Research Article

Kinetics of Peroxomonosulfate Oxidation of Indole in aqueous Ethanol Medium: A Mechanistic Study

Muniyappan Kavery*[1], Chandramohan Govindasamy[2], Stephen Johnson[3], Kiruthikajothi Kannan[1]

[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

Abstract

Kinetics of oxidation of indole by peroxomonosulfate (PMS) has been studied at 293 to 303 K in aqueous ethanol medium. The influence of [peroxomonosulphate], [indole], [H$^+$], ionic strength, percentage of Ethanol and temperature on the reaction rate was studied. The reaction follows a total second order, first order each with respect to [Indole] and [PMS]. 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 ethanol decreased the rate. Absence of any polymerization indicated a nonradical pathway. Activation and thermodynamic parameters ($\Delta E^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) have been computed. A suitable kinetic scheme based on these observations is proposed.

Keywords: Kinetics; Mechanism; Oxidation; Indole-PMS; Ethanol
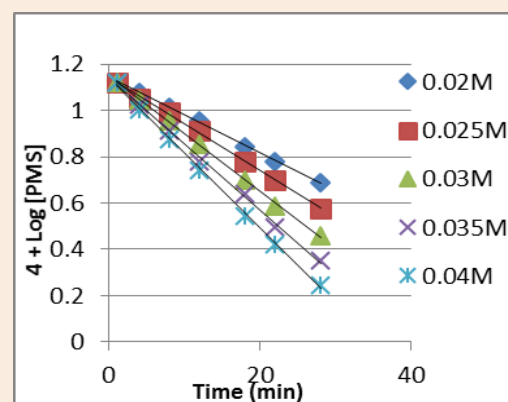
*Correspondence
Muniyappan Kavery,
Email: muni.kavery@gmail.com

Introduction

Peroxomonosulphate (PMS) ion, HSO_5^-, is a versatile anionic oxidant which is usually represented as OXONE, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Studies on the oxidation of organic compounds and inorganic complexes by PMS have been reported [1]. Oxidation of indole-3-acetic acid (IAA) has received much attention because of the involvement of the indole derivatives in significant biological processes. They have anti-inflammatory [2], tumor growth inhibitor [2], and antiviral, antitubercular, antibacterial, antiallergic and psychotropic activities [3]. The compounds serotonin and tryptophan were suggested to act as endogenous antioxidants [4]. IAA acts as a powerful plant harmone under the name AUXIN with much growth regulatory functions [5].

Oxidation of indole-3-acetic acid by dioxygen [6], Ce(IV) [6], 1,4-phenanthroline-manganese(II) complexes [7], hydrogen peroxide, persulphate, N-chlorosuccinimide, and sodium hypochlorite were reported [8]. Chlorophyll sensitized photo-oxidation [9], peanut peroxidise [10], horseradish and tobacco peroxidise [11] catalysed oxidation of IAA have been studied.

Although the oxidation of certain substituted indoles such as 2,3-dialkyl indoles by peroxodisulfate [12], PMS [12], peroxomonophosphoric [12], peroxodiphosphoric [12] acids has been already reported in the literature and oxidation of indoles by tetrabutylammoniumtribromide (TBATB) has been already reported in the literature, the lack of kinetic and mechanistic investigation on the oxidation of Indole by PMS in aqueous ethanol medium was investigated us to carry out this work and is presented as a first report in this study.

Experimental Methods

Materials and reagents

Indole (Qualigens, India) and PMS (E.I. Du Pont de Nemours Company, U.S.A) under the trade name Oxone were used as such. All the other chemicals and reagents such as sodium bisulphate, sulphuric acid, KI, and Ethanol used were of analytical grade. All the reagents were prepared in doubly distilled water.

Kinetic Measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess of the Indole over PMS. The temperature range was kept constant to 293-303 K. The solvent was 50% (v/v) aqueous ethanol used. The reactions were followed by monitoring the decrease in the concentration of PMS by using the iodometric method. The pseudo-first-order rate constants, k' (s^{-1}) were evaluated from the linear (r = 0.990–0.999) plots of log [PMS] against time. The second order rate constant, k_2, was evaluated from the relation $k_2 = k'/[Indole]$.

Product Analysis

A reaction mixture containing slight excess of PMS (0.125 M), Indole (0.05 M), and ethanol–water mixture was kept aside at room temperature for a day, so that the substrate was completely converted into product. 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 was filtered, washed and dried. The identity of this product isatin was confirmed from its ^{1}H NMR and. FT-IR spectra, as shown in Fig. 1.

IR and NMR Data

FT-IR (KBr) 3198 cm^{-1} (N-H Str), 1734 cm^{-1} (C=O Str) and 1581cm^{-1} (Amide C=O Str); ^{1}H NMR (DMSO) ppm = 6.9 - 8 (m,-5H, ArH, NH).
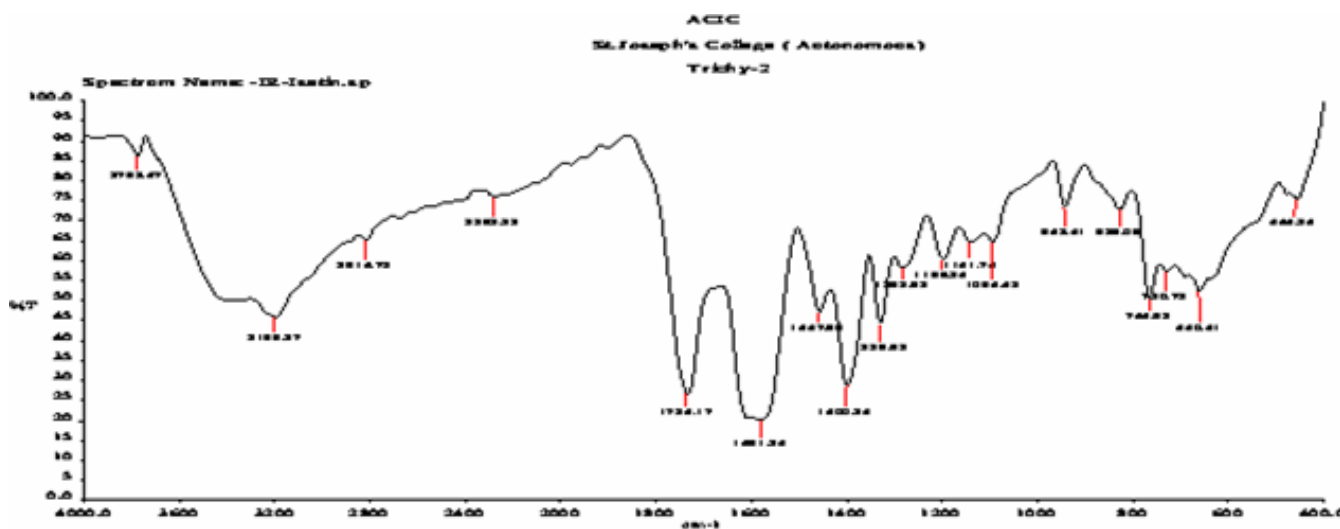

Figure 1 FT-IR spectrum of product

Results and Discussion

Factors influencing the rate of oxidation of [Indole] by PMS such as effects of (i) [Indole]$_0$, (ii) [PMS]$_0$, (iii) ionic strength (μ), (iv) [H$^+$], and (v) dielectric constant have been studied. Rate and activation parameters were evaluated.

Effect of [Indole]

The dependence of reaction rate on [Indole] was studied with fixed [PMS], [H$^+$], μ and ethanol (solvent) percentage but 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] (**Table 1 & Figure 2**). This indicates the first order dependence of rate on [Indole]. 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 3**). Such a kinetic behaviour indicates the absence of any self-decomposition of PMS [13].

Effect of [PMS]

It is observed that the reaction rate was unaffected as evident from the constant slopes of log [PMS] vs time plots for various [PMS]$_0$ ($1.0 \times 10^{-3} - 3.0 \times 10^{-3}$ mol dm^{-3}) at fixed [Indole]$_0$, [H$^+$]$_0$, μ, and percentage of ethanol (**Table 1 & Figure 4**). This observation confirms the first-order dependence of rate on [PMS].

Effect of μ

The influence of ionic strength (μ) maintained by the addition of sodium bisulfate on the reaction rate was found to be negligible (**Table 1**). This shows that the reaction occurs between a neutral species namely the Indole molecule and the mononegative ion HSO$_5^-$, the active species of the oxidant.

Effect of [H$^+$]

The reaction rates measured at constant [Indole], [PMS], μ, and percentage of ethanol but with various [H$^+$] ($5 \times 10^{-3} - 10 \times 10^{-2}$ mol dm^{-3}) were found to be the same (**Table 1**). Such a kinetic behaviour indicates the nonexistence of any protonation equilibrium with respect to both PMS and Indole under the present experimental conditions employed.

Effect of Dielectric Constant

So as to determine the effect of dielectric constant or polarity of the medium on rate, the oxidation of Indole by PMS was studied in aqueous ethanol mixtures of various compositions (**Table 1**). 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 [14], a neutral molecule (Indole) and a mononegative ion (HSO$_5^-$) suggesting a polar or ionic mechanism.

Table 1 Pseudo-First Order Rate Constant for the oxidation of Indole by Peroxosulfate

[Ind] X10^2	[PMS] X10^3	[H$^+$]	[μ]	[C$_2$H$_5$OH]	k' (10^4 s^{-1})		
(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	% (v/v)	293 K	298 K	303 K
2.0	2.0	0.02	0.3	50	2.70	4.33	6.28
2.5	2.0	0.02	0.3	50	3.38	5.40	7.76
3.0	2.0	0.02	0.3	50	4.05	6.52	9.55
3.5	2.0	0.02	0.3	50	4.75	7.56	10.96
4.0	2.0	0.02	0.3	50	5.42	8.69	12.44
3.0	1.0	0.02	0.3	50	-	-	9.45
3.0	1.5	0.02	0.3	50	-	-	9.57

3.0	2.0	0.02	0.3	50	-	-	9.55
3.0	2.5	0.02	0.3	50	-	-	9.65
3.0	3.0	0.02	0.3	50	-	-	9.47
3.0	2.0	0.005	0.3	50	-	-	9.63
3.0	2.0	0.02	0.3	50	-	-	9.55
3.0	2.0	0.05	0.3	50	-	-	9.56
3.0	2.0	0.09	0.3	50	-	-	9.42
3.0	2.0	0.10	0.2	50	-	-	9.58
3.0	2.0	0.02	0.3	50	-	-	9.55
3.0	2.0	0.02	0.4	50	-	-	9.49
3.0	2.0	0.02	0.5	50	-	-	9.62
3.0	2.0	0.02	0.3	40	8.26	12.07	15.88
3.0	2.0	0.02	0.3	45	5.83	9.47	12.63
3.0	2.0	0.02	0.3	50	3.83	7.32	9.55
3.0	2.0	0.02	0.3	55	2.66	4.59	6.46
3.0	2.0	0.02	0.3	60	1.23	2.64	4.00

[Indole]	: 0.03 mol dm^{-3}	[H$^+$]	: 0.02 mol dm^{-3}
μ	: 0.3 mol dm^{-3}	[PMS]	: 0.002 mol dm^{-3}
C$_2$H$_5$OH	: 50% (V/V)		

Table 2 Effect of temperature on the reaction rate

Temperature (K)	k_2 (10^2 mol^{-1} dm^3 s^{-1})	SD
293	1.3546	±0.0032
298	2.1685	±0.0020
303	3.1358	±0.0079

Table 3 Thermodynamic parameters

Thermodynamic parameters of Oxidation of Indole		Activation Parameters
Energy of Activation (Ea)	kJmol^{-1}	62.0082
Enthalpy (ΔH$^\#$)	kJ mol^{-1}	59.489 ± 0.0831
Entropy (ΔS$^\#$)	J K^{-1} mol^{-1}	− 77.2600 ± 0.5014
Free Energy (ΔG$^\#$)	kJ mol^{-1}	36.9326 ± 0.4205

Temperature Effect

The effect of temperature on k' (s^{-1}) was studied in the range of 293–303 K and it was observed that when increase the temperature, the rate of the reaction also increased. The results are shown in (Table 2). The Arrhenius plot of log k_2 vs $1/T$ was linear. From the above plot, the values of energy of activation (E_a) were calculated (**Figure 5 and Table 3**). 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 [15].
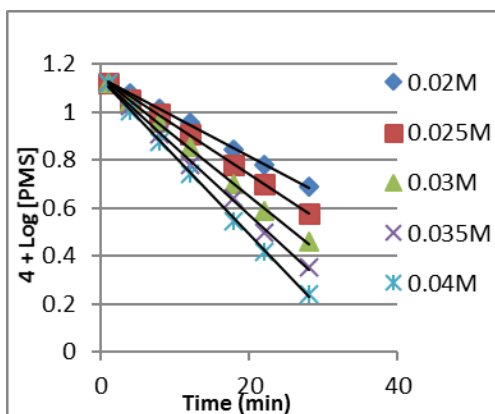
Figure 2 Variation of [Ind] @ 303 K
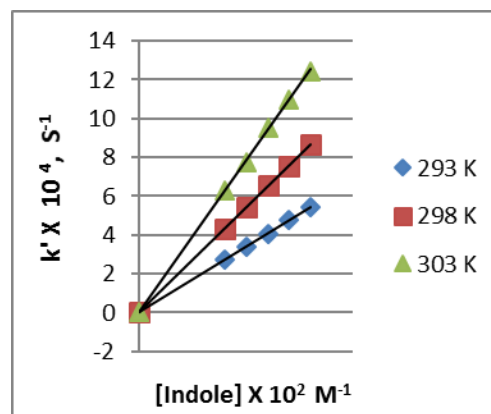
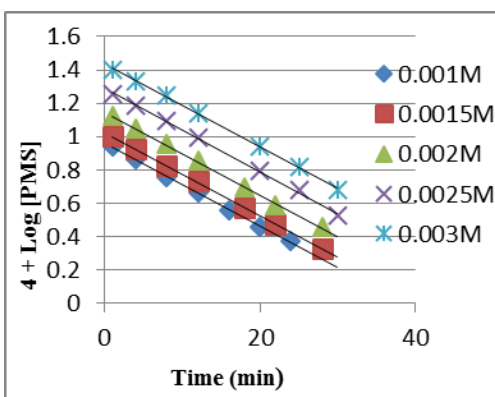

Figure 3 Evaluation of k_2
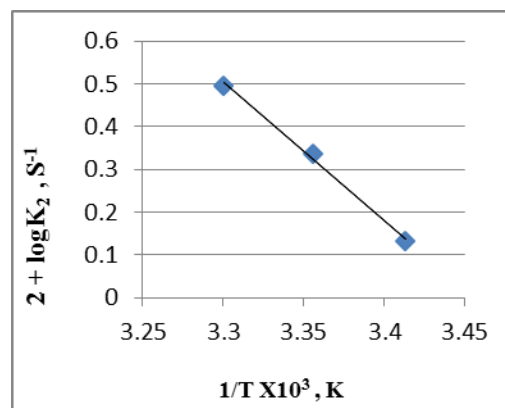

Figure 4 Variation of [PMS] @ 303 K

Figure 5 Evaluation of Ea

Stoichiometry

Solutions of Indole containing an excess of PMS were kept overnight at room temperature. Titrimetric estimation of the concentration of PMS consumed and assuming that all the Indole taken had reacted, the stoichiometry of Indole: PMS 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 [Indole] and [PMS], 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 PMS is given as follows:

-d [PMS]/dt = k_2 [PMS] [Indole]

Rate / [PMS] = k' (s^{-1}) = k_2 [Indole]

$k' = k_2$ [Indole], where k' = pseudo first order rate constant, k_2 = second order rate constant.

Mechanism

Based on the foregoing observations such as first-order dependence of rate each on [Indole], [PMS], zero-order dependence on [H$^+$], negligible effect of [μ], and the stoichiometry, the following mechanism (**Figure 6**) is suggested:
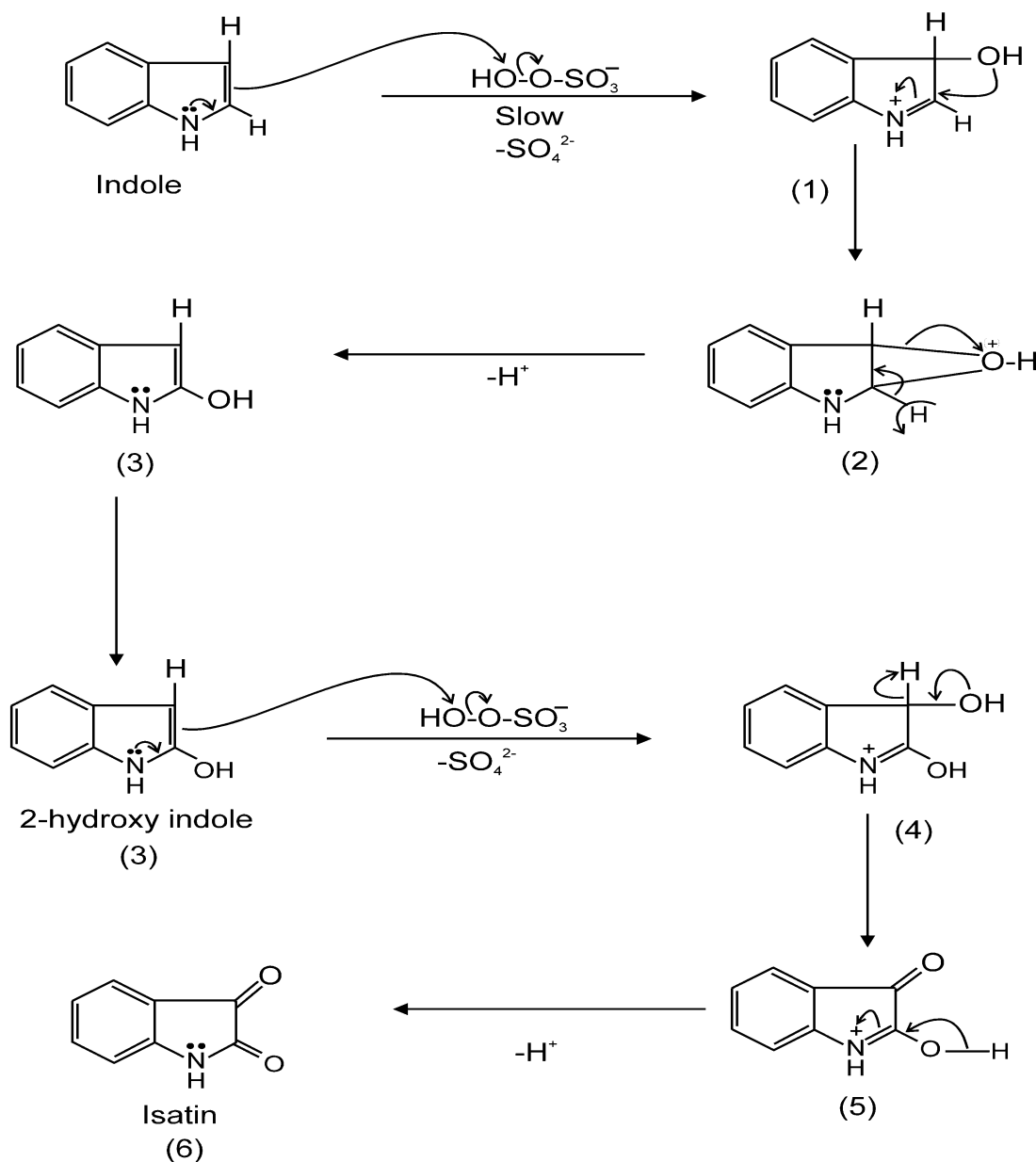
Figure 6

PMS ion is known to be a mild electrophilic reagent capable of substituting activated aromatic compounds. From our experimental results we suggest that the reaction proceeds through an electrophilic attack of the oxidant (PMS) at C-3 by a mechanism involving nucleophilic displacement of peroxide oxygen [16] to form Sulfuric acid mono-(3H-indol-3-yl) ester (**1**) as the rate determining step. Such a similar electrophilic attack on the C-3 of indoles is supported by earlier reports [16]. The compound (**1**) undergoes an intramolecular rearrangement to give 2-hydroxy-indole (**3**) through a cyclic intermediate (**2**). Infact, evidences for the involvement of a similar cyclic intermediate in the oxidations of *o*-benzoquinone [17], 3, 5-dimethyl-2, 6-diaryl 1-4-piperidones [18] and 2, 6-diphenyl-4-piperidones [19] by PMS were obtained. The second PMS ion attacks the compound **3** to form 2, 3-dihydroxy-indole (**4**) which gives isatin (**6**) has final products through the intermediate (**5**).

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 effect of ionic strength and $[H^+]$. From the data of the dielectric effect clearly reveals that the rate increases with decrease in the percentage of ethanol.

Acknowledgement

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