

# **CHAPTER V**

## **Kinetics of Oxidation of Indole by Chloramine-T**

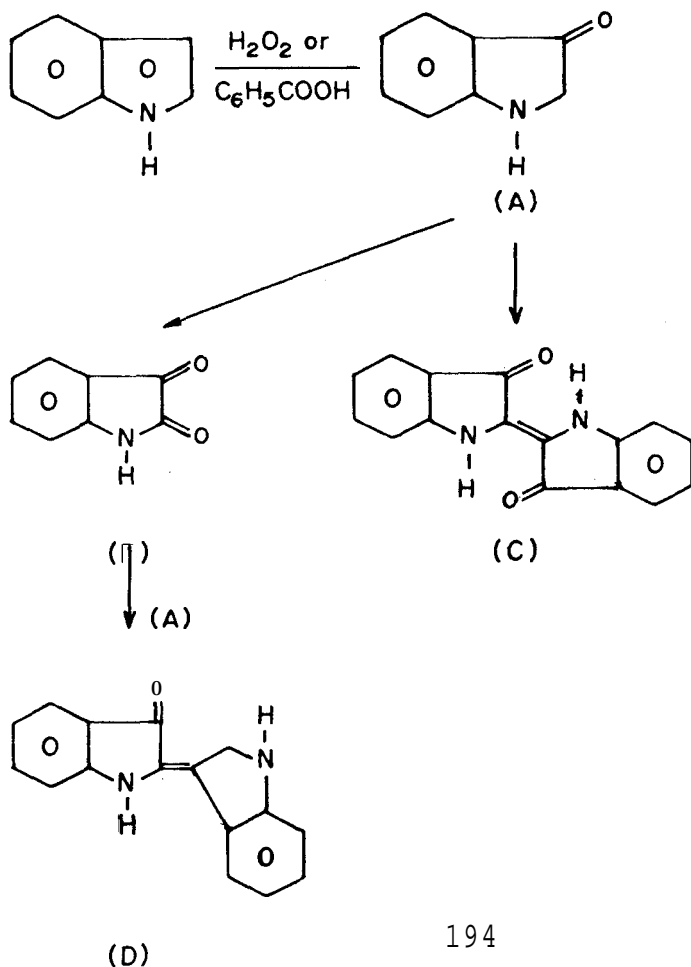
## GENERAL INTRODUCTION

Indole was first prepared by heating oxindole with Zn dust. Indole is a non-basic nitrogenous compound in which a benzene ring and a pyrrole nucleus are fused together in 2,3-positions of the pyrrole ring. Indole possesses an unpleasant odour when impure; the pure material has pleasant fragrance and is found in both natural and synthetic perfumes. Indole is a colorless, crystalline solid, melting at  $52^{\circ}\text{C}$  and boiling at  $254^{\circ}\text{C}$ . It is volatile with steam, soluble in benzene, ether and ligroin and may be recrystallized from water.

Indole is used in compounding perfumes and in the manufacture of tryptophan and indole acetic acid. The number of indole derivatives occurring in nature is legion, and many of them have high physiological potency. The importance of indoles in industry centres around the synthetic halogenated indigos (durable dyes, used principally for cellulose fabrics), and a valuable intermediate especially for synthesis of the derivatives of benzene and quinoline.

## OXIDATION OF INDOLE-A REVIEW

Indole is readily oxidised by a variety of reagents. The extent of oxidation depends upon the particular reagent and experimental condition, but indoxyl is frequently observed as an intermediate in the processes. Thus  $H_2O_2$  or perbenzoic acid converts indole to indoxyl (A) and thence to indigo (C) plus a small amount of indirubin (D). The last compound is presumably formed by condensation of indoxyl with the byproduct isatin (B)



Sodium perborate in acetone oxidizes **indole** to a mixture of indigo and leucoindigo, whereas alkaline persulphate affords indoxyl-O-sulphate (**indican**). Oxidative cleavage of **indole** is obtained by  $MnO_2$  or  $O_3$  which furnish **2-formamido benzoic acid** and **2-formamidobenzaldehyde** respectively.

Enzymatic oxidation of **indole** has attracted the attention of chemists for the past several decades. The metabolic oxidation of **indole** to indoxyl was attempted by Laroche and Desbordes<sup>155</sup>. **Indole** has been oxidized by sodium perborate<sup>156</sup> in presence of acetone and methyl paraoxone as promoter. The reaction rate was determined by measuring the intensity of fluorescence of the intermediate oxidation products of **indole** (indoxyl and indigo white). The reaction was found to obey **Michaelis-Menten** kinetics with respect to the substrate. The degree of oxidisability and their first order kinetics of a number of organic nitrogen compounds has been studied by Chudoba<sup>157</sup>. He found that **aminic**, quinolinic, pyrrolic, pyrrolidinic and indolic nitrogen split off as  $NH_3$ . Nitrogen from **imidazole** and pyrimidine rings splits off as ammonia and nitrogen.

Enzymatic oxidation of **indole** to oxindole by peroxide catalyzed by chloroperoxidase has been investigated by Corbett et al<sup>158</sup>. Oxidation kinetics were first order with respect to **indole upto 8mM**, which was the highest concentration of **indole** that could be investigated. On the

other hand, Z-methyl indole was not affected by  $H_2O_2$  and chloroperoxidase, but its presence inhibited the indole oxidation to a great extent. The isomer l-methyl indole was a poor substrate for chloroperoxidase oxidation, and a weak inhibitor of indole oxidation. These results suggest the possibility that chloroperoxidase oxidation of the carbon atom adjacent to the nitrogen atom in part results from hydrogen bonding of the substrate N-H to the enzyme active site.

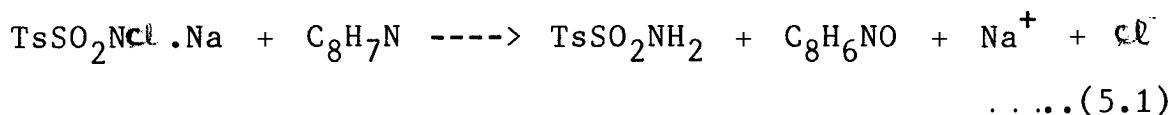
### SECTION-5.3

#### KINETICS OF OXIDATION OF **INDOLE** BY CHLORAMINE-T IN **NaOH** MEDIUM CATALYSED BY **OsO<sub>4</sub>**.

This section deals with the results of oxidation of indole (In) and its derivatives 5-chloro, 5-bromo and 5-methoxy indoles. As indole is less soluble in water, a 10% methanolic content (v/v) was maintained in the reaction mixture. For substituted indoles methanolic content of 30%(v/v) was maintained in the reaction mixture, as it was not homogeneous in 10% methanolic solution. Oxidation of methanol during the experimental period was taken into account while calculating the pseudo first order rate constants.

#### Stoichiometry

Reaction mixtures with varying amounts of known excess of CAT over indole in presence of NaOH and OsO<sub>4</sub> were equilibrated at 30 C for 24 hours. Determination of unreacted CAT in the reaction mixtures showed that every mole of indole consumed one mole of CAT, conforming to the following stoichiometry:



The reaction was made slightly acidic by adding dilute HCl and was diluted with water, when TsSO<sub>2</sub>NH<sub>2</sub> was

precipitated in bulk. The remaining  $\text{TsSO}_2\text{NH}_2$  in the reaction mixture was salted out. Then the reaction mixture was extracted with chloroform and the extract was evaporated to give a brown solid residue. The residue (four products, TLC) was subjected to column chromatography on silica gel (60-200 mesh) using gradient elution (dichloromethane to acetone). Of the four products, only two were in significant amount:

1) p-toluenesulphonamide, recrystallised from dichloromethane/petroleum ether (m.p.134-135.5°C) known m.p.137-140°C. Rf value (0.84) determined from TLC ( $\text{CH}_2\text{Cl}_2$ ).

2) Oxindole - recrystallised from dichloromethane/petroleum ether (m.p.118 - 120°C), known m.p.125 -127°C. Rf value (0.13) determined from TLC ( $\text{CH}_2\text{Cl}_2$ ). The IR (KBr) spectrum shows characteristic bands ( $\text{cm}^{-1}$ ) at 3217 (N-H stretch), 3070 and 3032 (aromatic C-H stretch), 2925 (aliphatic C-H stretch), 1701 (C=O stretch), 1619 (C=C stretch), 1473, 1333, 1234, 749, 674 and 552  $\text{cm}^{-1}$ .  $^1\text{H}$  spectrum ( $\text{CDCl}_3$ );- (relative to TMS); 7.22 - 6.83 (m,4H, aromatic C-H), 3.54 (s,2H aliphatic C-H) and 1.71 (s,1H, N-H).

Mass spectrum :- m/e: 133( $\text{M}^+$ ), 104( $\text{M}^+ - \text{CHO}$ ), 78( $\text{M}^+ - \text{C}_2\text{HNO}$ ), 77, 51 and 36.

## Results

The kinetics of oxidation of indole by CAT was investigated at several initial concentrations of the

reactants at constant temperature and ionic strength. The reaction was studied in two ranges.

(i) Low concentration of alkali and **indole**.

$[In]_0 = 8 \times 10^{-4}$  to  $80 \times 10^{-4}$  mol  $dm^{-3}$ ;  $[NaOH] = 8 \times 10^{-4}$  to  $40 \times 10^{-4}$  mol  $dm^{-3}$ .

(ii) High concentration of alkali and **indole**.

$[In]_0 = 30 \times 10^{-4}$  to  $150 \times 10^{-4}$  mol  $dm^{-3}$ ,  
 $[NaOH] = 25 \times 10^{-4}$  to  $100 \times 10^{-4}$  mol  $dm^{-3}$ .

This section deals with the results of oxidation of **indole** in range (i).

#### Effect of reactants

At constant  $[OH^-]$  with substrate in excess, plots of  $\log[CAT]$  Vs time were linear (Table -5.1, Fig -5.1) indicating a first order dependence of rate on  $[oxidant]_0$ . Values of pseudo-first order rate constants ( $k'$ ) are given in Table -5.2. The rate increases initially with increase in  $[In]$ , which levels off at higher  $[In]$ , [Table -5.3, Fig 5.2]. Plot of  $\log k'$  Vs  $\log [In]_0$  was linear ( $r=0.9919$ ,  $s=0.05$ ) with unit slope.

#### Effect of $[OH^-]$

At constant concentrations of CAT and In, the rate was found to be independent of  $[OH^-]$  (Table - 5.4).

#### Effect of $[OsO_4]$

The rate increased with increase in concentration of

$\text{OsO}_4$ , (Table -5.5). Plot of  $\log k'$  Vs  $\log[\text{OsO}_4]$  was linear ( $r=0.9955$ ,  $s=0.04$ , Fig - 5.3) with unit slope.

#### Effect of $[\text{Cl}^-]$

Addition of chloride ions in the form of  $\text{NaCl}$ , had no effect on the rate (Table - 5.6).

#### Effect of [p - toluenesulphonamide]

Addition of the reduced product, p-toluenesulphonamide had no effect on the rate (Table - 5.7).

#### Effect of ionic strength

The effect of varying the ionic strength of the medium by adding a concentrated solution of  $\text{NaClO}_4$  did not alter the rate of the reaction (Table - 5.8).

#### Effect of dielectric constant of the medium on the rate.

Rate studies were made in water-methanol mixtures of varying compositions. The rate decreased with increase in methanol content of the reaction mixture (Table - 5.9). Plot of  $\log k'$  Vs  $1/D$  gave a straight line ( $r=0.9923$ , Fig - 5.4) with negative slope. Blank experiments with methanol, however showed that there is slight decomposition of solvent (~2%) under experimental conditions. This was allowed for in the calculation of the net reaction rate constant for the oxidation of indole.

### **Effect of temperature**

The reaction was studied at different temperatures (298.7 to 310.6K) (Table - 5.10). From the Arrhenius plots of  $\log k'$  Vs  $1/T$  ( $r=0.9850$ , Fig-5.5), kinetic and thermodynamic parameters were evaluated (Table - 5.11).

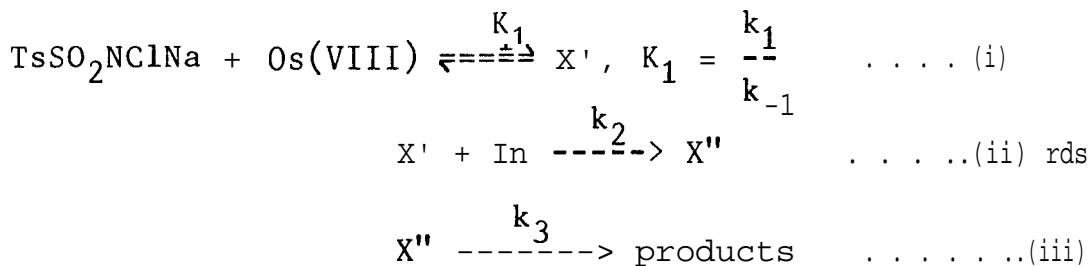
### **Test for free radicals.**

Addition of reaction mixture to aqueous acrylamide did not initiate polymerization showing the absence of free radical species.

## Discussion

Chloramine-T acts as an oxidising agent in both acidic and alkaline media. In general CAT undergoes a two electron change in its reaction, the products being p-toluene-sulphonamide (PTS) and sodium chloride. The reduction potential of CAT/PTS is pH dependent and decreases with increase in pH of the medium, having values of 1.14 V at pH 0.65 and 0.5 V at pH 12. Depending on the pH of the medium, CAT furnishes different types of reactive species in solution such as  $\text{TsSO}_2\text{NHCl}$ ,  $\text{TsSO}_2\text{NCl}_2$ ,  $\text{HOCl}$  and possibly  $\text{H}_2\text{OCl}^+$  in acid solutions, as well as  $\text{TsSO}_2\text{NHCl}$  and  $\text{OCl}^-$  ions in alkaline solution. It has been suggested that the reactivity of CAT in weakly alkaline solutions is due to the formation of conjugate acid  $\text{TsSO}_2\text{NHCl}$  from  $\text{TsSO}_2\text{NCl}^-$  in a base retarding step. Therefore the possible oxidant species of CAT in alkaline solutions are  $\text{TsSO}_2\text{NHCl}$  and  $\text{OCl}^-$ .

The observed first order dependence of rate on  $[\text{CAT}]_0$  and nearly first order in  $[\text{Indole}]$  which becomes zero at higher  $[\text{Indole}]$  and the rate independence of  $[\text{OH}^-]$  can be explained by Scheme - 5.1.



Scheme -5.1

According to Scheme - 5.1, rate =  $k_2 [X'] [In]$  . . . (5.2)

Assuming steady state for  $[X']$ , we get

$$\frac{d[X']}{dt} = k_1 [CAT][Os(VIII)] - k_{-1} [X'] - k_2 [X'] [In] = 0$$

$$\text{or } [X'] = \frac{k_1 [CAT][Os(VIII)]}{k_{-1} + k_2 [In]} \quad \dots (5.3)$$

Substituting for  $[X']$  in equation (5.2), we get

$$\text{rate} = \frac{k_2 k_1 [CAT] [Os(VIII)] [In]}{k_{-1} + k_2 [In]} \quad \dots (5.4)$$

At low  $[In]$ ;  $k_2 [In] \ll k_{-1}$  and hence

$$\text{rate} = K_1 k_2 [CAT] [Os(VIII)] [In] \quad \dots (5.5)$$

Equation (5.5) accounts for the first order each in  $[CAT]$ ,  $[Os(VIII)]$  and  $[In]_0$ . When  $[In]$ , is increased,

$k_2 [In]_0 \gg k_{-1}$  and

$$\text{rate} = k_1 [CAT] [Os(VIII)] \quad \dots (5.6)$$

The negative dielectric effect observed, confirms the dipole-dipole nature of the rate limiting step in the reaction sequence. Further the mechanism is supported by the low enthalpy of activation. The value of  $\Delta S^\ddagger$  shows that there is the formation of a more ordered transition state.

The activation enthalpies and entropies of oxidation of indole and substituted indoles are linearly related by plotting  $\Delta H^\ddagger$  Vs  $\Delta S^\ddagger$  ( $r=0.9999$ , Fig-5.6). From the slope, the computed value of isokinetic temperature ( $\beta$ ) is 325 K.

Further verification of the isokinetic relation was done by Exner criterion in which  $\log k'_{248.7}$  Vs  $\log k'_{310.6}$  is plotted. This results in a straight line ( $r=0.9964$ , Fig 5.6) from which  $T$  is 325 K. The values of  $\beta$  from both the plots are higher than the experimental temperature (303 K) indicating enthalpy as a controlling factor. The linear correlation and the consistency of  $\Delta G^\ddagger$  values (Table-5.11) indicate that **indoles** (substituted) undergo oxidation via the same mechanism.

The detailed mechanism of oxidation of **indole** and substituted **indoles** by CAT catalyzed by  $\text{OsO}_4$  in alkaline medium is shown in Scheme 5.2.  $\text{Os(VIII)}$  exists<sup>159</sup> in alkaline medium as  $[\text{OsO}_4(\text{OH})]^-$  which on further coordination with  $\text{OH}^-$  gives  $[\text{OsO}_4(\text{OH})_2]^{2-}$ . Since the reactions were carried out under comparable conditions of alkalinity and there is independence of  $[\text{OH}^-]$  in the oxidation of **indole** and substituted **indoles**, it is unlikely that  $[\text{OsO}_4(\text{OH})_2]^{2-}$  reacts with the substrate. CAT first coordinates with  $\text{OsO}_4$ , activating chloramine-T via stabilization of the nitrogen's anionic charge and polarizing the nitrogen-chlorine band. In basic solution,  $\text{OsO}_4$  is known to bind with one or even two hydroxide anion(s). Hence in this case the hydroxide anion(s) can be replaced by CAT. Then, the base catalyzed **indole** chlorination via activated chloramine-T ( $\text{X}'$ ) affords **3-chloroindolenine** and a nitrogen-protonated

chloramine-T/osmium tetroxide complex (both of which constitute the complex X'' in Scheme - 5.1). Hydration of nitrogen-protonated chloramine-T/osmium tetroxide complex results in p-toluenesulphonamide and a hydroxide anion/osmium tetroxide complex. Hydration of 3-chloroindolenine to 3-chloro 2-hydroxy indolenine followed by base catalyzed removal of hydrogen chloride affords 2-hydroxy indole, which is in equilibrium with its more stable keto form oxindole. The low sensitivity of  $k_2'$  (second order rate constant Table 5.11) to ring substituents indicates significant bond formation between the substrate and the oxidant in the rate limiting step. A plot of  $\log k'$  Vs  $\sigma_P$ , the Hammett parameter for the ring substituents of substituted **indoles** is shown in Fig-5.7. The Hammett correlations <sup>160,161</sup> were fitted with the  $\sigma = \sigma_1 + \sigma_{R\text{-scale}}$ . The observed sensitivity to ring substituents for this reaction is  $\rho^+ = -1.0$ . It can also be seen in Table - 5.11, that the rate decreases as the ring substituent becomes more electron withdrawing.

Table - 5.1, Fig - 5.1

Effect of oxidant concentration on the rate  
(representative run).

$[In]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OH^-] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ , MeOH = 10% (v/v),  
 $\mu = 0.5 \text{ mol dm}^{-3}$ , temp :  $29.4^\circ\text{C}$ .

Time in min	Titre value ml.	log (a-x)
0	12.0	1.08
31	9.9	1.00
60	8.4	0.92
100	6.2	0.79
140	4.7	0.67
180	3.4	0.53

Table - 5.2

Effect of oxidant concentration on the rate  
(consolidated table).

$[In]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OH^-] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ , MeOH = 10% (v/v),  
 $\mu = 0.5 \text{ mol dm}^{-3}$ , temp:  $29.4^\circ\text{C}$ .

$[CAT]_0 \times 10^4$ mol $\text{dm}^{-3}$	$k' \times 10^5 \text{ s}^{-1}$
6.0	9.88
7.0	9.57
7.5	9.20
8.0	9.37
8.5	10.01
9.0	9.40
10.0	9.18

Table - 5.3, Fig. 5.2

Effect of concentration of indole on the rate of reaction

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[NaOH] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $MeOH = 10\% (v/v)$ ,  $\mu = 0.5 \text{ dm}^{-3}$ ,  
temp:  $29.4^\circ C$ .

$[In], \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
8.0	2.98
10.0	4.00
20.0	7.39
25.0	9.37
30.0	10.68
40.0	12.76
50.0	15.98
60.0	15.76
80.0	15.84

Table - 5.4

Effect of sodium hydroxide concentration on the rate of reaction

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $MeOH = 10\% (v/v)$ ,  
 $\mu = 0.5 \text{ mol dm}^{-3}$ , temp:  $29.4^\circ C$ .

$[OH^-] \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
8.0	9.98
10.0	10.10
20.0	9.37
25.0	10.06
30.0	10.07
40.0	10.07

Table - 5.5, Fig - 5.3

Effect of osmium tetroxide concentration on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{OsO}_4] \times 10^6$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
3.93	1.74
7.86	4.07
11.78	6.46
15.70	9.37
19.62	12.56
23.60	13.75
31.40	16.95

Table - 5.6

Effect of chloride ion concentration on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{OsO}_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}.$$

$$\text{MeOH} = 10\% \text{ (v/v)}, \mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{NaCl}] \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
1.0	11.10
5.0	10.99
8.0	10.85

Table - 5.7

Effect of p-toluenesulphonamide (PTS) concentration on the rate

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 $[NaOH]_0 = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4]_0 = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ .  
 MeOH = 10% (v/v),  $\mu = 0.5 \text{ mol dm}^{-3}$ , temp: 29.4°C.

[PTS] x 10 <sup>4</sup> mol dm <sup>-3</sup>	k' x 10 <sup>5</sup> s <sup>-1</sup>
0.0	9.37
1.0	9.17
3.0	9.45
5.0	9.17

Table - 5.8

Effect of ionic strength on the reaction

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[NaOH]_0 = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4]_0 = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ .  
 MeOH = 10% (v/v),  $\mu = 0.5 \text{ mol dm}^{-3}$ , temp: 29.4°C.

Ionic strength mol dm <sup>-3</sup>	k' x 10 <sup>5</sup> s <sup>-1</sup>
0.5	9.37
0.75	9.45
1.0	9.52

Table - 5.9, Fig - 5.4

Effect of varying dielectric constant on the rate

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[NaOH] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}$ .  
 $\mu = 0.5 \text{ mol dm}^{-3}$ , temp:  $29.4^\circ\text{C}$ .

Methanol % v/v	D	$10^2/D$	$k' \times 10^5 \text{ s}^{-1}$
10	72.37	1.38	9.37
15	69.93	1.43	8.51
20	-67.48	1.48	6.76
30	62.71	1.60	3.96

Table - 5.10, Fig - 5.5

Effect of temperature on the rate of reaction

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{S}]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{OsO}_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}.$$

MeOH = 30% (v/v),  $\mu = 0.5 \text{ mol dm}^{-3}$

Temp	Indole	5-Methoxyindole	5-Bromoindole	5-chloroindole
K	$k' \times 10^5 \text{ s}^{-1}$	$k' \times 10^5 \text{ s}^{-1}$	$k' \times 10^5 \text{ s}^{-1}$	$k' \times 10^5 \text{ s}^{-1}$
298.7	6.12	7.25	2.63	2.38
302.4	7.30	9.02	3.78	3.37
306.5	8.79	10.61	5.22	5.17
310.6	12.07	13.01	7.41	7.47

Table - 5.11

Kinetic and thermodynamic parameters for the oxidation of indole and substituted indoles by chloramine-T in NaOH medium catalysed by  $\text{OsO}_4$

	$E_a$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ JK <sup>-1</sup> mol <sup>-1</sup>	$k' \times 10^5$ s <sup>-1</sup> at 29.4°C.	$k'_2 = k' / [S]_0$ 1 mol <sup>-1</sup> s <sup>-1</sup>
Indole	43.2	40.7	127.6	-189.7	7.30	$2.92 \times 10^{-2}$
5-Methoxyindole	37.2	34.7	126.8	-208.1	9.02	$3.61 \times 10^{-2}$
5-Bromoindole	66.6	64.1	129.2	-118.1	3.80	$1.52 \times 10^{-2}$
5-Chloroindole	69.0	66.5	129.4	-110.8	3.50	$1.40 \times 10^{-2}$

# LEGEND

## INDOLE

- a Indole
- b 5-Methoxy indole
- c - 5-Bromo indole
- d- 5-Chloro

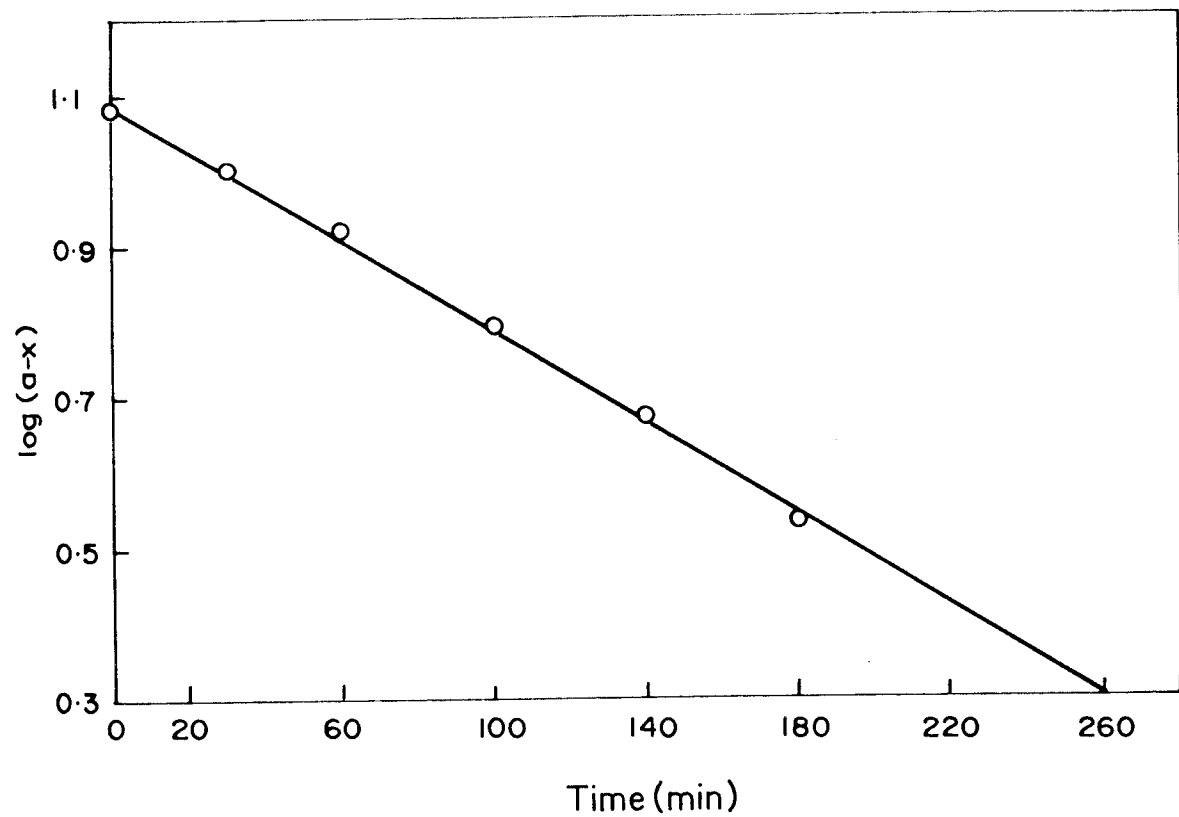


FIG. 5·1

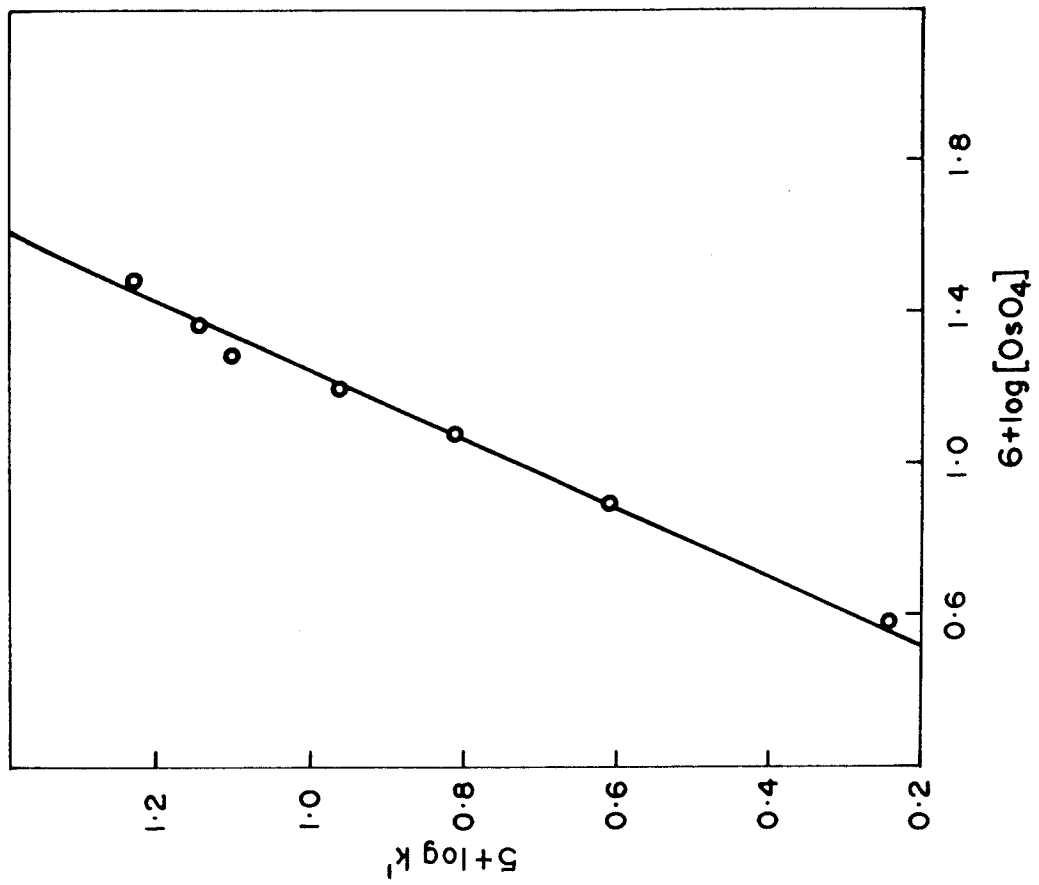


FIG. 5.3

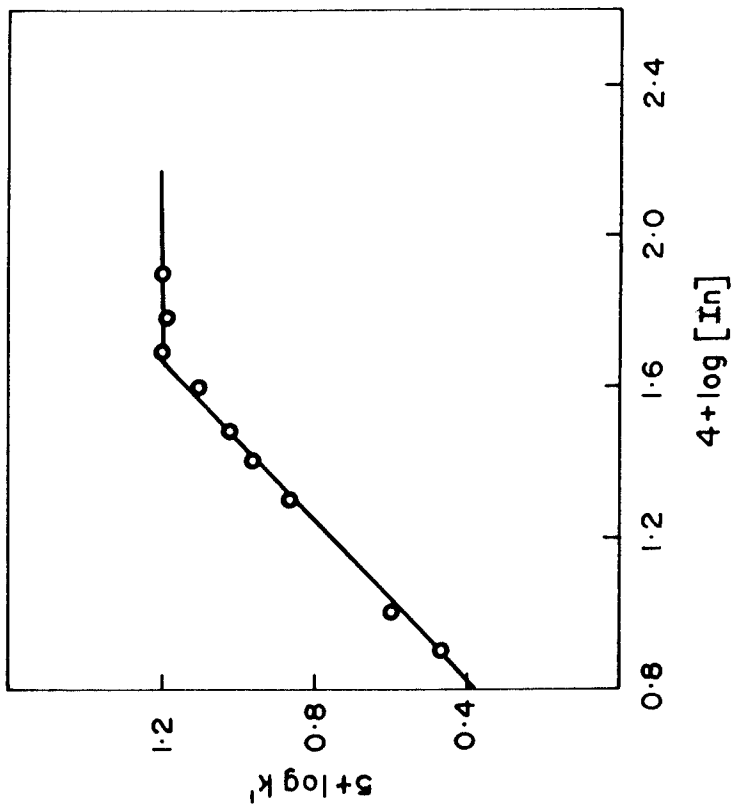


FIG. 5.2

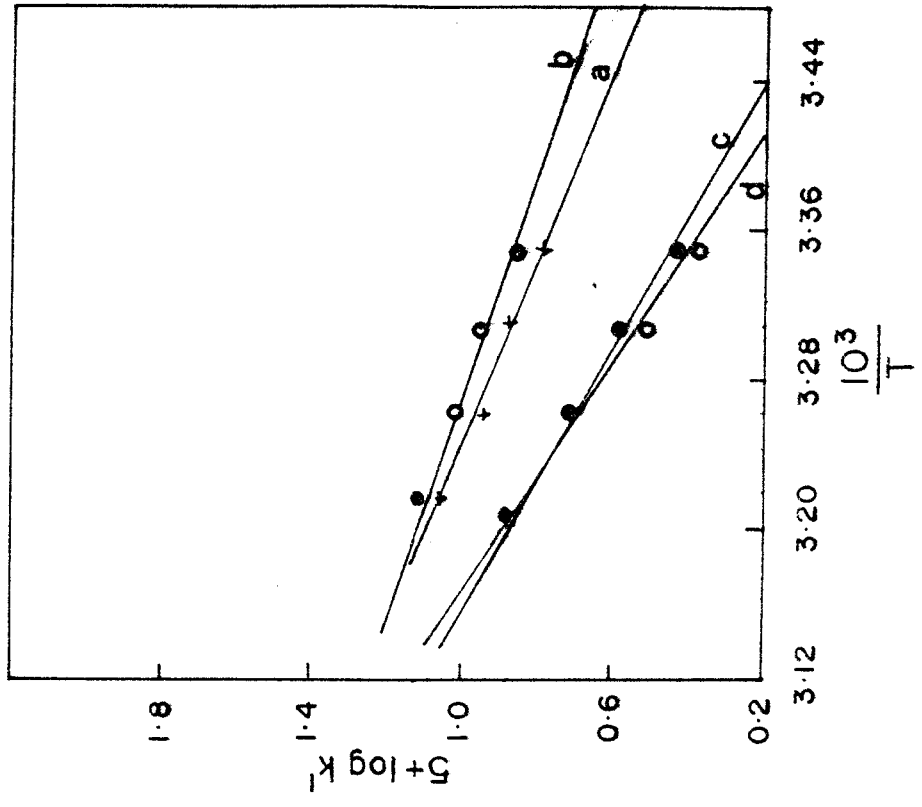


FIG. 5.5

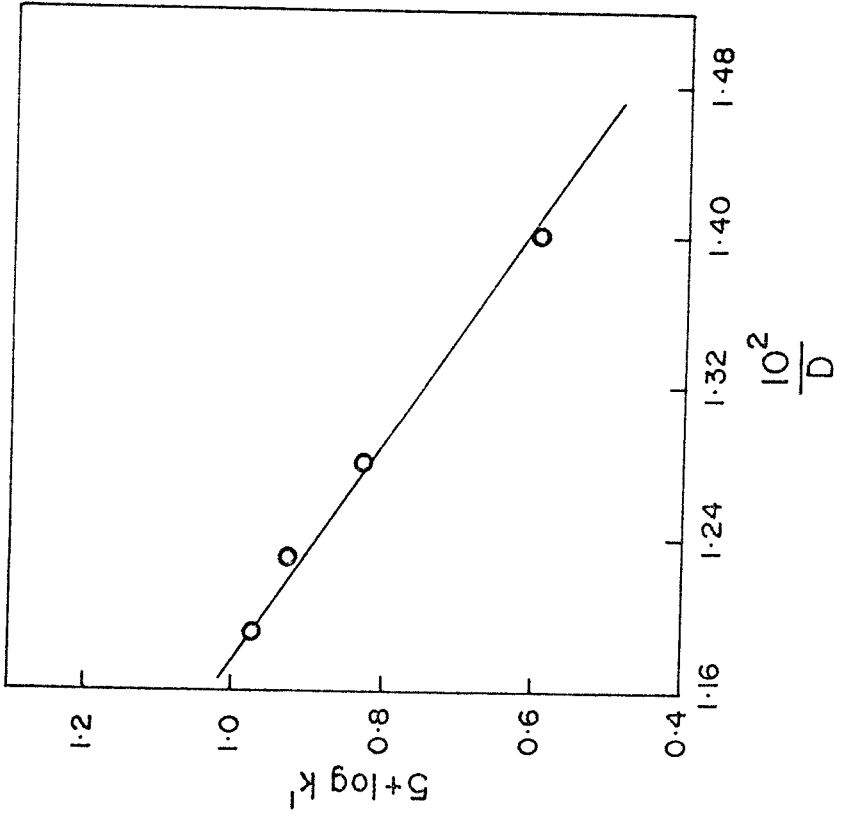


FIG. 5.4

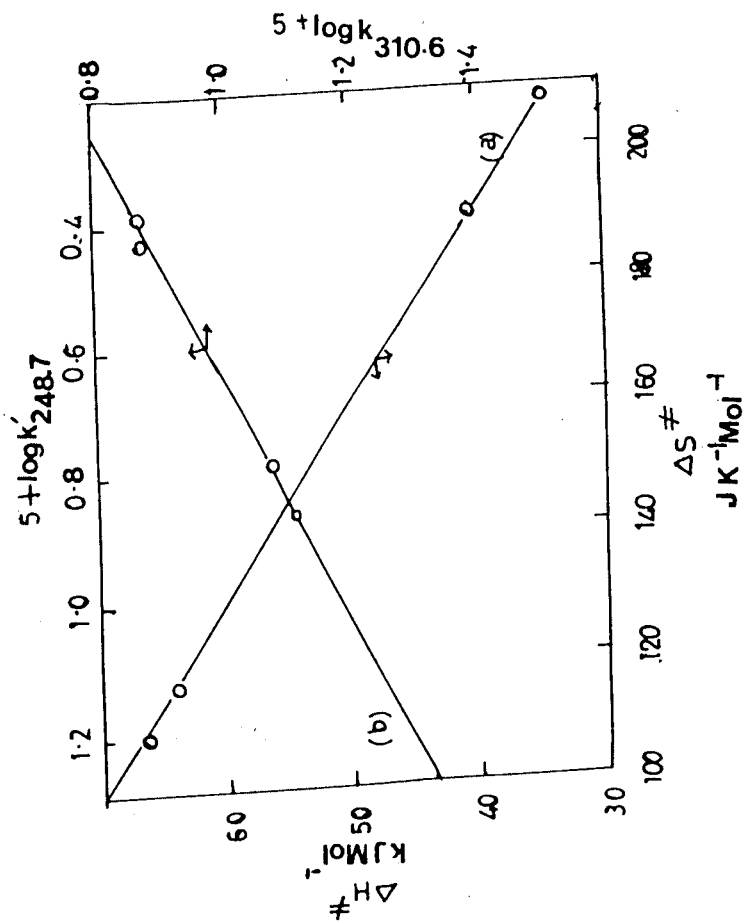


FIG. 5.6

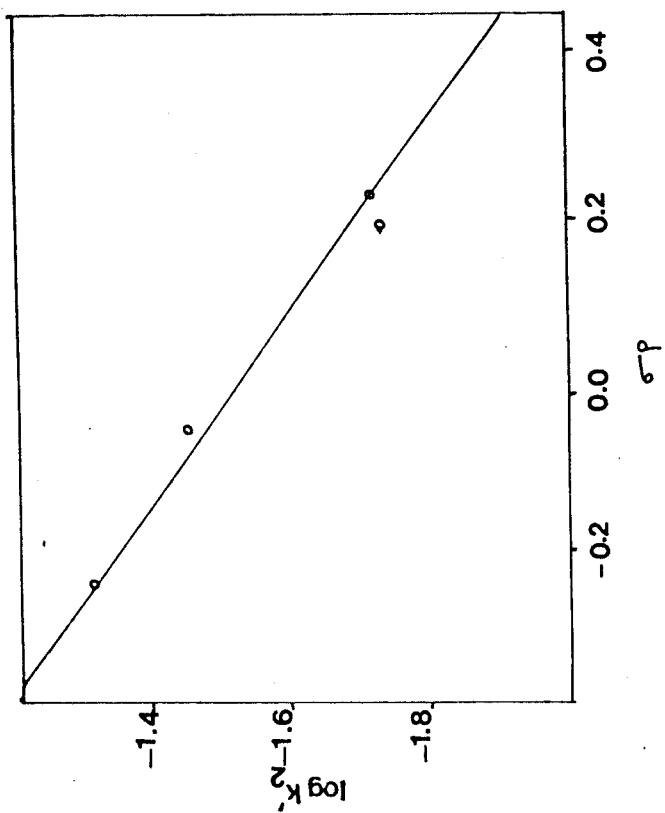
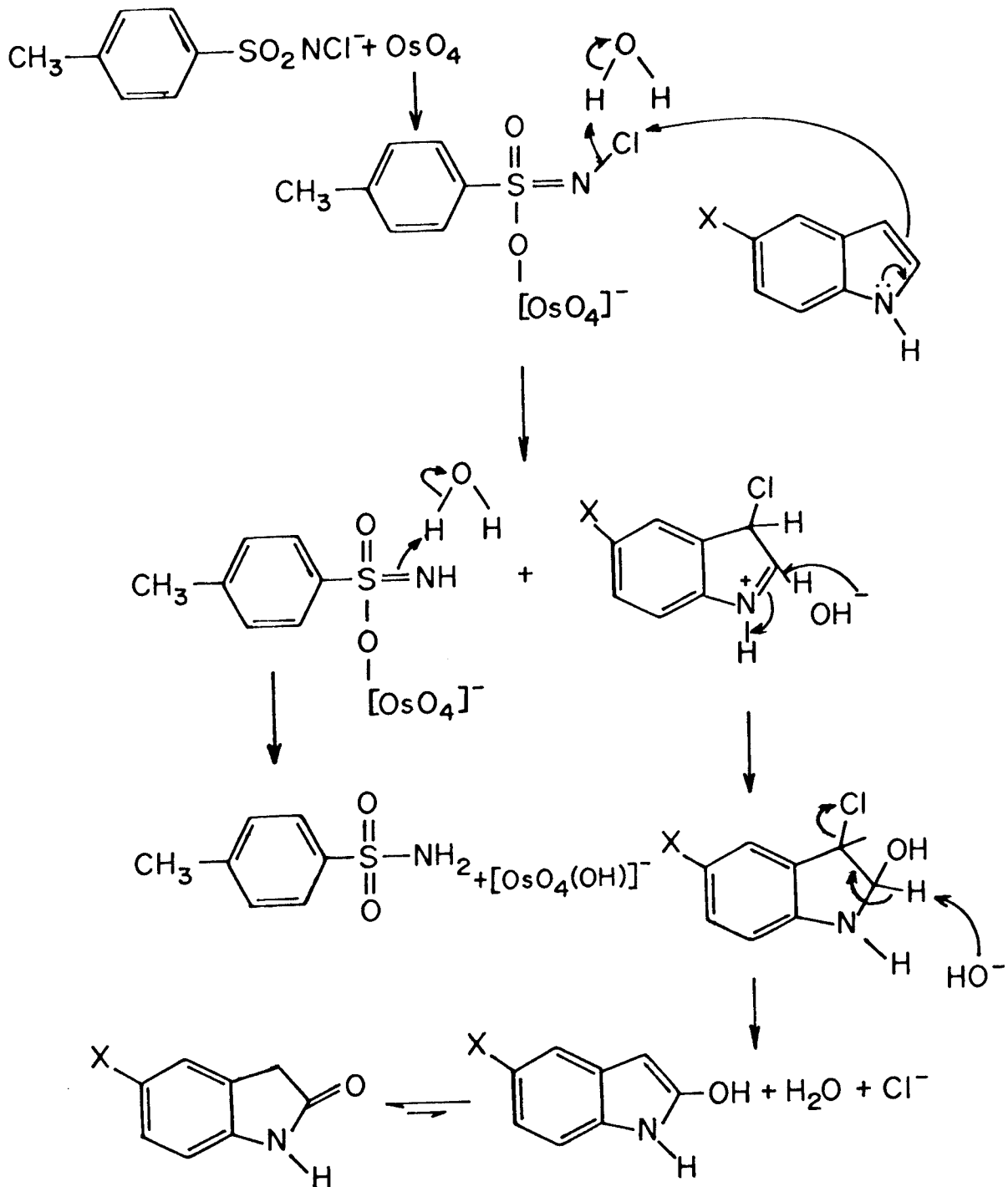


FIG. 5.7



Scheme 5.2

## SECTION-5.4

### KINETICS OF OXIDATION OF **INDOLE** BY CHLORAMINE-T IN **NaOH** MEDIUM CATALYSED BY **OsO<sub>4</sub>**.

This section deals with the oxidation of indole by CAT at high concentrations of alkali and indole. The stoichiometry and the products of oxidation were the same in both the ranges, which has been described in Section 5.3.

#### Results

##### Effect of reactants

At constant [OH<sup>-</sup>] with substrate in excess, plots of log [CAT] Vs time were linear (Table-5.12, Fig-5.8) indicating a first order dependence of rate on [oxidant]<sub>0</sub>. Values of pseudo-first order rate constants (k') are given in Table - 5.13. The rate was found to be independent of [In]<sub>0</sub> (Table-5.14).

##### Effect of [OH<sup>-</sup>]

At constant concentrations of CAT and indole, the reaction rate decreases with increase in [OH<sup>-</sup>] (Table-5.15) Plot of log k' Vs log [OH<sup>-</sup>] was linear (r=0.9958, s=0.05, Fig-5.9) with unit negative slope.

##### Effect of [OsO<sub>4</sub>]

The rate increased with increase in concentration of OsO<sub>4</sub> (Table-5.16). Plot of log k' Vs log [OsO<sub>4</sub>] was linear (r=0.9995, s=0.01, Fig-5.10) with unit slope.

### Effect of [Cl<sup>-</sup>]

Addition of chloride ions in the form of NaCl did not affect the rate (Table-5.17).

### Effect of [p-toluenesulphonamide].

Addition of p-toluenesulphonamide ( $1 \times 10^{-4}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>) to the reaction mixture had no effect on the rate (Table-5.18).

### Effect of ionic strength

The effect of varying the ionic strength of the medium by adding a concentrated solution of NaClO<sub>4</sub> had negligible effect on the rate (Table-5.19).

### Effect of dielectric constant of the medium on the rate.

Rate studies were made in water-ethanol mixtures of varying compositions. The rate decreased with increase in methanol content of the reaction mixture (Table-5.20). Plot of log k' Vs 1/D gave straight lines (r=0.9995, Fig-5.11) with negative slopes. Blank experiments with methanol, however showed that there is a slight decomposition of solvent (-2%) under experimental conditions. This was allowed for in the calculation of the net reaction rate constant for the oxidation of **indole**.

### Effect of temperature

The reaction was studied at different temperatures (298.3 to 313 K) (Table-5.21). From the Arrhenius plots of

$\log k'$  Vs  $1/T$  ( $r=0.9970$ , Fig-5.12), kinetic and thermodynamic parameters were evaluated (Table-5.22).

#### Solvent isotope studies

Solvent isotope studies in  $D_2O$  medium were made and the values of  $k'_{D_2O}$  and  $k'_{H_2O}$  were  $6.82 \times 10^{-5} s^{-1}$  and  $14.59 \times 10^{-5} s^{-1}$  at experimental conditions,  $[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[In]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[NaOH] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}$ , MeOH = 10% (v/v),  $\mu = 0.5 \text{ mol dm}^{-3}$ ,  $t=29.4^\circ C$ , giving a solvent isotope effect of  $k'_{H_2O}/k'_{D_2O} = 2.14$ .

#### Test for free radicals

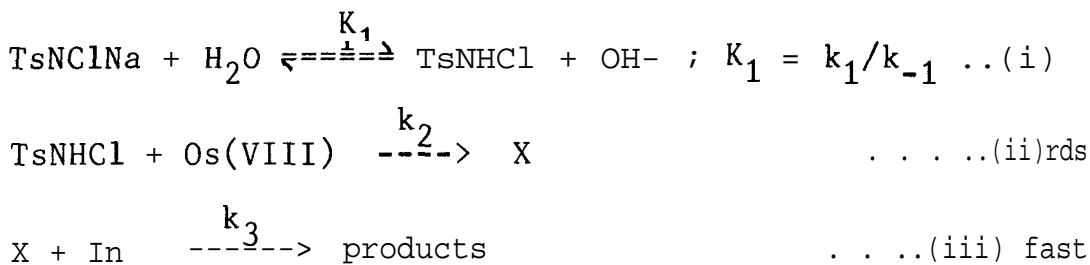
Addition of reaction mixture to aqueous acrylamide did not initiate polymerization showing the absence of free radical species.

## Discussion

The rate law for the oxidation of indole by CAT at high concentration of NaOH catalyzed by  $OsO_4$  is of the form,

$$\frac{-d[CAT]}{dt} = \frac{k [CAT] [OsO_4]}{[OH^-]} \dots\dots(5.7)$$

Since the rate law is independent of  $[In]_0$ , complex formation between the oxidant and  $OsO_4$  in the rate determining step is envisaged. Such a behavior has been reported by Mushran and co-workers<sup>121</sup> during the oxidation of  $\beta$ -hydroxy acids by CAT in alkaline medium. Retardation of the rate of chloraminometric reactions in alkaline medium has been observed by several workers<sup>118,119,120</sup>. It can be proposed that  $TsSO_2NHCl$  formed by the hydrolysis of CAT, is the oxidizing species under these conditions, as shown in Scheme-5.2:



Scheme - 5.3

From the above Scheme we get

$$\text{rate} = k_2 [TsNHCl] [Os(VIII)] \dots\dots(5.8)$$

Applying steady state conditions to  $[TsNHCl]$  we get,

$$\frac{d[\text{TsNHCl}]}{dt} = k_1 [\text{CAT}] [\text{H}_2\text{O}] - k_{-1} [\text{TsNHCl}] [\text{OH}^-] - k_2 [\text{TsNHCl}][\text{Os(VIII)}] = 0 \dots \dots (5.9)$$

Assuming that  $k_{-1} [\text{OH}^-] \gg k_2 [\text{Os(VIII)}]$  we get

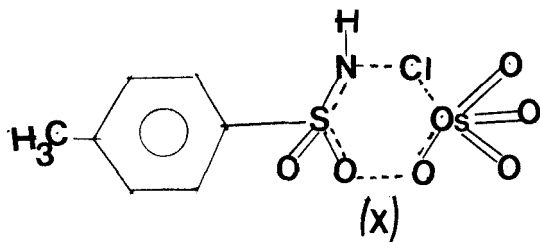
$$[\text{TsNHCl}] = \frac{k_1 [\text{CAT}] [\text{H}_2\text{O}]}{k_{-1} [\text{OH}^-]} = \frac{K_1 [\text{CAT}] [\text{H}_2\text{O}]}{[\text{OH}^-]} \dots (5.10)$$

Substituting for  $[\text{TsNHCl}]$  in equation (5.8)

$$\text{rate} = \frac{K_1 K_2 [\text{CAT}] [\text{H}_2\text{O}] [\text{Os(VIII)}]}{[\text{OH}^-]} \dots (5.11)$$

Equation (5.11) accounts for the observed first order each in  $[\text{oxidant}]$ ,  $[\text{catalyst}]$  and  $[\text{OH}^-]$ .

At high  $[\text{In}]_0$  the reaction rate decreases with increase in  $[\text{OH}^-]$ . The variation of  $[\text{In}]$  was studied by keeping  $[\text{OH}^-]$  constant  $[0.005\text{mM}]$ . The reaction rate becomes independent of  $[\text{In}]$  from  $3 \times 10^{-5}$  mole to  $15 \times 10^{-5}$  mole. Hence it is probable that the change in mechanism may be attributed (from that of Scheme - 5.1) to the fact that the oxidation of indole does not occur with either  $\text{OsO}_4$  or CAT alone. It can be assumed that a complex of these two serve as an oxidant<sup>31</sup>. Based on the oxidizing capacity observed, a cyclic structure X involving the oxygen and chlorine atom of the oxidant and the metal atom of the catalyst is proposed.



The structure X shows that the electron density around the nitrogen is lowered, resulting in a weakening of the N-Cl bond. Subsequent oxidizing capacity of N-chlorotoluene p-sulphonamide is increased after complexation, which results in a fast interaction of complex X with the appropriate form of the substrate.

The negligible salt and ionic strength effect on the rate is in agreement with the slow step (ii) of Scheme -5.2.

The solvent isotope effect,  $k'_{\text{H}_2\text{O}}/k'_{\text{D}_2\text{O}} = 2.14$  is noted under these experimental conditions. This is generally correlated with the greater basicity<sup>115</sup> of  $\text{OD}^-$  compared to  $\text{OH}^-$  ions which supports the initial equilibrium and the rate determining step in Scheme - 5.2. It is also seen that the rate decreases with increase in dielectric constant of the medium confirming the dipole-dipole nature of the rate limiting step in the reaction sequence.

Further, the mechanism is supported by the low enthalpy of activation. The value of  $\Delta S^\ddagger$ , though negative is small and indicates very little rearrangement in the transition state pointing towards the loose nature of the activated complex.

Table - 5.12, Fig - 5.8

Effect of chloramine-T concentration on the rate of reaction  
(representative run).

$$[In]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3}, [NaOH] = 5.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp} : 29.4^\circ\text{C}.$$

Time min	Titre value ml	log (a-x)
0	14.7	1.17
10	12.8	1.11
32	10.6	1.03
45	9.2	0.96
67	6.8	0.83
89	5.3	0.72
135	3.3	0.52

Table - 5.13

Effect of chloramine-T concentration on the rate of reaction  
(consolidated table).

$$[In]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3}, [NaOH] = 5.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[OsO_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp}: 29.4^\circ\text{C}.$$

$[CAT]_0 \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
6.0	9.09
7.0	8.69
7.5	8.29
8.0	8.69
8.5	8.29
9.0	8.49
10.0	8.49

Table - 5.14

Effect of **indole** concentration on the rate of reaction

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{NaOH}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{OsO}_4] = 15.7 \times 10^{-6} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{In}]_0 \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5$ s <sup>-1</sup>
30.0	8.98
50.0	8.70
70.0	8.69
80.0	8.58
90.0	8.72
100.0	6.86
150.0	6.27

Table - 5.15, Fig - 5.9

Effect of hydroxide **concentration** on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{OsO}_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{OH}^-] \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5$ s <sup>-1</sup>
25.0	13.47
40.0	12.25
50.0	8.69
60.0	7.29
75.0	5.58
100.0	4.24

Table - 5.16, Fig - 5.10

Effect of osmium tetroxide concentration on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}, \text{MeOH} = 10\% \text{ (v/v)},$$

$$\mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{OsO}_4] \times 10^6$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
3.93	2.55
7.86	4.71
15.70	8.69
23.60	11.89
27.50	14.49
31.40	16.20

Table - 5.17

Effect of added salt (sodium chloride) on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{OsO}_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}.$$

$$\text{MeOH} = 10\% \text{ (v/v)}, \mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

$[\text{NaCl}] \times 10^4$ mol dm <sup>-3</sup>	$k' \times 10^5 \text{ s}^{-1}$
1.0	8.70
5.0	8.88
8.0	8.75

Table - 5.18

Effect of p-tolluenesulphonamide concentration on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}], = 7.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{OsO}_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}.$$

$$\text{MeOH} = 10\% \text{ (v/v)}, \mu = 0.5 \text{ mol dm}^{-3}, \text{temp: } 29.4^\circ\text{C}.$$

[PTS] x 10 <sup>4</sup> mol dm <sup>-3</sup>	k' x 10 <sup>5</sup> s <sup>-1</sup>
0.0	8.69
1.0	8.69
3.0	8.89
5.0	8.68

Table - 5.19

Effect of ionic strength on the rate

$$[\text{CAT}]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}, [\text{In}], = 7.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{NaOH}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{OsO}_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}.$$

$$\text{MeOH} = 10\% \text{ (v/v)}, \text{temp: } 29.4^\circ\text{C}.$$

Ionic strength mol dm <sup>-3</sup>	k' x 10 <sup>5</sup> s <sup>-1</sup>
0.25	8.59
0.5	8.69
0.75	7.59
1.00	6.39

Table - 5.20, Fig - 5.11

Effect of varying dielectric constant on the rate

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[NaOH] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}$ .  
 $\mu = 0.5 \text{ mol dm}^{-3}$ , temp:  $29.4^\circ\text{C}$ .

MeOH % v/v	D	$10^2/D$	$k' \times 10^5 \text{ s}^{-1}$
10	72.37	1.38	8.69
15	69.93	1.43	6.82
20	67.48	1.48	5.34
30	62.71	1.60	3.17

Table - 5.21, Fig - 5.12

Effect of temperature on the rate

$[CAT]_0 = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[In]_0 = 7.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
 $[NaOH] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OsO_4] = 15.6 \times 10^{-6} \text{ mol dm}^{-3}$ .  
 MeOH = 10% (v/v),  $\mu = 0.5 \text{ mol dm}^{-3}$ .

Temp K	$k' \times 10^5 \text{ s}^{-1}$
298.3	5.69
302.4	8.69
305.9	11.23
309.0	13.98
313.0	19.28

Table - 5.22

Kinetic and thermodynamic parameters for the oxidation of indole by CAT in NaOH medium catalysed by OsO<sub>4</sub>

Parameters	Value
E <sub>a</sub> kJ mol <sup>-1</sup>	63.10
ΔH <sup>‡</sup> kJ mol <sup>-1</sup>	60.60 ± 0.01
ΔG <sup>‡</sup> kJ mol <sup>-1</sup>	98.20 ± 0.20
ΔS <sup>‡</sup> JK <sup>-1</sup> mol <sup>-1</sup>	-123.00 ± 0.10
log A	9.30 ± 0.01

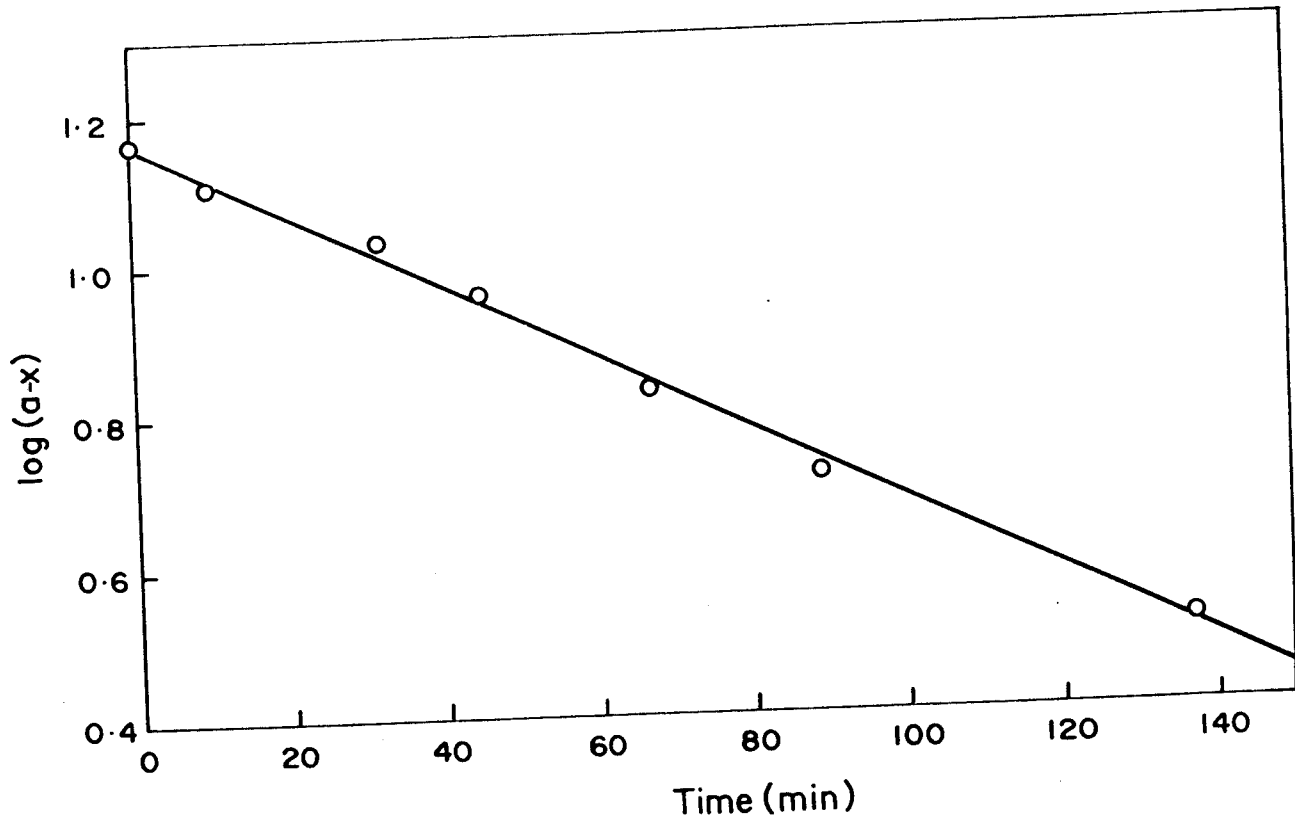


FIG. 5·8

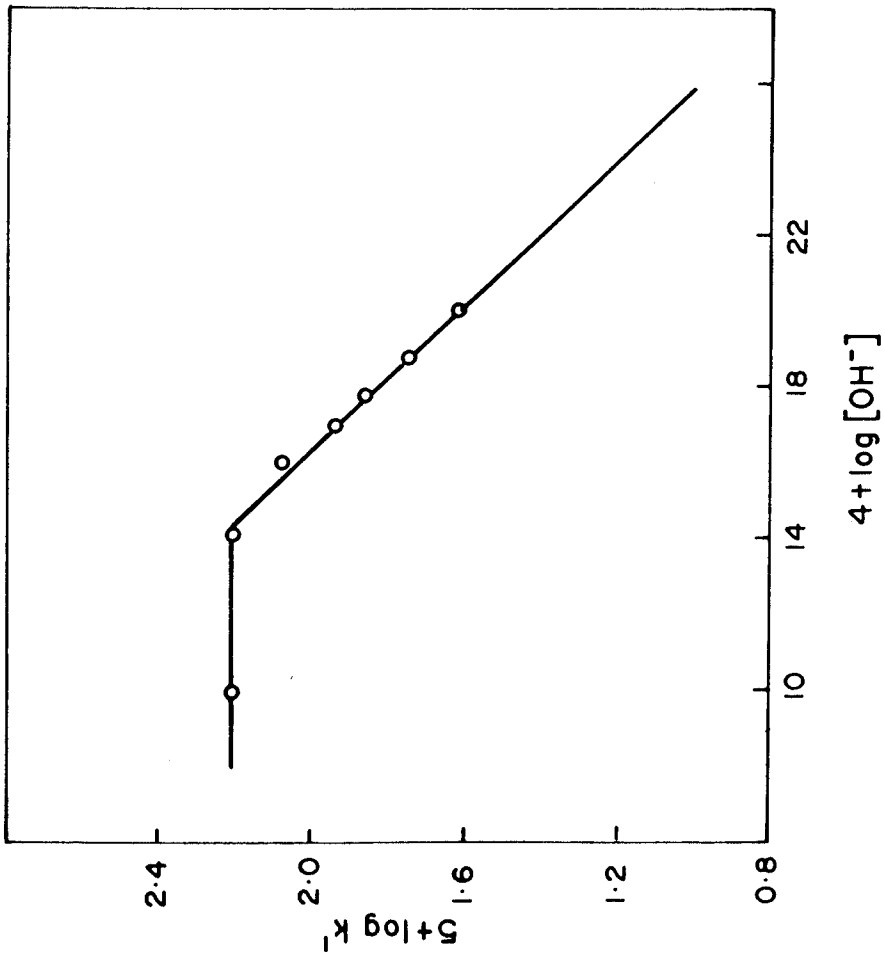


FIG. 5.9

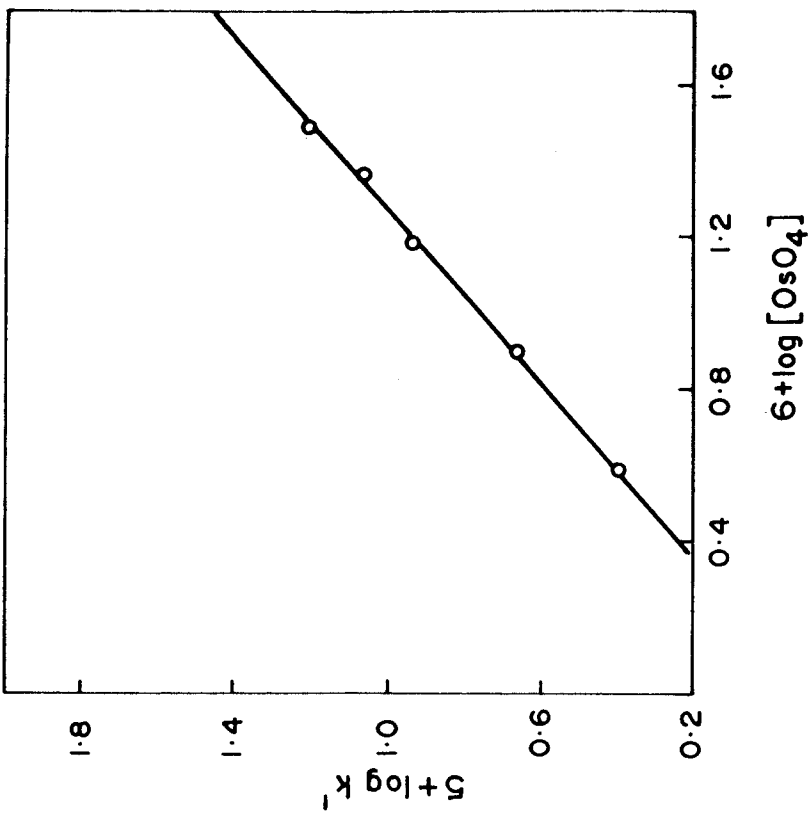


FIG. 5.10

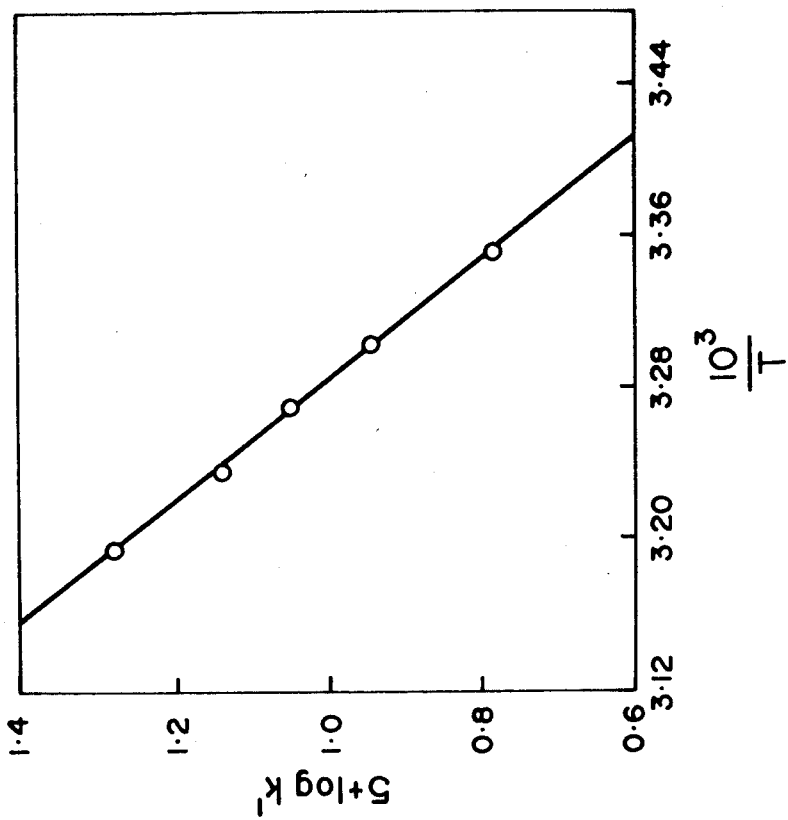


FIG. 5.12

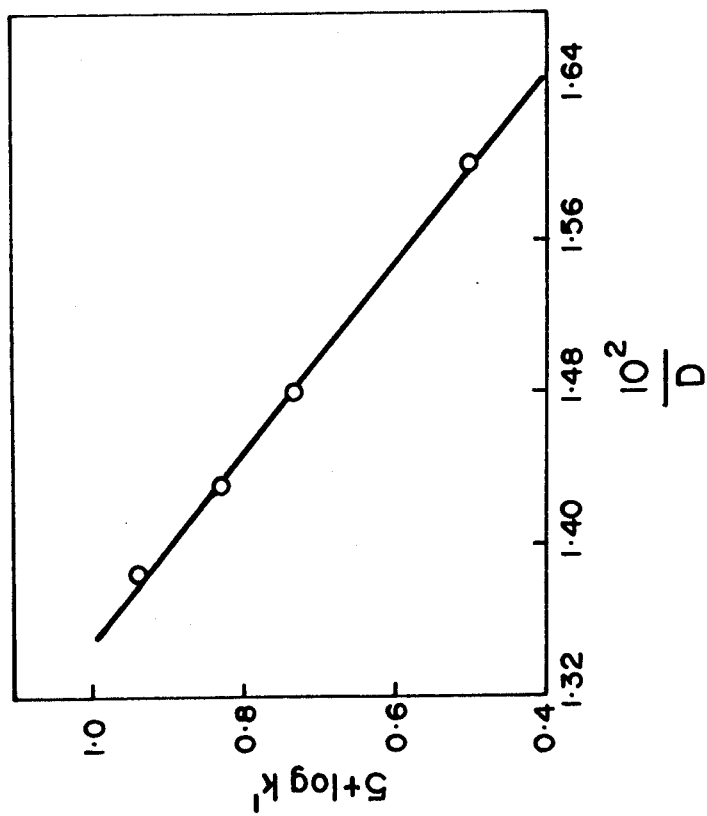
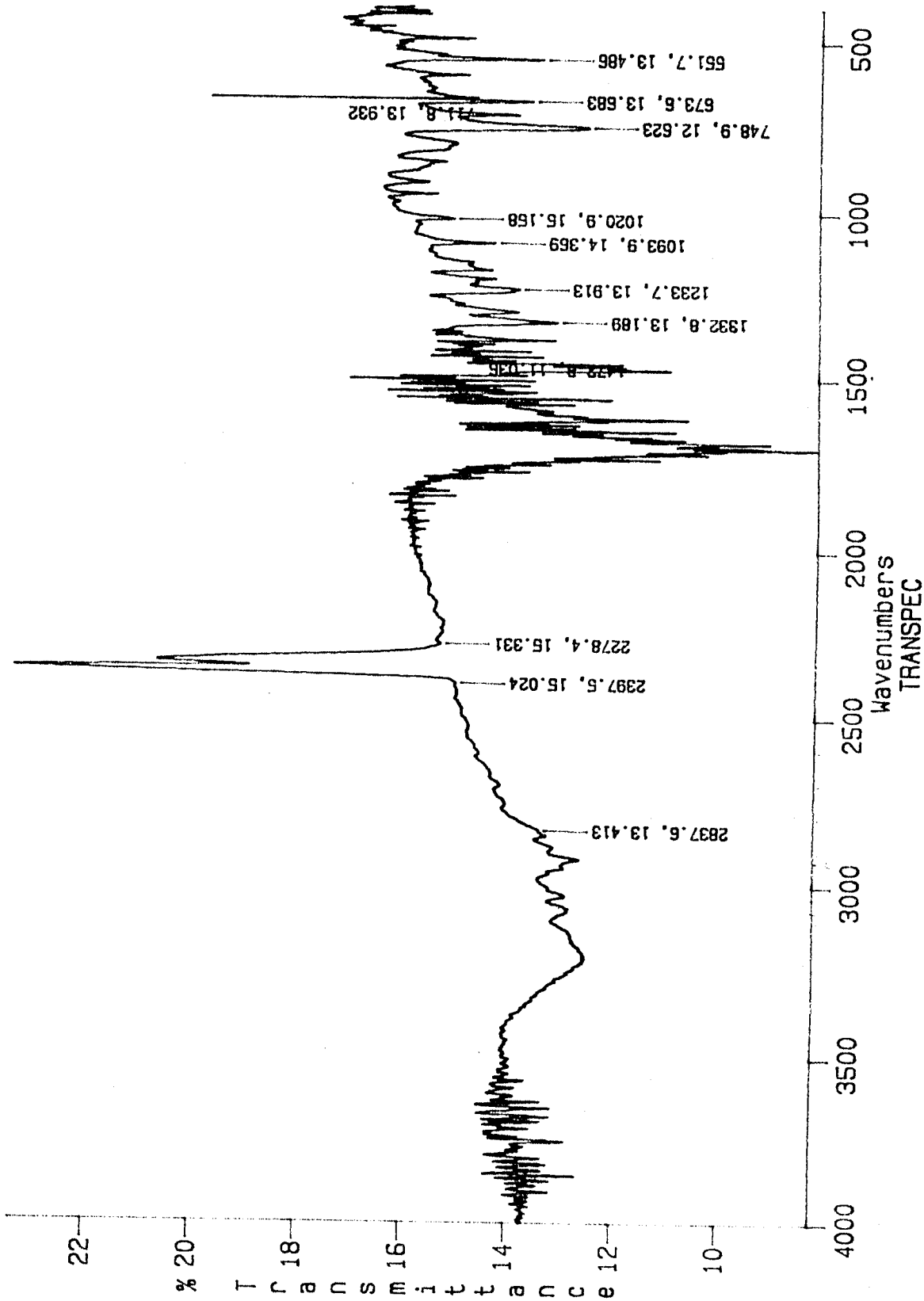
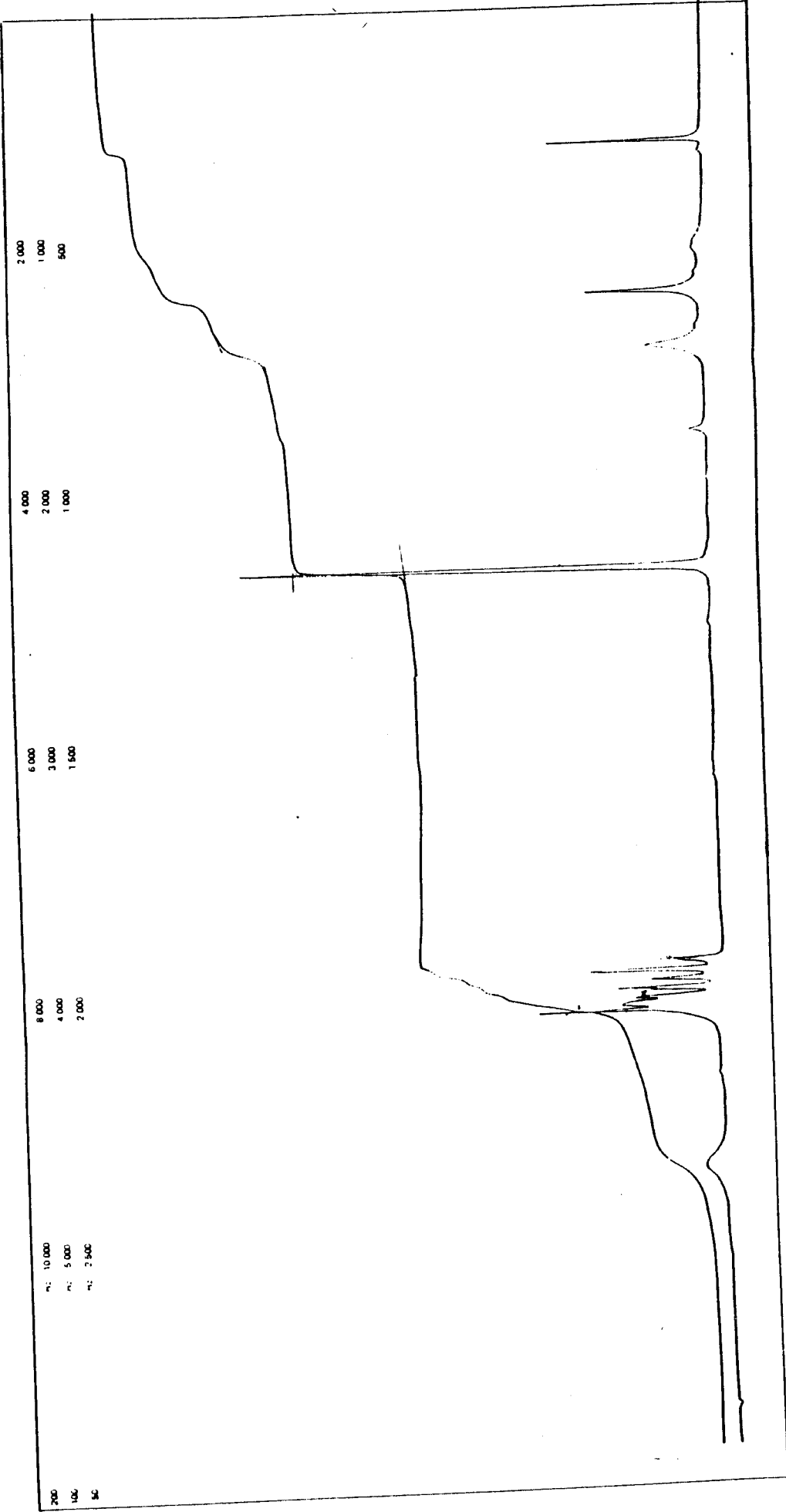


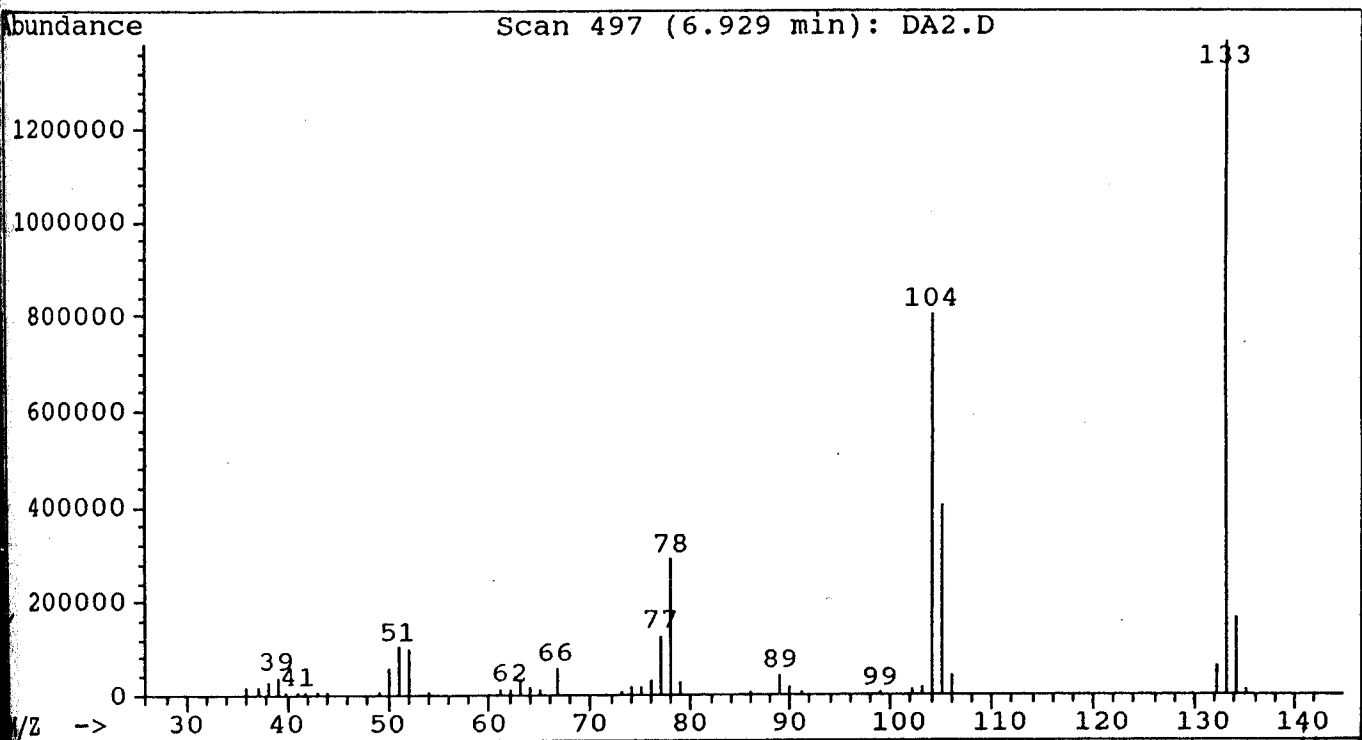
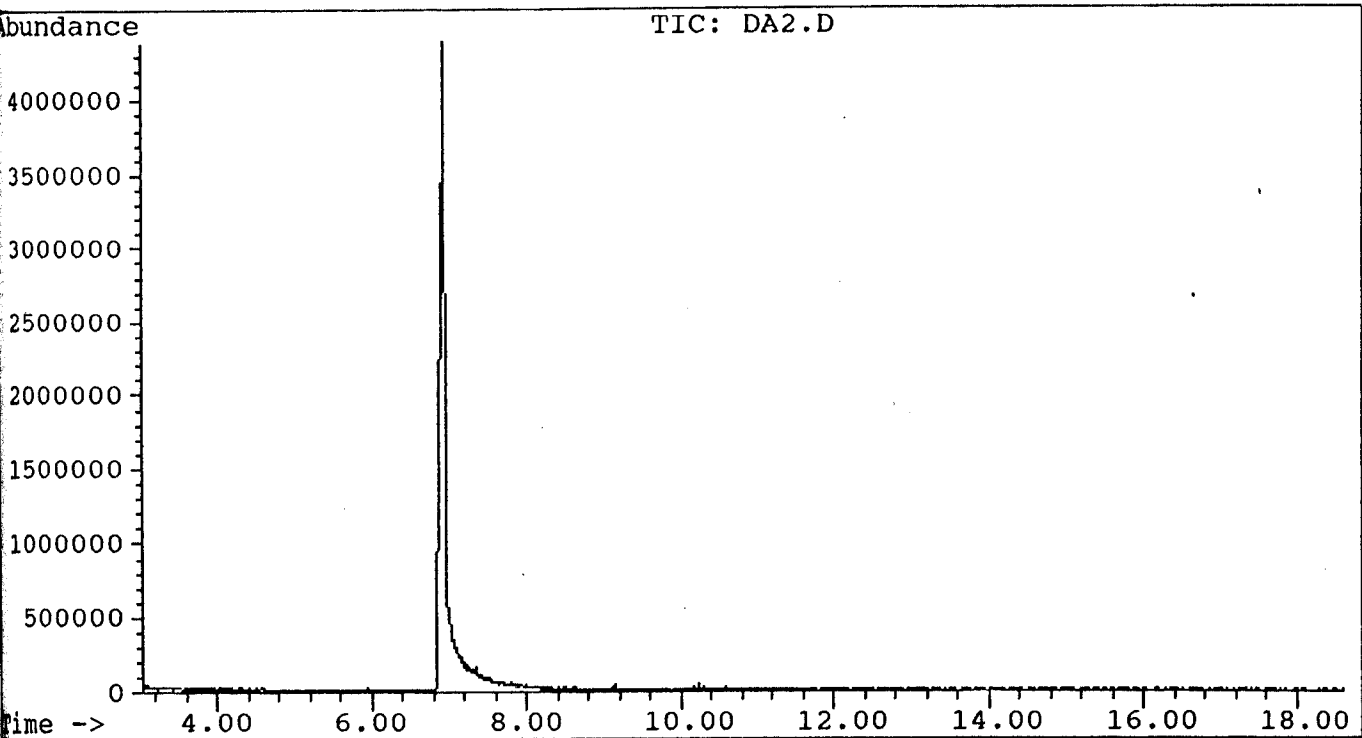
FIG. 5.11



FT - IR of oxindole



1H spectrum of oxindole



Mass spectrum of oxindole

## SUMMARY

Mechanistic and kinetic aspects of oxidation of some organic compounds such as aromatic aldehyde, secondary alcohols, aliphatic esters and a heterocyclic system, indole by the aromatic sulphonyl haloamines are reported in this thesis.

The  $\alpha$ ,  $\beta$ -unsaturated aromatic aldehyde cinnamic aldehyde (CA) was oxidised by CAT in presence of different acids like  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and in  $\text{NaOH}$  medium at  $40^\circ\text{C}$ . In  $\text{HClO}_4$  medium, a Michaelis-Menten kinetics is obeyed with a first order dependence of rate on  $[\text{CAT}]$  and a fractional order in  $[\text{CA}]$  which becomes zero at higher  $[\text{CA}]$ ,. Rate dependence on  $[\text{H}^+]$  varies from inverse fractional to fractional order and the rate- $\text{H}^+$  profile is of the inverted bell type. In  $\text{HCl}$  medium, the rate shows a first order dependence each in  $[\text{CAT}]$ ,  $[\text{H}^+]$  and  $[\text{Cl}^-]$ . Michaelis-Menten kinetics is obeyed with respect to  $[\text{CA}]$ ,. The observed rate law is of the form,

$$\frac{-d[\text{CAT}]}{dt} = k[\text{CAT}][\text{CA}]^x[\text{H}^+][\text{Cl}^-],$$

where  $x$  is fractional. In  $\text{H}_2\text{SO}_4$  medium the rate is found to be first order dependent on  $[\text{CAT}]$  and fractional orders are observed with respect to  $[\text{CA}]$ , and  $[\text{H}^+]$ . The rate law is of the form,

$$\frac{-d[\text{CAT}]}{dt} = k[\text{CAT}][\text{CA}]^y[\text{H}^+]^z$$

where the values of  $y$  and  $z$  are 0.83 and 0.72 respectively. In all the three acid media  $\text{TsNHCl}$  is considered to be the possible oxidising species. In  $\text{NaOH}$  medium, the rate law observed is,

$$\frac{-d[\text{CAT}]}{dt} = \frac{k[\text{CAT}][\text{OsO}_4][\text{H}_2\text{O}]}{[\text{OH}^-]}$$

Formation of a complex between  $\text{TsNHCl}$  (formed in an alkali retarded step) and  $\text{OsO}_4$  is envisaged as the rate limiting step to form the products.

Five secondary alcohols **propan-2-ol**, **butan-2-ol**, **pentan-2-ol**, **hexan-2-ol** and **heptan-2-ol** were oxidised by CAB in presence of  $\text{HCl}$  at  $40^\circ\text{C}$ . The rate shows a first order dependence each on  $[\text{CAB}]_0$  and  $[\text{alcohol}]_0$  and is fractional in  $[\text{HCl}]$ . Schemes were proposed to account for oxidation of alcohols through acid dependent, acid independent and chloride **catalysed** paths. Attempts made to correlate rates with the Taft substituent constants gave a negative value of  $\rho^*$  showing that electron releasing groups increase the rate. The rates of oxidation are found to be governed by both polar and steric effects.

Aliphatic esters like methyl, ethyl, propyl, isopropyl and butyl acetates were oxidised by BAT in hydrochloric acid medium at  $40^\circ\text{C}$ . The reaction shows a first order with respect to  $[\text{BAT}]_0$  and fractional orders in [ester], and  $[\text{H}^+]$ . The rate levels off at high  $[\text{H}^+]$  and **Michaelis-Menten**

kinetics is obeyed for the  $[\text{ester}]_0$ . The observed kinetic behaviour can be explained by the reaction of BAT with acid (and possibly water) in a reversible step to form the active oxidant which then reacts with the ester to form the products. An isokinetic relationship was observed with  $\beta = 374\text{K}$  indicating enthalpy as a rate controlling factor. Attempts were made to arrive at a linear free energy relationship through Taft treatment. Electron releasing groups in the ester moiety increase the rate with  $\rho^* = -3.85$ . Direct oxidation of ester before hydrolysis has been proposed.

The fused heterocyclic systems, indole and 5-substituted indoles were oxidised by CAT in NaOH medium catalysed by  $\text{OsO}_4$  at 302.413 in two different ranges - at high  $[\text{In}]_0$  and  $[\text{NaOH}]$  where rate law (i) holds, while at low  $[\text{In}]_0$  and  $[\text{NaOH}]$  experimental rate law (ii) is obeyed.

$$\frac{-d[\text{CAT}]}{dt} = \frac{k[\text{CAT}][\text{Os(VIII)}][\text{In}]^0}{[\text{OH}^-]} \dots\dots\dots(i)$$

$$\frac{-d[\text{CAT}]}{dt} = k[\text{CAT}][\text{Os(VIII)}][\text{In}]^x \dots\dots (ii)$$

where  $0 < x < 1$ . Effects of substituents like -Cl, -Br, -OCH<sub>3</sub> at the 5-position in indole, on the rate has been studied. An isokinetic relation was observed with  $\beta = 325\text{K}$ , indicating enthalpy as the rate controlling factor. The initial formation of a complex between CAT and  $\text{OsO}_4$  is envisaged, which reacts with the substrate to form the products.

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APPENDIX

Regression analysis of the experimental data

Regression coefficient 'r' is given by the formula<sup>1</sup>.

$$r = \frac{\overline{XY} - \bar{X} \cdot \bar{Y}}{S_X \cdot S_Y}$$

where  $S_X = \sqrt{\frac{\Sigma X^2}{n} - \left(\frac{\Sigma X}{n}\right)^2}$

and  $S_Y = \sqrt{\frac{\Sigma Y^2}{n} - \left(\frac{\Sigma Y}{n}\right)^2}$

Using the above equations for a given set of X and Y values,  $S_X$  and  $S_Y$  can be calculated and 'r' the regression coefficient can be obtained.

Standard deviation 's' of the points from the regression line can be calculated by the formula,

$$s = \sqrt{\frac{nS_Y^2 - \frac{n(\overline{XY} - \bar{X} \cdot \bar{Y})^2}{S_X^2}}{n - 2}}$$

Also 'r' can be calculated by the formula  $r = m \frac{\sigma_X}{\sigma_Y}$ ,

where the standard deviation in X, namely  $\sigma_X = \sqrt{\frac{\Sigma X^2}{n} - (\bar{X})^2}$ ,

the standard deviation in Y, namely  $\sigma_Y = \sqrt{\frac{\Sigma Y^2}{n} - (\bar{Y})^2}$  and m is the slope for a given straight line for a set of X and Y values.

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