PMS	$KBrO_3$

Energy of Activation (E_a)	$kJmol^{-1}$	21.088	53.7387
Enthalpy ($\Delta H^{\#}$)	$kJ\ mol^{-1}$	18.652	51.2195
Entropy ($\Delta S^{\#}$)	$J\ K^{-1}\ mol^{-1}$	-270.05	-284.4568
Free Energy ($\Delta G^{\#}$)	$kJ\ mol^{-1}$	98.070	137.4099

Table 2.Pseudo-First Order Rate Constant for the oxidation of 3-MI by PMS in Ethanol Solvent

[3-MI] X10^2 (mol dm^{-3})	[PMS] X10^3 (mol dm^{-3})	[H^+] (mol dm^{-3})	[μ] (mol dm^{-3})	EtOH % (v/v)	k' (10^4 s^{-1}) 283 K	288 K	293 K	298K
2.0	2.0	0.02	0.3	50	4.45	5.31	5.89	7.13
2.5	2.0	0.02	0.3	50	5.52	6.32	7.32	8.75
3.0	2.0	0.02	0.3	50	6.55	7.69	8.70	10.63
3.5	2.0	0.02	0.3	50	7.38	9.26	10.16	12.23
4.0	2.0	0.02	0.3	50	8.81	10.30	11.64	14.14
3.0	1.0	0.02	0.3	50	-	-	8.45	-
3.0	1.5	0.02	0.3	50	-	-	8.70	-
3.0	2.0	0.02	0.3	50	-	-	8.41	-
3.0	4.0	0.02	0.3	50	-	-	8.42	-
3.0	5.0	0.02	0.3	50	-	-	8.81	-
3.0	2.0	0.005	0.3	50	-	-	8.49	-
3.0	2.0	0.02	0.3	50	-	-	8.70	-
3.0	2.0	0.05	0.3	50	-	-	8.12	-
3.0	2.0	0.09	0.3	50	-	-	8.24	-
3.0	2.0	0.02	0.1	50	-	-	8.51	-
3.0	2.0	0.02	0.2	50	-	-	8.62	-
3.0	2.0	0.02	0.3	50	-	-	8.70	-
3.0	2.0	0.02	0.5	50	-	-	8.33	-
3.0	2.0	0.02	0.3	40	7.89	10.21	13.08	16.89
3.0	2.0	0.02	0.3	45	5.14	7.94	10.41	13.84
3.0	2.0	0.02	0.3	50	2.08	5.89	8.70	9.25
3.0	2.0	0.02	0.3	55	1.04	2.64	4.80	6.11
3.0	2.0	0.02	0.3	60	0.14	0.98	1.98	2.38

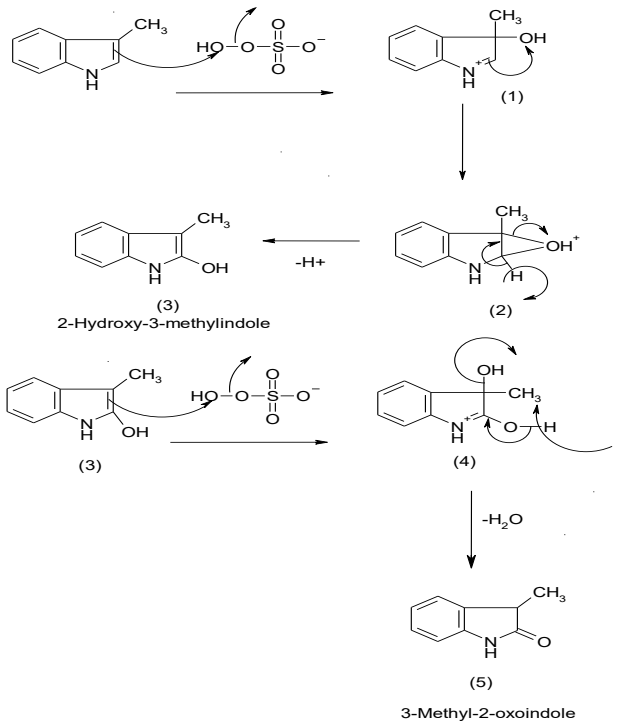
Table 3. Pseudo-First Order Rate Constant for the oxidation of 3-MI by $KBrO_3$ in Ethanol Solvent

[3-MI] X10^2 (mol dm^{-3})	[$KBrO_3$] X 10^3 (mol dm^{-3})	[H^+] (mol dm^{-3})	[μ] (mol dm^{-3})	Ethanol % (v/v)	k' (10^4 s^{-1}) 283 K	288 K	293 K	298 K
2.0	2.0	0.02	0.3	50	2.10	2.98	4.88	6.12
2.5	2.0	0.02	0.3	50	2.91	3.80	5.61	7.32
3.0	2.0	0.02	0.3	50	3.50	4.92	6.56	8.92
3.5	2.0	0.02	0.3	50	4.23	5.89	7.42	10.65
4.0	2.0	0.02	0.3	50	5.01	6.72	8.51	12.11
3.0	1.0	0.02	0.3	50	-	-	6.21	-
3.0	2.0	0.02	0.3	50	-	-	6.34	-
3.0	3.0	0.02	0.3	50	-	-	6.56	-
3.0	4.0	0.02	0.3	50	-	-	6.04	-
3.0	5.0	0.02	0.3	50	-	-	6.18	-
3.0	2.0	0.005	0.3	50	-	-	6.51	-
3.0	2.0	0.02	0.3	50	-	-	6.56	-
3.0	2.0	0.05	0.3	50	-	-	6.42	-
3.0	2.0	0.09	0.3	50	-	-	6.24	-

3.0	2.0	0.02	0.1	50	-	-	6.20	-
3.0	2.0	0.02	0.2	50	-	-	6.15	-
3.0	2.0	0.02	0.3	50	-	-	6.56	-
3.0	2.0	0.02	0.5	50	-	-	6.22	-
3.0	2.0	0.02	0.3	40	4.81	8.21	12.01	16.25
3.0	2.0	0.02	0.3	45	2.63	6.52	9.81	12.56
3.0	2.0	0.02	0.3	50	1.79	4.18	6.56	8.29
3.0	2.0	0.02	0.3	55	0.98	1.89	3.21	4.67
3.0	2.0	0.02	0.3	60	0.11	0.55	1.29	2.14

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:



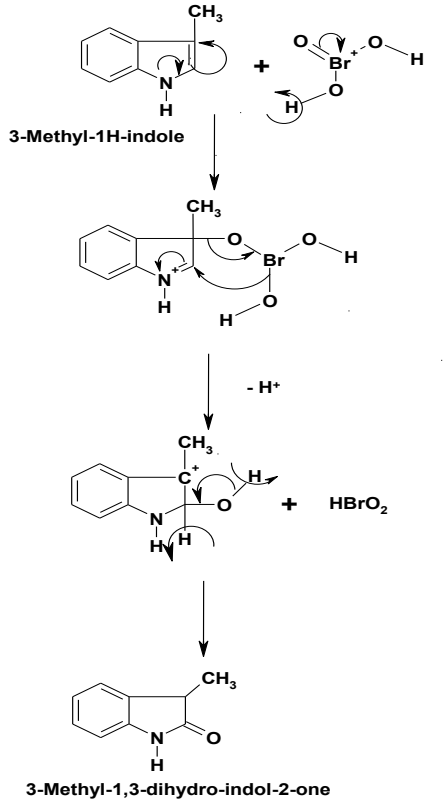
PMS exists as HSO_5^- ion in solution and the ion is weak nucleophile. It is suggested that the reaction proceeds through an electrophilic attack of the oxidant (PMS)[20-21] at the nucleophilic site C_3 of 3-MI by a mechanism involving displacement of sulphate ion to 3-hydroxy-3-Methylindole (1) as the rate determining step. Compound (1) undergoes intramolecular rearrangement [22] 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.

$KBrO_3$ – 3-MI: Based on the foregoing observations such as first-order dependence of rate each on [3-MI],[$KBrO_3$], zero-order dependence on [H^+], negligible effect of [μ], and the stoichiometry, the following mechanism is suggested:

Our results suggest that the reaction proceeds through an electrophilic attack of the oxidant (bromated ion) at nucleophilic site C-3 of 3-Methylindole by a mechanism involving nucleophilic displacement of bromated ion [23]. Presence of electron releasing methyl group increases the reaction rate. 3-Methylindole reacts with H_2BrO_3 forming a bromated ester intermediate.

This intermediate breaks down fatly to produce 3-Methyloxindole as the product. The mechanism was supported by the observed rate laws, first order in oxidant, first order in substrate and second order in [H^+]. This was further confirmed by the solvent influence on the reaction the rate was found to increase considerably upon increase in

solvent content of the medium. This was due the fact the reaction was facilitated by the increase in polarity or nucleoplicity. The addition of acrylonitrile, which is a good trapper of free radicals, did not have any retarding effect on the reaction. It indicates no free radical's participation in the reaction



CONCLUSION

The mechanism was supported by the observed rate laws, first order in oxidant first order in substrate and second order in [H^+]. Follows first order with respect to 3-Methylindole, Oxidants ($KBrO_3$ and PMS) then overall follows second order reaction. The results indicate that there is no ionic strength and [H^+]. On comparing the results, it is clear that $KBrO_3$ reacts slower (redox potential of $KBrO_3$ E^0 = 2.01 V)[23] than that of Peroxomonsulphate (PMS) (E^0 = 1.82 V)[24].

REFERENCE

1. Al-Kazwini, A. T., O'Neill, Peter, Adams, G. E., Cundall, R. B., Lang, G. and Junino, A., 1991. J Chem Soc, Perkin Trans 2, 1941.
2. Balon, M., Munoz, M., Guardado, P., Hidalgo, J. and Carmona, C., 1993. J Org Chem, 58, 7469.
3. Muniyappan. K., Chandramohan. G. and Stephen. J. 2013. J. Korean Chem. Soc. Vol. 57, No. 2, 210 – 215.
4. Chandramohan. G., Kalyanasundharam. S. and Renganathan R. 2002. Int. J. Chem Kinet. 34: 569-574
5. O. R.Suárez-Castilho, L. Beiza-Granados, M. Meléndez-Rodri´guez, A. Alvarez-Hernández; *J. Nat. Prod.*, 69, 1596 (2006).
6. R. J. Sundberg; *Chemistry of Indoles*; Academic Press: New York, (1970).
7. W. J. Houlihan; *Ed. Indoles*; Wiley-Interscience: New York; Part 1, Part 2 and Part 3 (1972).
8. M. T. Yokoyama, J. R. Carlson; *Appl. Microbiol.* 27, 540-548 (1974).
9. M. T. Yoko yama, J. R. Carlson, E. O. Dickinson; *Am. J. Vet. Res.* 36: 1349-1352 (1975).
10. B. Witkop, Justus Liebigs; *Ann. Chem.*, 558, 98 (1947).
11. William B. Lawson, Abraham Patchornik, Bernhard Witkop,;*J. Am. Chem. Soc.*, 80 (17), 4748–4749 (1958).
12. Hiroshi Ushiro, Katsuji Takai, Yoichi Noda, Shuh Narumiya, Takashi Tokuyama, Osamu Hayaishi; *J. Biol. Chem.*, 253, 9002-9008 (1978).
13. G. Chandramohan, S. Kalyanasundharam, R. Renganathan; *Int J Chem Kinet*., 34, 569–574 (2002).
14. MuniyappanKavery, Chandramohan Govindasamy, Stephen Johnson, Kiruthikajothi Kannan; *Chem. Sci. Rev Lett.,* 3 (11), 345-352 (2014).
15. MuniyappanKavery, Chandramohan Govindasamy, Stephen Johnson; *Journal of the Korean Chemical Society*, 57 (2), 210 – 215 (2013).
16. K. Muniyappan, G. Chandramohan, J. Stephen, A. Peiyasami; *Research Journal of Chemical Sciences*, 4(8), 7-11, (2014)
17. A. Periyasami, N. Kumaraguru; *Eur. Chem. Bull.* 2023, 12(12), 2613-2621.
18. Anis, S. S. *J. Chim. Phys.* 1992, 89, 659.

19. Cherkupally Sanjeeva Reddy and Padma Sunitha, manjari, Kinetics and mechanism of acid bromate oxidation of substituted 4-oxo acids, *Indian J. of Chemistry*, 49A, 418 - 434 (2010)
20. Chandramohan. G., Kalyanasundharam. S. and Renganathan R., 2002. Int. J. Chem Kinet. 34: 569-574.
21. Ando,W.; Miyazaki, H.; Akasaka, T. *J. Chem. Soc. Chem. Commun.* 1983, 518.
22. Laidler, K. J., 1965. "Chemical Kinetics"; Tata-McGraw Hill:New Delhi; p. 229.
23. Latimer, W .M. The Oxidation of the Elements and Their Potential in Aquwous Solutions; Prentice-Hall: Englewood Cliffs, NJ, 1956, p. 78.
24. Steela, W. V.; Appelman, E. H. 1982. J. ChemThermodyn., 14, 337.