Kinetic and Mechanistic Investigation of the Oxidation of Indole Using Peroxomonosulphate in Acetone Medium

Muniyappan K.[1], Chandramohan G.[2] , Stephen J.[3] and Periyasami A.[4]
[1]Research and Development Centre, Bharathiar University, Coimbatore – 641046, Tamil Nadu, INDIA
[2]Dept of Chemistry, A.V.V.M.S.P College, Poondi, 613503, Tamil Nadu, INDIA
[3]MAM College of engineering, Siruganur, Trichy-621105, Tamil Nadu, INDIA
[4]Dept of Chemistry**,** SVVCAS, Dharmapuri**,** Tamil Nadu, INDIA

Abstract

The kinetic study of oxidation of indole using peroxomonosulphate was carried out in aqueous acetone medium in the temperature variation of 293-308 K. The influence of [indole], [peroxomonosulphate], [H^+], ionic strength, percentage of acetone and temperature on the rate of reaction was carried out. The order with respect to [peroxomonosulphate] and [indole] was also one. The total reaction was second order, first order each with respect to [Indole] and [PMS]. No effect of [H^+] on the rate was observed while increase of [H^+]. Variations of ionic strength had no effect and Increase of percentage of aqueous acetone decreased the rate. Suitable mechanism in conformity with the kinetic observations has been proposed and Activation and thermodynamic parameters have been computed basis of the observed data. The product isatin was confirmed from the IR and NMR spectral analysis.

Keywords: Kinetics, mechanism, oxidation, indole, peroxomonosulphate (PMS).

Introduction

Peroxomonosulfate (heretofore written as PMS) in aqueous solution to be HSO_5^- is an active ingredient of oxone. Oxone is a commercial name of this triple salt of potassium ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). Oxone is a versatile and environmentally benign oxidant with wide applications such as bleaching, cleaning and disinfection agent[1]. Peroxomonosulfuric acid a derivative of H_2O_2 when one of the H atoms of the latter is substituted by sulfuric acid group[2-4]. Thus it is this weak peroxide linkage (-O-O-) that undergoes cleavage during electron transfer reactions[5-12]. However, such peroxo compounds are exceptionally sensitive to the traces of metal-ions as has been observed in trace metal-ion catalysis in large number of reactions of peroxo acids[13].

The oxidation of 2,3-dialkyl indoles by peroxodisulphate, PMS, peroxomonophosphoric, peroxodiphosphoric acids and oxidation of 3-methylindole by PMS in ethanol solvent [14], oxidation of indoles by tetrabutylammoniumtribromide (TBATB), IAA oxidation[15] by PMS has been already reported in the literature. The main objectives of the present study are kinetic investigation of oxidation of indole by PMS in acetone medium, identify the oxidation product, mechanism of the reaction and computing the thermodynamic parameters.

Material and Methods

Indole (qualigens, India) and PMS (from Du Pont, U.S.A) and other name is oxone were used as such. All the other chemicals and reagents such as sodium bisulphate, H_2SO_4, KI, and acetone used were of anala R grade. All the reagents were prepared in doubly distilled water.

Kinetic Measurements: The kinetic run of the indole-PMS system was carried out in a mixture of acetone and water (50 % aqueous acetone v/v). The reaction in the indole –PMS system was conducted under the pseudo first order conditions with iodometrically. The concentration of the indole was at least ten times excess over that of the PMS. Pseudo-first-order rate constants (k') calculated from plots of log [PMS] versus time were reproducible within ±5%

Product Analysis Stoichiometry: The stoichiometry of the reaction was determined by equilibrating reaction mixtures of various [peroxomonosulphate]/[Indole] ratios at 303 K for 48 hours keeping all the other reagents constant. Estimation of unconsumed [peroxomonosulphate] revealed that one mole of indole consumed two moles of peroxomonosulphate The final product also identified by UV, FT-IR, and NMR spectral and elemental analysis. The IR spectrum was recorded using KBr pellets.

IR and NMR Data: FT-IR (KBr) 3198 cm^{-1} (N-H Str), 1734 cm^{-1} (C=O Str) and 1600 cm^{-1} (Amide C=O Str); ^{1}H NMR (DMSO) ppm = 6.9 - 8 (m,-5H, ArH, NH).

Results and Discussion

Effect of [Indole]: The dependence of reaction rate on [Indole] was studied with fixed [PMS], [H$^+$], μ and acetone (solvent) percentage by using various initial concentrations of indole (2.0

$\times 10^{-2} - 4.0 \times 10^{-2}$ mol dm^{-3}). It was found that the rate increases with increase in indole concentrations (table-1 and figure-1). This indicates the indole concentrations followed by first oder reaction. Such a kinetic behaviour was commonly observed the first order with respect to [indole] is confirmed by the straight lines passing through origin in the plots of log k'(s^{-1}) versus log [indole] (figure-2). Such a kinetic behaviour indicates that there is no self-decomposition of PMS[16].

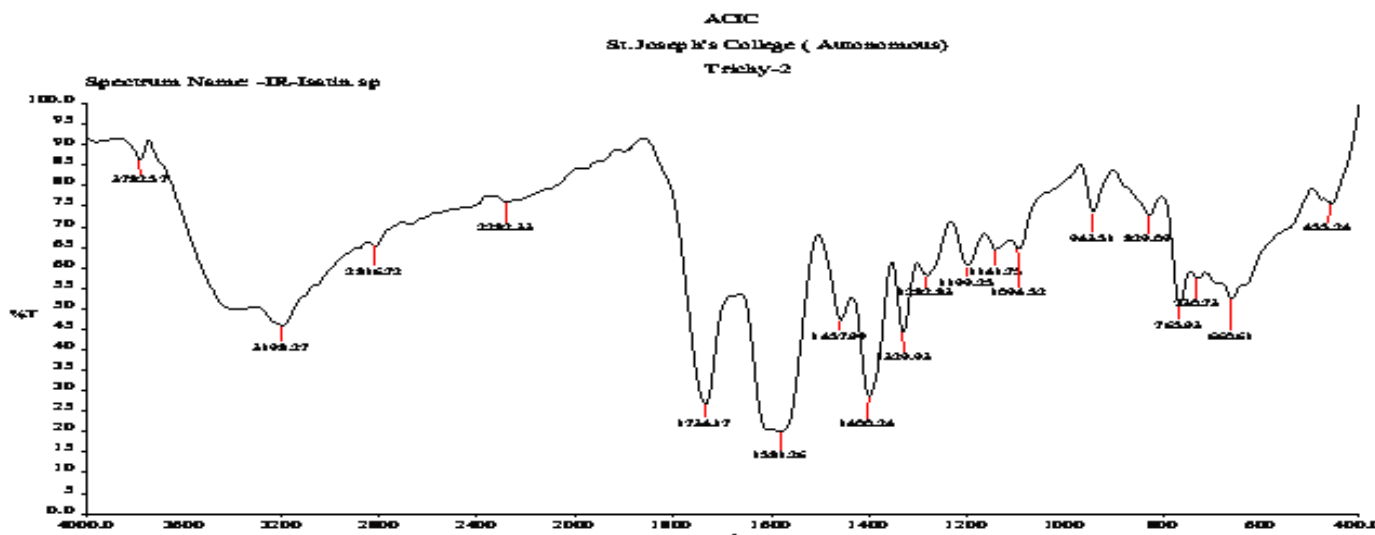**Figure-1**
FT-IR spectrum of product

Table-1
Variation of indole concentrations on the reaction rate at 303 K
[H$^+$]: 0.02 mol dm^{-3}, CH$_3$COCH$_3$: 50%. μ: 0.3 mol dm^{-3}, [PMS]: 0.002 mol dm^{-3}

[Indole] X mol dm^{-3}	0.020	0.025	0.30	0.035	0.040
k′ X 10^{-4} s^{-1}	4.70	5.86	6.96	8.31	9.54

Table-2
Variation of oxidant on reaction rate at 303 K
[H$^+$]: 0.02 mol dm^{-3}, [Indole]: 0.03 mol dm^{-3}, , CH$_3$COCH$_3$: 50%, μ: 0.3 mol dm^{-3}

[Oxidant] X mol dm^{-3}	0.001	0.0015	0.002	0.0025	0.003
k′ X 10^{-4} s^{-1}	6.71	6.62	6.96	6.89	6.60

Table-3
Variation of concentrations of Ionic strength at 303 K
[H$^+$]: 0.02 mol dm^{-3}, [Indole]: 0.03 mol dm^{-3}, CH$_3$COCH$_3$: 50%., [PMS]: 0.002 mol dm^{-3}

[μ] X mol dm^{-3}	0.20	0.30	0.40	0.50
k′ X 10^{-4} s^{-1}	6.65	6.96	6.71	6.70

Table-4
Variation of concentrations of H$^+$ ion at 303 K
[Indole]: 0.03 mol dm^{-3}, CH$_3$COCH$_3$: 50%, μ: 0.3 mol dm^{-3}, [PMS]: 0.002 mol dm^{-3}

[H$^+$] X mol dm^{-3}	0.005	0.02	0.03	0.05	0.09
k′ X 10^{-4} s^{-1}	6.49	6.96	6.68	6.26	6.47

Table-5
Effect of solvent variations at 303 K
[Indole]: 0.03 mol dm^{-3}, [H$^+$]: 0.02 mol dm^{-3}, μ: 0.3 mol dm^{-3}, [PMS]: 0.002 mol dm^{-3}

H$_2$O : CH$_3$COCH$_3$	55:45	50:50	45:55	40:60
k′ X 10^{-4} s^{-1}	10.45	6.96	5.90	3.81

Table-6
Variation of temperature on the reaction rate

Temperature (K)	293	298	303	308
$k_2 \times 10^{-2}$ s^{-1}	1.16	1.41	2.35	3.39

Table-7
Rate and Activation Parameters at 303K

Thermodynamic parameters of Oxidation of Indole	Activation Parameters
Energy of Activation (Ea) kJ mol^{-1}	51.83
Enthalpy ($\Delta H^{\#}$) kJ mol^{-1}	49.31
Entropy ($\Delta S^{\#}$) J K^{-1} mol^{-1}	-113.51
Free Energy ($\Delta G^{\#}$) kJ mol^{-1}	83.70

Effect of [PMS]: The kinetics of oxidation of indole has been studied at various initial concentration of the PMS (1.0×10^{-3} – 3.0×10^{-3} mol dm^{-3}) and at fixed concentrations of other reactants. The plot of log [PMS] versus time yields a straight line (table-2 and figure-3).This indicates confirms the first-order dependence of rate on [PMS].

Effect of ionic strength: In order to test if the reaction is ionic or not, reactions were conducted at different μ values by using different concentrations of the salt, NaHSO$_4$, while the other additives were maintained constant. For all the compounds, it was noticed that increase of μ did not alter the reaction rate significantly (table-3).

Effect of [H$^+$]: At fixed [PMS], [Indole], percentage of aqueous acetone and μ, experiments involving different initial concentrations of [H$^+$] (0.005 – 0.09 mol dm^{-3}) were carried out. It was noticed that the rate constants $k'(s^{-1})$ obtained for the substrate of indole (table-4). There is no influence of added concentration of H$^+$ ions.

Effect of Dielectric Constant: The effect of dielectric constant on the rate of oxidation was investigated. It was found that the rate constants decreased with increase in composition of acetone (table-5). However, there was no linearity plot obtained for log k' versus time. This may be due to the charge development in the transition state involving a more polar activated complex than the reactants.[17]

Temperature Effect: The reaction was carried out at four different (293, 298, 303 and 308 K) temperatures to study the effect of temperature on the rate of reaction. It was observed that when increase the temperature, the rate of the reaction also increased (Table-6). The thermodynamic parameters (E$_a$, $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$) were calculated (table-7 and figure-4) by Arrhenius plot of log k$_2$ versus 1/T was linear.

Test for Free Radical Intermediates: There was no induced polymerisation of acrylonitrile monomer, ruling out the possibility of free radical formation during the course of the reaction.
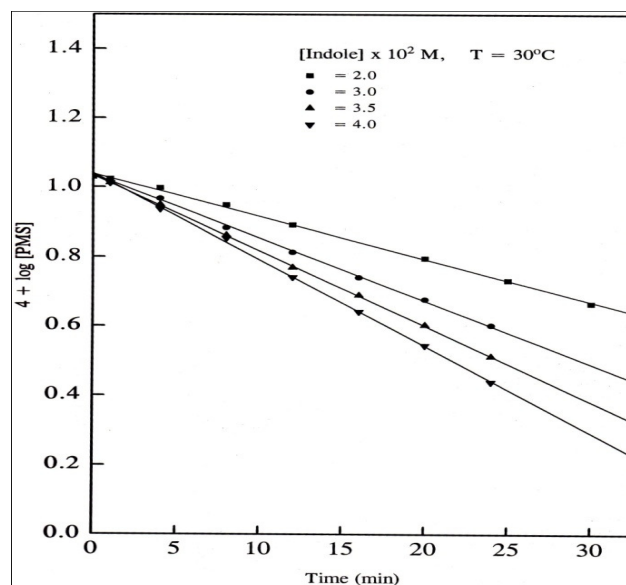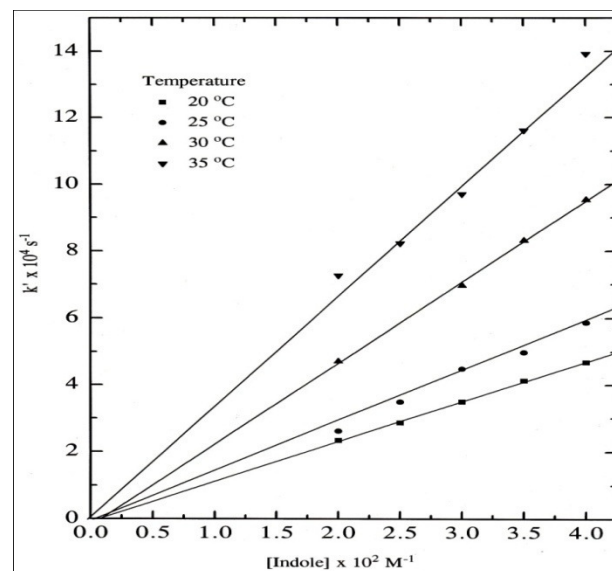

Figure-1
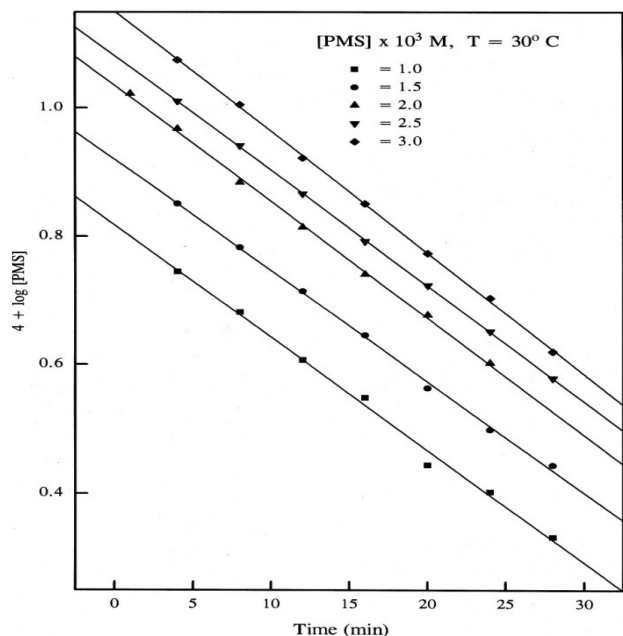**Effect of [Indole]**

Figure-2
Evaluation of k$_2$

Figure-3
Effect of [PMS]
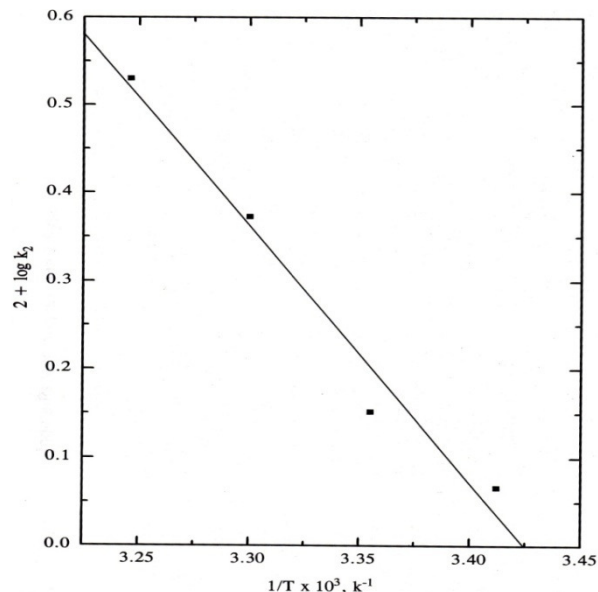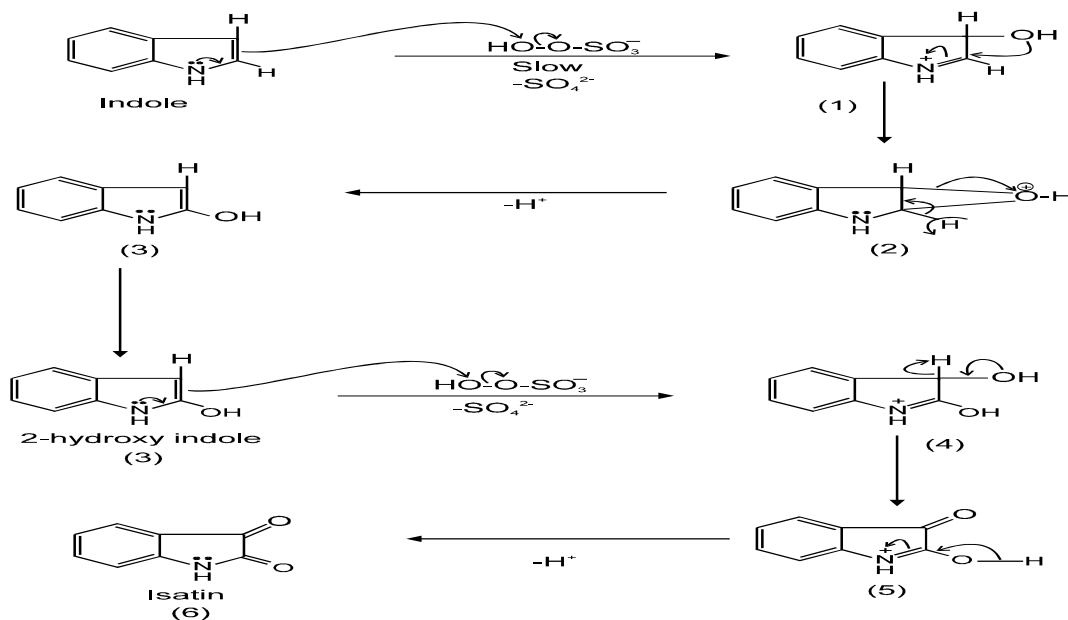

Figure-4
Evaluation of E₂

Scheme-1

PMS exists as HSO_5^- ion in solution and the ion is a weak nucelophile. It is suggested that OH^+ ion of the PMS attack at nucleophilic centre C-3 of indole to get product of isatin (6) through the various intermediate compound (1-5).

Mechanism: The following mechanism (scheme-1) is suggested based on the observations.

strength and [H^+]. From the data of the dielectric effect clearly reveals that the rate inversely proportional to percentage of acetone.

Conclusion

Indole and PMS reaction involves of a peroxo linkage, follows first order with respect to Indole and PMS and overall follows second order reaction. The results indicate that there is no ionic

Acknowledgement

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