



**Kinetics and mechanism of electron transfer reactions:
Oxidation of pyridine by peroxomonosulphate in Aqueous acid medium**

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Abstract: Kinetic pathway of oxidation of pyridine by peroxomonosulphate in an aqueous acid medium has been studied. The reaction is second-order viz first-order dependence with respect to peroxomonosulphate and pyridine. Activation parameters have also been evaluated the activation energy (E_a) (49 ± 4) kJ mol^{-1} , and the entropy of activation $-(110 \pm 10) \text{ JK}^{-1} \text{ mol}^{-1}$. The derived Kinetic rate law accounts for experimental observations, and a plausible reaction mechanism has also been suggested.

Key Words: Kinetics, mechanism, pyridine, peroxomonosulphate, acid medium.

Introduction

Peroxomonosulphuric acid is considered mono-substituted hydrogen peroxide with the replacement of one of the hydrogens by the HSO_3^- group. The chemistry of peroxomonosulphuric acid is not much understood compared to that of peroxodisulphuric acid.

Peroxomonosulphuric acid¹ has a sulphur atom at the centre, which is tetrahedrally surrounded by a per hydroxyl group, a hydroxyl group and two oxo groups. The proton in HSO_3^- is highly acidic, whereas another proton is weakly acidic. Thus, the first proton is a sulphuric acid, and the second is a hydroxide proton. The acid is dibasic HSO_5^- . However, in the solution phase, it is reportedly forming an internal hydrogen bonding. In reactions of peroxodisulphate, typically, sulphate free radical is formed; thus, the reaction mechanism becomes a chain reaction mechanism. However, in the case of peroxomonosulphuric acid, despite the peroxide linkage²⁻⁴, no such free radical formation has been indicated. Therefore, reactions of peroxomonosulphuric acid are considered to be non-chain reactions.⁵⁻⁶

The title reaction was undertaken to attempt the kinetics of the reaction with the sole aim of understanding the role of peroxide linkage on the nitrogen nucleophile of pyridine.

Secondly, the attack of the oxidant on the pyridine⁷⁻⁸ nitrogen is an important observation in which the reaction yields the formation of pyridine N-oxide⁹⁻¹⁰ product in most of the reactions, particularly with those compounds having peroxide linkage. This aspect was much used to understand the mode of attack of peroxides on the nitrogen of pyridine.

Experimental

The reagents employed in this study were of pro analysed grade and used without further treatment.

The solution of peroxomonosulphate was prepared by dissolving the requisite amount of potassium salt of peroxomonosulphate in double distilled water. The solution is quite transparent and was standardized iodometrically¹¹. It is a double salt of the formula

2KHSO₅, KHSO₄, K₂SO₄ (Aldrich) and is known by its trade name 'OXONE'. The trace metal ions do not catalyse or inhibit the reactions. The solution of pyridine was also prepared in doubly distilled water. Doubly distilled water was employed for the preparation of the reagent solutions and also for kinetic work.

Kinetic procedure

The Kinetics of the reaction was monitored by allowing the reactions to occur in a water bath thermostated at $\pm 0.1^\circ\text{C}$ unless specified otherwise. The reactions were initiated by adding peroxomonosulphate solution of the desired concentration. The time was recorded when half of the peroxomonosulphate solution from the pipette was released into the reaction mixture. An aliquot of (5 cm³) was withdrawn periodically, and the concentration of remaining peroxomonosulphate was estimated iodometrically¹²⁻¹⁴.

The kinetics were carried out under pseudo-first-order conditions where the concentration of pyridine was sufficiently higher than that of the oxidant ($[\text{Py}] \gg [\text{PMS}]$).

Pseudo-first-order plots of $\log [\text{PMS}]_t$ versus time (t) were made. Second-order plots were made wherever concentrations of the reactants were comparable by plotting $\log \frac{[\text{Py}]_t}{[\text{PMS}]_t}$ versus time or $\log \frac{[\text{PMS}]_t}{[\text{Py}]_t}$ versus time. Rate measurements in triplicate were reproducible to within $\pm 6\%$.

Product Analysis

The oxidation product of pyridine was identified spectrophotometrically to be pyridine N-oxide as the λ_{max} of the spectrum corresponded closely to that of the standard spectrum of pyridine N-oxide.

Results

Peroxomonosulphate Dependence

The concentration of peroxomonosulphate (heretofore written as PMS) was varied from 1×10^{-3} to 5×10^{-3} mol dm⁻³ at fixed concentrations of pyridine to be 5×10^{-2} and 1.0×10^{-1} mol dm⁻³ respectively keeping pH constant to be 4.02 at 40 °C.

The pseudo-first-order plots were made (Fig.1), and the pseudo-first-order rate constants (k' , sec⁻¹) were calculated, independent of initial concentrations of peroxomonosulphate. This further justified the order with respect to the oxidant to be one.

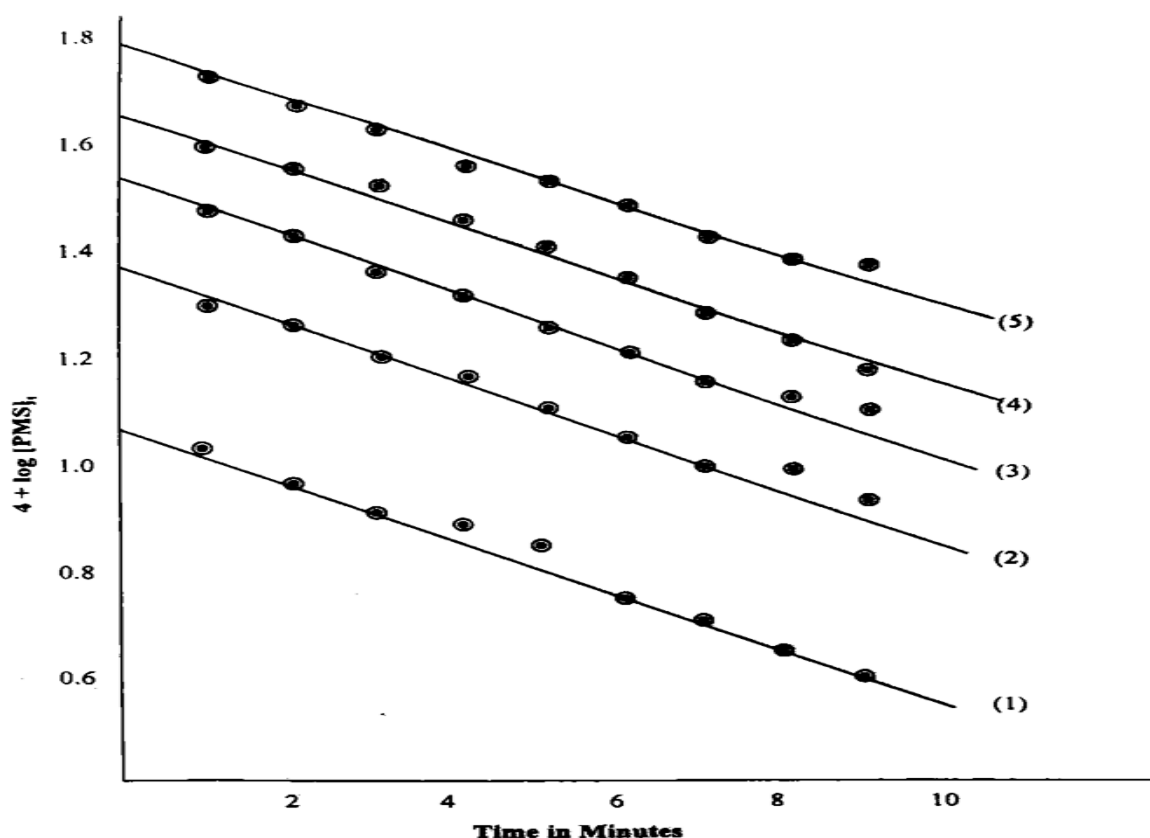


Fig.1 PSEUDO FIRST ORDER PLOTS

[Py]= 1.0×10^{-1} mol dm⁻³; pH = 4.02 and 45° C

[PMS] = (1) 1.0×10^{-3} mol dm⁻³; (2) 2.0×10^{-3} mol dm⁻³; (3) 3.0×10^{-3} mol dm⁻³;

(4) 4.0×10^{-3} mol dm⁻³; (5) 5.0×10^{-3} mol dm⁻³;

Pyridine Dependence

The concentration of pyridine was varied from 1.0×10^{-2} to 1.0×10^{-1} mol dm⁻³ at three different but fixed concentrations of [PMS]= 1×10^{-3} , 2×10^{-3} and 3×10^{-3} mol dm⁻³ respectively keeping other parameters of the reaction constant such as pH = 4.02 and 40 °C. A plot of pseudo-first-order rate constant (k' , sec⁻¹) against the concentration of pyridine yielded a straight line passing through the origin, indicating first order with respect to pyridine(Fig 2).

However, second-order plots were also made(Fig.3) wherever reaction conditions of the reactants were comparable; these second-order rate constants calculated from these plots and those calculated from pseudo-first-order rate constants are in agreement indicating an overall reaction to be second-order reactions.

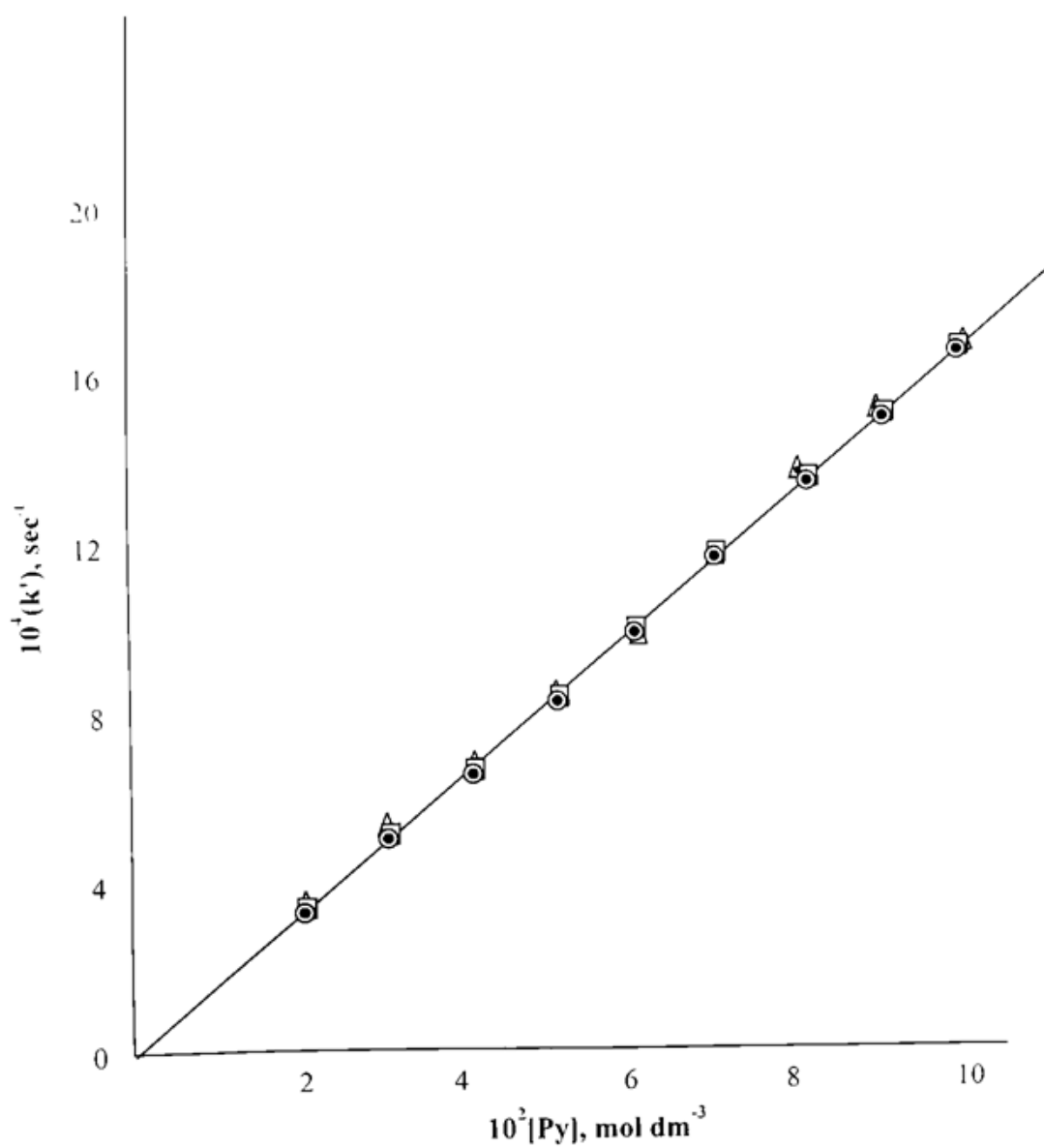


Fig. 2 VARIATION OF PYRIDINE

[PMS] \circ , $1 \times 10^{-3} \text{ mol dm}^{-3}$; Δ , $2 \times 10^{-3} \text{ mol dm}^{-3}$;

\blacksquare , $3 \times 10^{-3} \text{ mol dm}^{-3}$; pH = 4.02; and 40° C

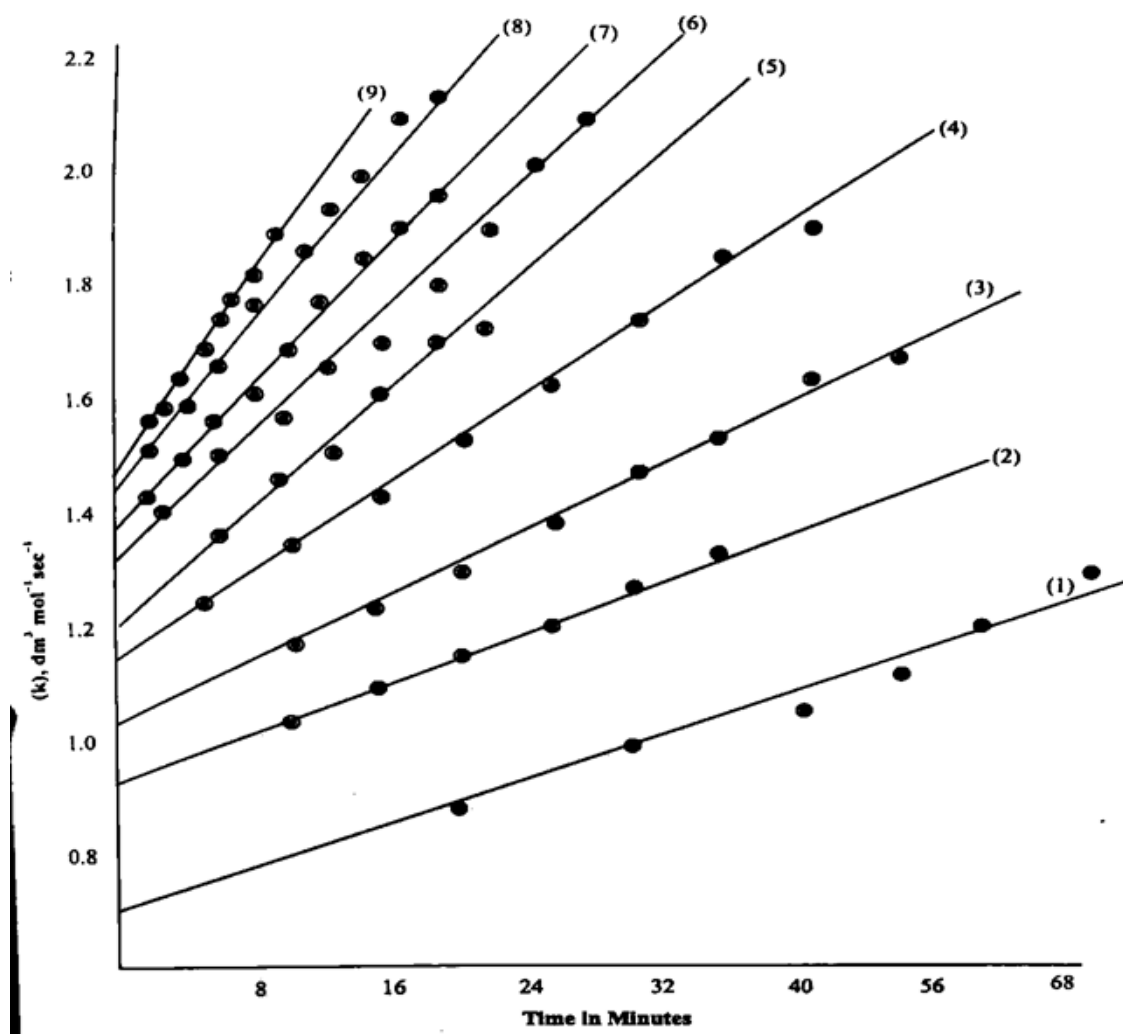


Fig. 3 SECOND ORDER PLOTS

[PMS] = 3×10^{-3} mol dm⁻³; pH = 4.02; and 40° C

[Py] = (1) 2×10^{-2} mol dm⁻³; (2) 3×10^{-2} mol dm⁻³; (3) 4×10^{-2} mol dm⁻³;

(4) 5×10^{-2} mol dm⁻³; (5) 6×10^{-2} mol dm⁻³; (6) 7×10^{-2} mol dm⁻³;

(7) 8×10^{-2} mol dm⁻³; (8) 9×10^{-2} mol dm⁻³; (9) 10×10^{-2} mol dm⁻³;

Effect of Ionic Strength (I)

The effect of ionic strength was studied by employing NaNO₃ and lithium perchlorate, respectively, at fixed concentrations of other reaction ingredients viz [PMS] = 2.0×10^{-3} mol dm⁻³, [Py] = 5.0×10^{-2} mol dm⁻³; pH = 4.02 and 40° C.

The pseudo-first-order rate constants were found to be independent of ionic strength.

pH Dependence

The pH variation was made keeping fixed concentrations of sodium acetate with the variation of the concentration of acetic acid from pH 2.8 to 4.74 at fixed concentrations of other ingredients, $[PMS]=2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Py] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ at three temperatures such as 35, 40 and 45° C respectively.

The pseudo-first-order rate constant increases with increasing pH, as is evident from Fig. (4). In order words rate decreases with increasing hydrogen ion concentration Fig. (5).

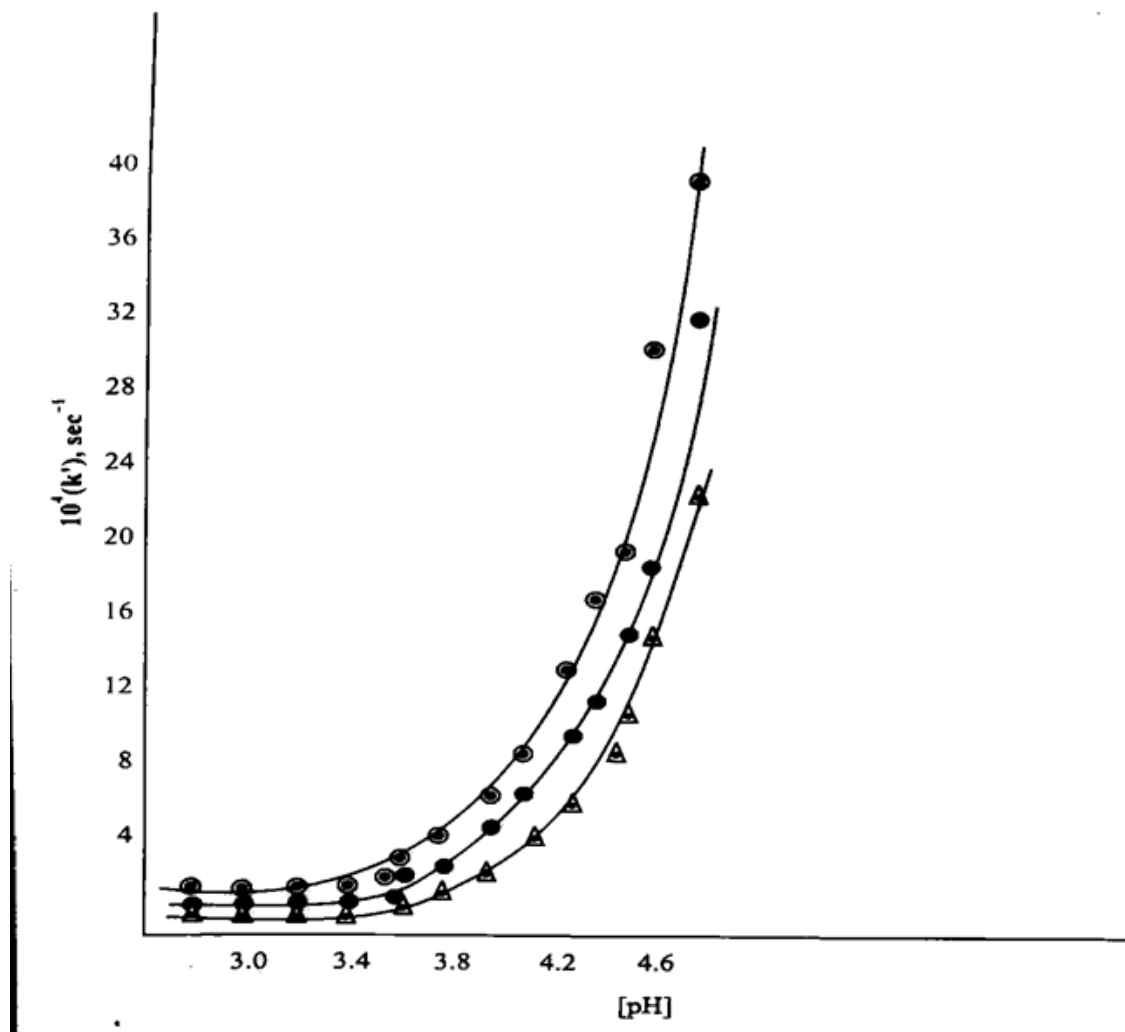


Fig. 4 A PLOT OF $[k']$ VERSUS $[pH]$

$[Py] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $[PMS] = 2 \times 10^{-3} \text{ mol dm}^{-3}$

and Δ , 35° C ; \bullet 40° C ; \circ , 45° C

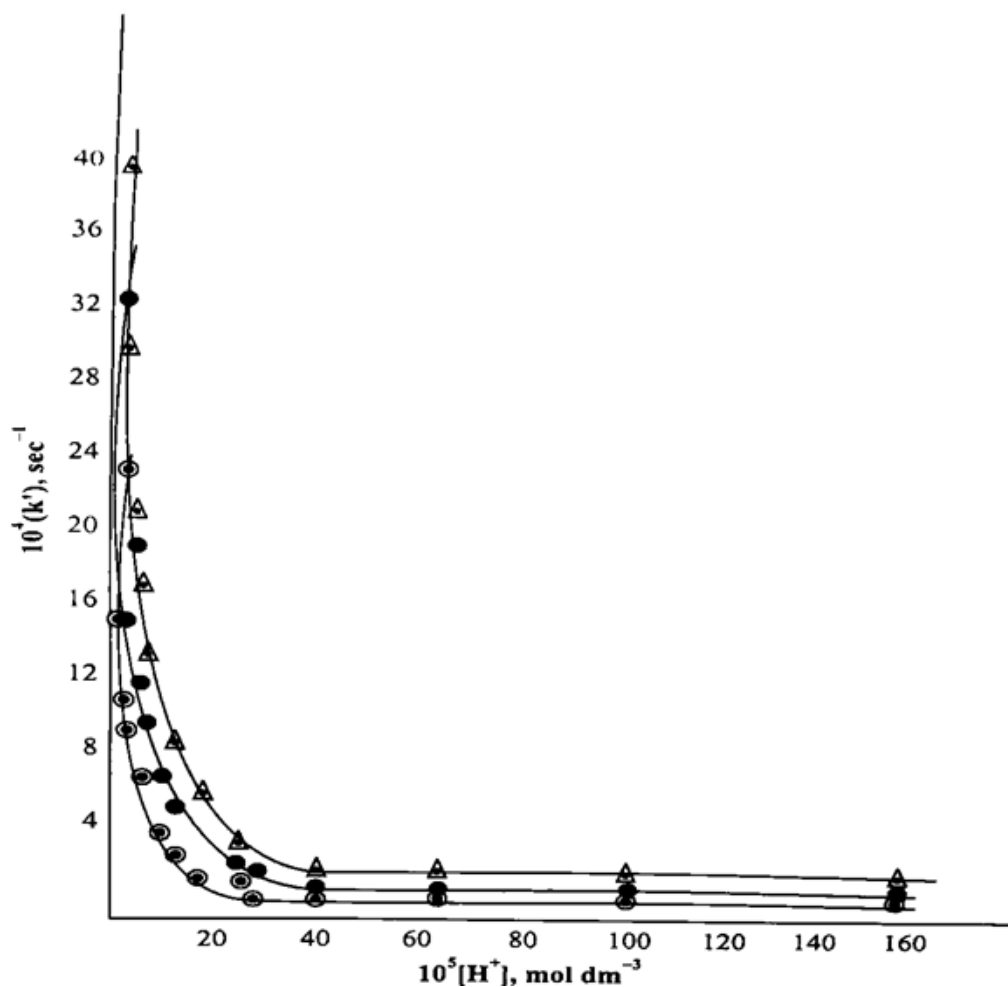


Fig. 5 VARIATION OF HYDROGEN ION

$$[\text{Py}] = 5 \times 10^{-2} \text{ mol dm}^{-3}; [\text{PMS}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

and ○, 35° C; ● 40° C; △, 45° C

Temperature Dependence

The effect of temperature was studied at fixed concentrations of the reaction components viz $[\text{PMS}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Py}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{pH} = 4.02$ at three temperatures such as 35, 40 and 45° C respectively.

A plot of $\log k (\text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1})$ versus $[T]^{-1}$ was made that yielded a straight line as in Fig.(6) The activation energy (E_a) was calculated to be $(49 \pm 4) \text{ kJ mol}^{-1}$, and the entropy of activation was calculated in a conventional manner to be $-(110 \pm 10) \text{ JK}^{-1} \text{ mol}^{-1}$.

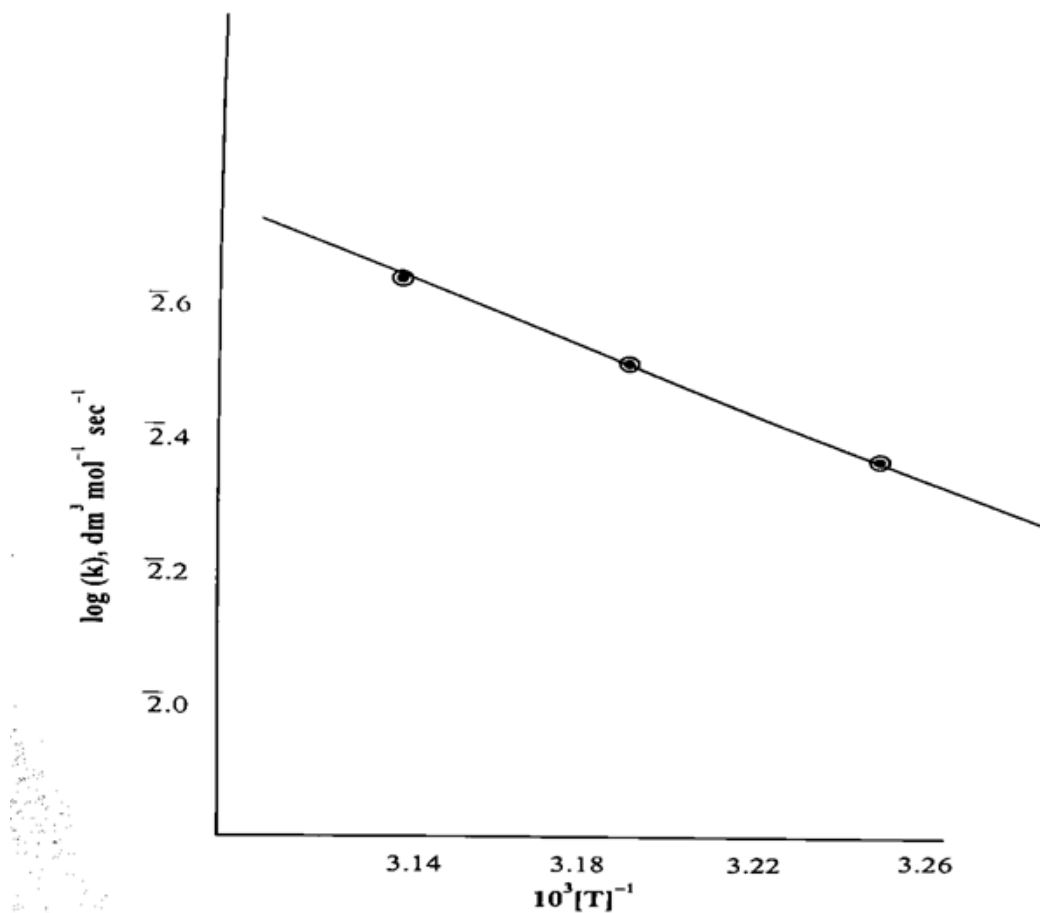


Fig. 6 A PLOT OF LOG[k] VERSUS $[T]^{-1}$

$[\text{Py}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{PMS}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{pH}] = 4.02$

Discussion

Peroxomonosulphate reactions are usually non-chain reactions. Considering the pH of the reaction in the reaction mixtures, peroxomonosulphate should mainly exist in the form of HSO_5^- . The species SO_5^{2-} is not expected in such a medium. However, pyridine is in the form of protonated pyridinium ion. Since the ionic strength does not affect the reaction rate, the reaction of the species of like charges is not expected. If this is taken into account, the following reaction mechanism can be suggested for this reaction:



The loss of peroxomonosulphate leads to the following rate law

$$-\frac{d[PMS]}{dt} = \frac{k \cdot K_1 [PMS][Py]}{[H^+] + K_1} \quad (3)$$

Where [Py] and [PMS] are the gross analytical concentrations of pyridine and peroxomonosulphate respectively.

Since $[H^+] \gg K_1$ the rate equation (3) reduces to the equation (4) of (5)

$$-\frac{d[PMS]}{dt} = \frac{k \cdot K_1 [PMS][Py]}{[H^+]} \quad (4)$$

$$\text{or } k = -\frac{d[PMS]}{dt} / [PMS][Py] = \frac{k \cdot K_1}{[H^+]} \quad (5)$$

A plot of 'k' versus $[H^+]$ was made that yielded as straight line passing through the origin at lower pH of the reaction mixture (Fig. 7).

However, at higher $[H^+] \ll k_1$, and the rate equation (3) changes to equation (6).

$$-\frac{d[PMS]}{dt} = k' [PMS][Py] \quad (6)$$

Or

$$k = k'$$

Where, k is an observed second order rate constant. These rate constants are collected in Table 1.

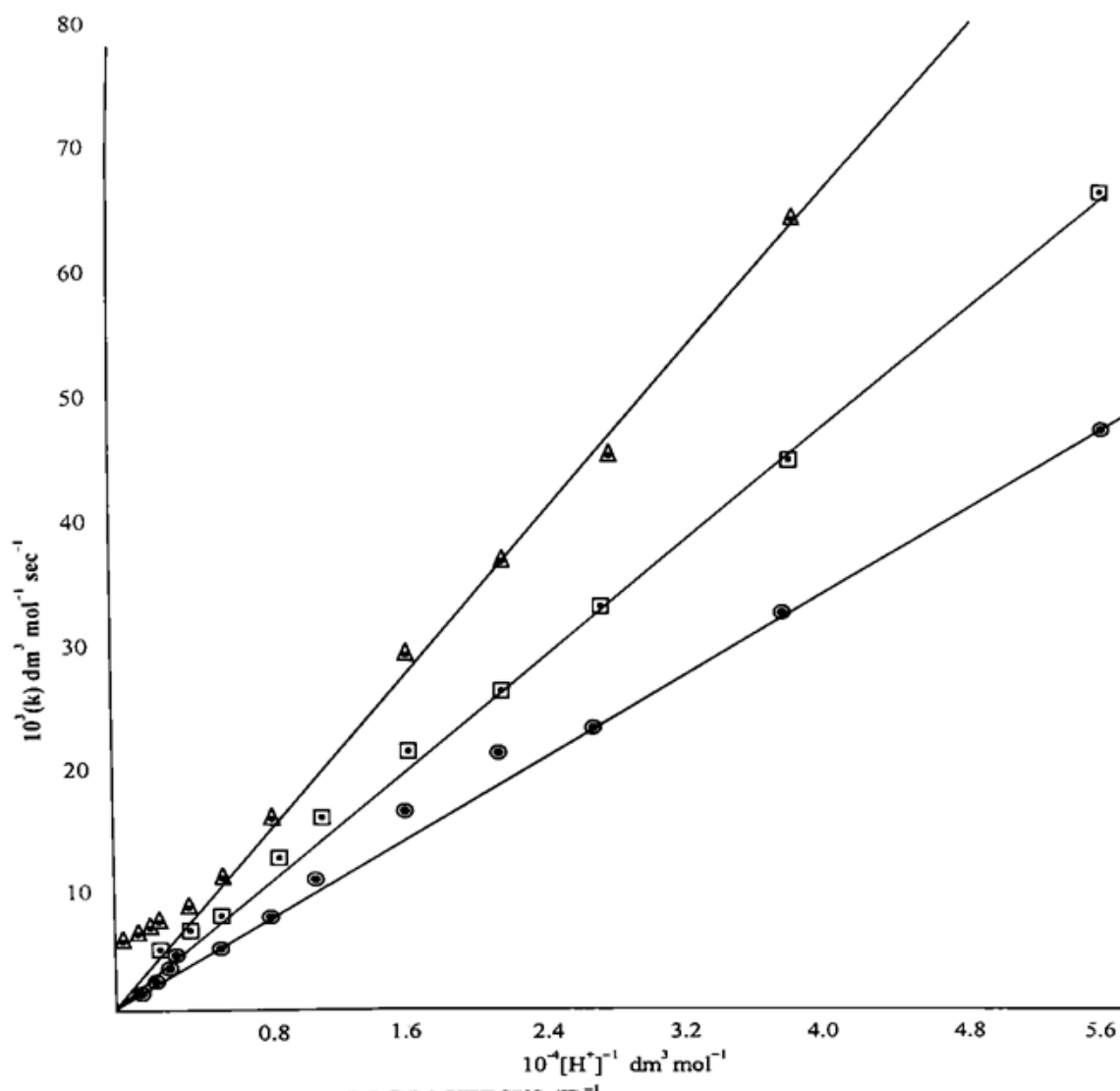


Fig. 7 A PLOT OF LOG[k_i] VERSUS [T]⁻¹

[Py] = 5 x 10⁻² mol dm⁻³; [PMS] = 2 x 10⁻³ mol dm⁻³

and ○, 35° C; ●, 40° C; Δ, 45° C

So far as the mode of electron transfer from pyridine to peroxomonosulphateos concerned, the following transition state suffice the purpose.

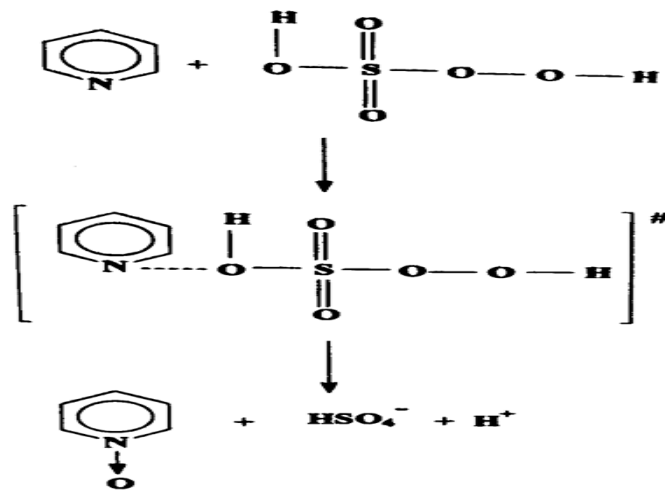


TABLE 1

Pseudo first order rate constants (k' , sec^{-1}) and second order rate constants (k , $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$) in the reaction of peroxomonosulphate and pyridine in acidic medium.

pH=4.02, 40 °C

$10^3[\text{PMS}]$ mol dm^{-3}	$10^2[\text{Py}]$ mol dm^{-3}	$10^4[k']$ sec^{-1}	$10^2[k]$ $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$
1.0	5.0	8.44	1.70(1.68)
2.0	5.0	8.44	1.70(1.68)
3.0	5.0	8.44	1.70(1.68)
4.0	5.0	8.44	1.70(1.68)
5.0	5.0	8.44	1.70(1.68)
1.0	10.0	17.2	1.76(1.72)
2.0	10.0	17.2	1.76(1.72)
3.0	10.0	17.2	1.76(1.72)
4.0	10.0	17.2	1.76(1.72)
5.0	10.0	17.2	1.76(1.72)
1.0	2.0	3.45	1.70(1.72)
1.0	3.0	5.18	1.78(1.72)

1.0	4.0	6.90	1.72(1.72)
1.0	5.0	8.63	1.75(1.72)
1.0	6.0	10.2	1.76(1.70)
1.0	7.0	12.1	1.74(1.72)
1.0	8.0	13.9	1.72(1.73)
1.0	9.0	15.3	1.74(1.70)
1.0	10.0	17.2	1.76(1.72)
2.0	2.0	3.45	1.70(1.72)
2.0	3.0	5.18	1.78(1.72)
2.0	4.0	6.90	1.72(1.72)
2.0	5.0	8.63	1.75(1.72)
2.0	6.0	10.2	1.76(1.70)
2.0	7.0	12.1	1.74(1.72)
2.0	8.0	13.9	1.72(1.73)
2.0	9.0	15.3	1.74(1.70)
2.0	10.0	17.2	1.74(1.72)

3.0	2.0	3.45	1.76(1.72)
3.0	3.0	5.18	1.79(1.72)
3.0	4.0	6.90	1.76(1.72)
3.0	5.0	8.63	1.71(1.72)
3.0	6.0	10.2	1.79(1.70)
3.0	7.0	12.1	1.71(1.72)
3.0	8.0	13.9	1.74(1.73)
3.0	9.0	15.3	1.76(1.70)
3.0	10.0	17.2	1.78(1.72)

Figures in parentheses were obtained from pseudo first order rate constants.

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