

## Kinetics and mechanism of the hydroxylation of some naphthalene sulphonic acid derivatives by peroxodisulphate

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Oxidation of 1,8-dihydroxynaphthalene-3,6-disulphonic acid (CTA) and 1-amino-4-naphthalene sulphonic acid (ANS) by potassium peroxodisulphate leads to hydroxylation of these organic compounds. These oxidations may proceed through inner-sphere electron transfer as in case of ANS or by outer-sphere mechanism in case of CTA. The homolytic fission of  $S_2O_8^{2-}$  is the rate determining step in the oxidation of CTA by  $S_2O_8^{2-}$ , whereas, the intramolecular electron transfer in the precursor compounds is the rate determining step in the mechanism of oxidation of ANS. Hydroxylation takes place in para-position of benzene ring in CTA and ortho-position in ANS. The thermodynamics activation parameters were calculated. Rate of oxidation of both CTA and ANS in methanol-water solvent mixtures is decreased by increasing methanol content in the medium.

**Keywords:** Oxidation, Hydroxylation, Peroxodisulphate, Kinetics, Chromotropic acid, 1-Amino-4-naphthalene sulphonic acid  
**IPC Code (s):** C07C7/00

Peroxodisulphates are desirable oxidizing agents because their products pose little or no threat to human or animal life<sup>1</sup>, and/or are non-toxic to the environment. They have applications in water treatment for the destructive oxidation of hazardous wastes<sup>2</sup> and in chemical heaters, which are defined as exothermic chemical processes capable of liberating substantial chemical energy as a replacement for combustion<sup>3</sup>.

Naphthalene sulphonic acids are one of the most important starting compounds for the synthesis of dyes and have wide biological application. Chromotropic acid (CTA) is one of the most widely used intermediates for the manufacture of Kock acid that is very important product in the field of dye chemistry<sup>4</sup>. It is used in the determination of methanol concentration of humans<sup>5</sup>, and microquantitative determination of Cr(VI) in water<sup>6</sup>.

Nitro and amino substituted aromatic compounds are nitrogen sources for the green alga *Scenedesmus oblique*. This model was tested by incubation of the alga with 1-amino naphthalene 4-sulphonic acid<sup>7</sup>.

Present work was done to study the effect of different substituted groups in naphthalene rings on the rate of its hydroxylation and to ascertain the most suitable conditions to control rate of formation of the oxidation products in their industrial preparation.

### Experimental Procedure

#### Materials

All chemicals were of analytical reagent grade, obtained from either Merck or Aldrich and were used without further purification. Aqueous solutions of disodium salt dihydrate of 1,8-dihydroxynaphthalene-3,6-disulphonic acid [chromotropic acid (CTA),  $(H_2O)_2C_{10}H_6(SO_3Na)_2$ ], sodium salt of 1-amino-4-naphthalene sulphonic acid (ANS) ( $NH_2C_{10}H_6SO_3Na \cdot 4H_2O$ ), potassium peroxodisulphate, sodium nitrate were prepared by accurate weighing of the appropriate compound and dissolving in requisite amount of water. Stock solution of NaOH was standardized against standard HCl.

Pure methanol of BDH quality was distilled before use. Its stability towards  $S_2O_8^{2-}$  was checked, no reaction was observed during the time taken for measurement.

#### Kinetic studies

Kinetic studies of hydroxylation of CTA and ANS were carried out by monitoring the absorption of the oxidation products, at their maximal wavelengths, on a Milton and Roy 601 spectrophotometer. All the reactants, except  $K_2S_2O_8$ , were equilibrated at the required temperature. The required amount of separately equilibrated  $K_2S_2O_8$  stock solution was then added, and after rapid mixing, the absorbance was recorded.

Pseudo-first order conditions were maintained in all runs by using a large excess of  $[S_2O_8^{2-}]$  (more than 10-fold) over [CTA] and [ANS].

#### Oxidation products

The oxidation products of both CTA and ANS were obtained by mixing an aqueous solution of  $5 \times 10^{-3}$  mole of organic compound with alkaline solution of 0.027 mole of  $K_2S_2O_8$ . The solution was concentrated by evaporation on a water bath, for two hours of cooling reddish brown compounds precipitated which were filtered and recrystallized from water.

[CTA, Found: C, 34.30; H, 2.25; S, 18.11. Calcd. C, 34.09; H, 2.27; S, 18.18] and [ANS, Found: C, 50.63; H, 3.84; S, 13.35; N, 5.91. Calcd. C, 50.21; H, 3.76; S, 13.38; N, 5.86].

IR spectra of the isolated products, exhibit the presence of a very broad band in the region  $2500-3500\text{ cm}^{-1}$  that may be attributed to  $\nu\text{ OH}^-$  acid band and bands at  $3200-3500\text{ cm}^{-1}$  may be due to the presence of  $\nu\text{-OH}$  phenolic in case of CTA, and  $\nu\text{-OH}$  phenolic,  $\nu\text{-NH}_2$  in case of ANS.

The UV-Vis absorption spectra of the oxidation products of CTA and ANS were recorded on Shimadzu UV-160 IPC spectrophotometer and shown in Figs 1 and 2, respectively. The maxima and molar absorptivities of the oxidation products are in agreement with those reported earlier<sup>8,9</sup>.

## Results and Discussion

#### Kinetics of hydroxylation of CTA

The oxidation kinetics of CTA was studied at 510 nm, where the product has maximum absorption, over the temperature range  $25-45^\circ\text{C}$ ,  $0.0125-0.025$  [OH<sup>-</sup>] range,  $0.005-0.05$   $[S_2O_8^{2-}]$  and  $(3-10) \times 10^{-4}$  organic compound concentrations.

Plots of  $A_t$  versus  $t$  (s) give straight lines, where  $A_t$  is the absorbance at time  $t$ . This indicates that the reactions, at large excess of  $[S_2O_8^{2-}]$ , is zero order with respect to CTA (Fig. 3).

Results recorded in Table 1 show that the specific rate  $k_{\text{obs}}$ , was unaffected when the concentration of organic compound is varied at constant  $[S_2O_8^{2-}]$ . At constant [OH<sup>-</sup>],  $k_{\text{obs}}$ , varies linearly with  $[S_2O_8^{2-}]$  at different temperatures as shown in Fig. 4. Also  $k_{\text{obs}}$  is found to be independent of [OH<sup>-</sup>] (Table 1), this behavior is described by Eq. (1),

$$d[\text{product}]/dt = k_1 [S_2O_8^{2-}] \quad \dots (1)$$

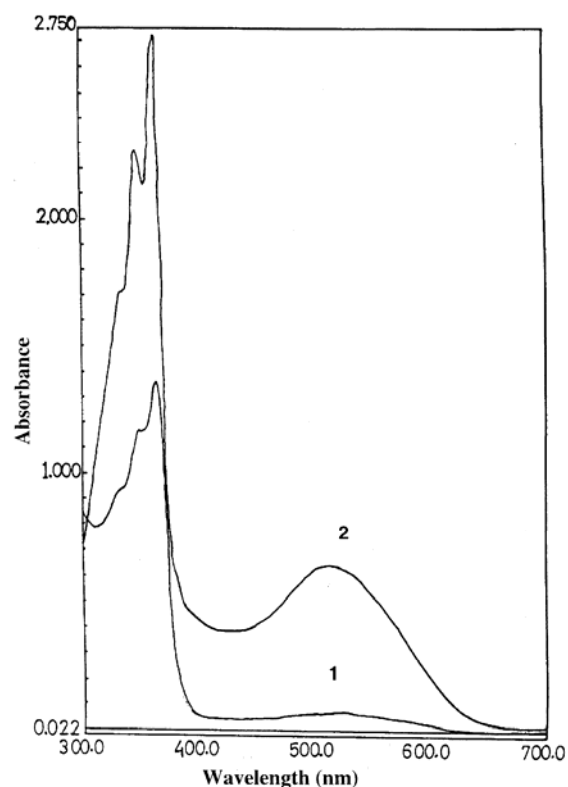


Fig. 1 — UV-visible spectrum of CTA (1) and the final product (2)

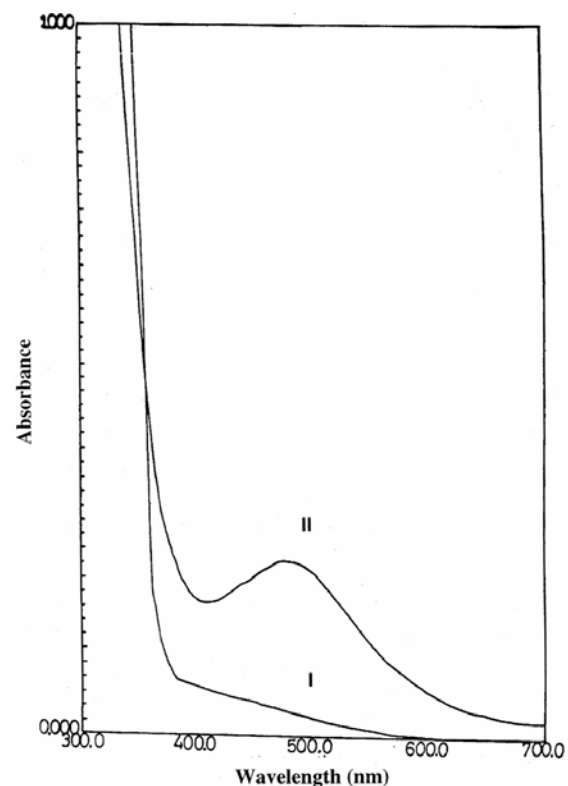


Fig. 2 — UV-visible spectrum of ANS (I) and the final product (II)

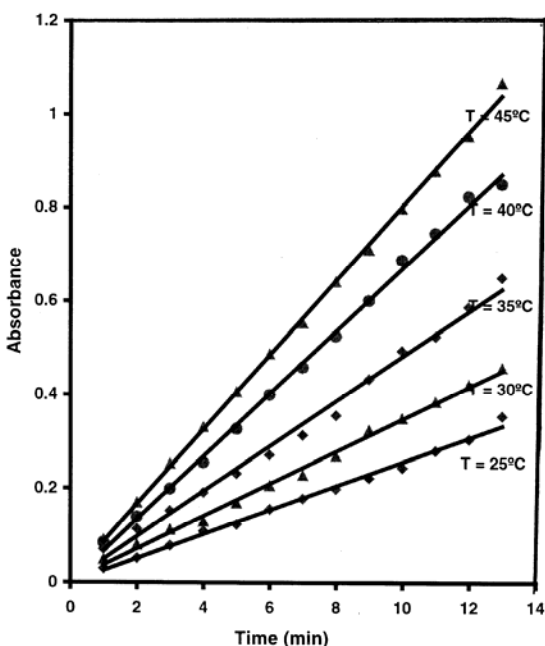


Fig. 3 — Variation of absorbance with time at different temperatures

Table 1 — Dependence of rate on  $[S_2O_8^{2-}]$ ,  $[CTA]^a$ ,  $[OH^-]^b$  and temperatures at  $I = 0.3 \text{ mol dm}^{-3}$

$10^2 [S_2O_8^{2-}]$ , $\text{mol dm}^{-3}$	$10^4 k_{\text{obs}}, \text{s}^{-1}$				
	T = 25°C	T = 30°C	T = 35°C	T = 40°C	T = 45°C
5.0	7.05	9.40	13.07	18.21	22.33
4.5	6.34	8.63	12.03	16.78	20.07
4.0	5.69	7.67	10.70	14.89	17.82
3.5	4.99	6.71	9.36	13.02	15.88
3.0	4.27	5.75	8.02	11.17	13.38
2.5	3.55	4.80	6.69	9.31	11.77
2.0	2.85	3.83	5.35	7.45	8.91
1.5	2.13	2.88	4.01	5.58	6.71
1.0	1.42	1.92	2.69	3.73	4.48
0.5	0.67	0.86	1.17	1.66	2.01

$[CTA]^a = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $10^4 k_{\text{obs}} = 5.69, 5.72, \text{ and } 5.76 \text{ s}^{-1}$  at  $10^4 [CTA]$  of 3, 7, 10  $\text{mol dm}^{-3}$ , respectively, at 30°C,  $[S_2O_8^{2-}] = 0.03 \text{ mol dm}^{-3}$ .

$[OH^-]^b = 0.015 \text{ mol dm}^{-3}$ ,  $10^4 k_{\text{obs}} = 2.66, 2.71, 2.66 \text{ and } 2.69 \text{ s}^{-1}$  at  $10^2 [OH^-]$  of 1.25, 1.75, 2.00, and 2.50  $\text{mol dm}^{-3}$  respectively, at 35°C,  $[S_2O_8^{2-}] = 0.01 \text{ mol dm}^{-3}$ .

The thermodynamic parameters  $\Delta H^*$  and  $\Delta S^*$  of the reaction obtained from a least-squares fit of the Arrhenius plot are  $44.16 \text{ kJ mol}^{-1}$  and  $132.10 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively.

Kinetic studies on the oxidation of CTA by  $[S_2O_8]^{2-}$  were also carried out in different wt% MeOH in the range of 10.2–18.8. Table 2 shows that the overall rate of oxidation decreases with increasing wt% of methanol in the reaction medium.

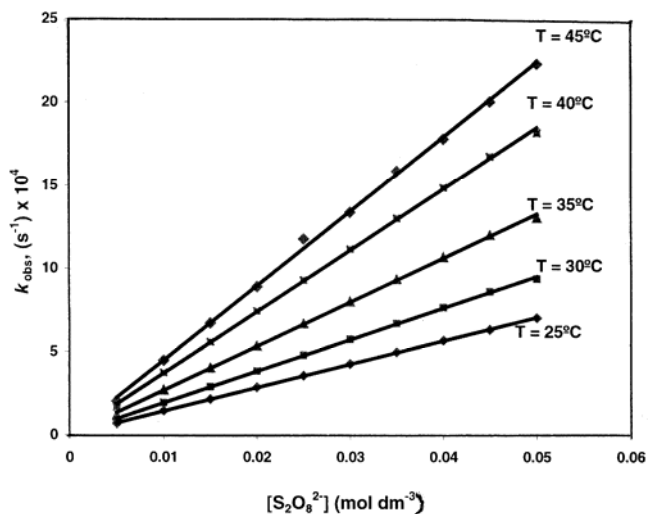


Fig. 4 — Plot of  $k_{\text{obs}}$  versus  $[S_2O_8^{2-}]$  at different temperatures

Table 2 — Dependence of rate of oxidation on solvent at  $[S_2O_8^{2-}] = 0.01 \text{ mol dm}^{-3}$ ,  $[CTA] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[OH^-] = 0.015 \text{ mol dm}^{-3}$ ,  $I = 0.3 \text{ mol dm}^{-3}$ , and  $T = 35^\circ\text{C}$

MeOH, wt%	$10^4 k_{\text{obs}}, \text{s}^{-1}$
0.00	2.69
10.2	1.04
14.4	0.830
18.8	0.787

The question of the identity of the active intermediate in redox activations of peroxodisulphate has been considered<sup>10</sup>. The problem arises because  $SO_4^-$  generated by the thermal or photolytic decomposition of peroxodisulphate is shown to undergo the radical interconversion reaction (2) given by,



However, these studies are carried out in the absence of any added oxidizable substrates, and these conditions obviously favour the radical exchange reaction. On the other hand, in the presence of oxidizable substrates, it has been established on the basis of chemical competition studies<sup>10,11</sup> that the reactive intermediate produced in the redox activation of peroxodisulphate is the sulphate ion. Therefore, these studies showed that various substrates compete favourably with water for the sulphate ion.

In fact, it has been stated that the reaction shown in Eq. (2) is probably slow and occurs only in the absence of scavengers for sulphate ion<sup>12</sup>. E.S.R. studies<sup>13</sup> have provided evidence for the existence of  $SO_4^-$  ion in peroxodisulphate oxidations.

The rate determining step in the oxidation reaction of CTA by  $[S_2O_8]^{2-}$  must be homolytic fission into two sulphate ions, since the oxidation rate is first-order dependent on  $[S_2O_8^{2-}]$  and zero-order with respect to [CTA]. The independence of the reaction rate on  $[OH^-]$  means that this anion does not get incorporated in the rate-determining pathway.

It was reported that alkaline peroxodisulphate oxidation of phenols results in their hydroxylation, this reaction is known as Elbs reaction<sup>14,15</sup> and has been thoroughly studied and found to proceed by a radical mechanism. The stereo chemistry of this hydroxylation reaction is usually governed by the substituent already present in the reacting phenolic compound. In this reaction the second hydroxy group enters at para position that is already present, but if that position is blocked, the ortho position is favoured<sup>16</sup>.

On the basis of the kinetic results, the mechanism shown in Scheme 1 is proposed for the oxidation of CTA by  $S_2O_8^{2-}$ .

The homolytic fission in the first step is followed by deprotonated equilibrium of CTA ion forming (I), which is a resonating form of (II). Then, hydrogen free radical from (II) is substituted by  $SO_4^-$  in the two benzene rings forming (III), which is transformed to (IV) by bond rearrangement. Then, compound (IV) reacts with water resulting in the formation of the hydroxy anion (V)  $OH^-$  abstracts  $SO_3^-$  radical from (V) forming the hydroxy anion (VI) and  $HSO_4^-$ .

Immediately, protonation of (VI) at the oxygen atom in the para-position takes place by  $H^+$  from  $HSO_4^-$  with the formation of 1,4,5,8-tetrahydroxynaphthalene-3,6-disulphonate(VII). On acidification, the final product 1,4,5,8-tetrahydroxynaphthalene-3,6-disulphonic acid is formed. The presence of free radical during the reaction was confirmed by addition of acrylonitrile to the reaction mixture, when polymerization took place.

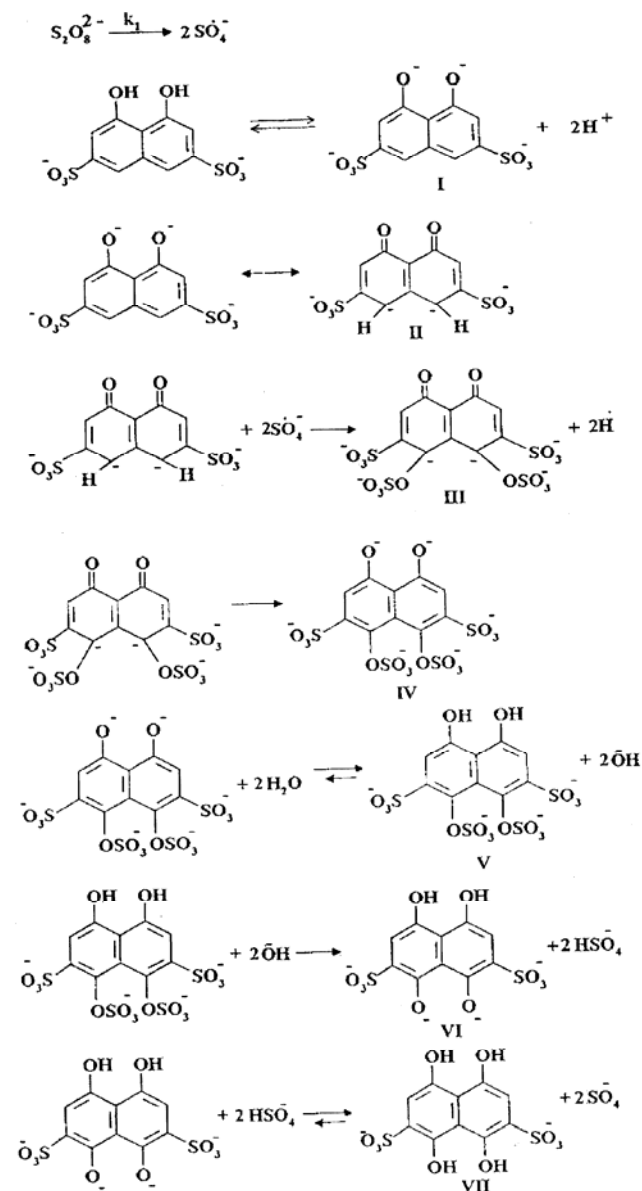
A number of investigators<sup>17-21</sup> have provided evidence concerning the formation of aromatic radical cations through oxidation by  $SO_4^{\cdot-}$ . Therefore, an alternative mechanism for the oxidation of CTA by persulphate may be proposed as shown in Scheme 2. This mechanism involves oxidation of CTA to a radical cation (II), nucleophilic addition of  $OH^-$  to give (III) followed by proton loss forming (IV) which hydrolyses with water to give (V).

#### Kinetics of hydroxylation of ANS

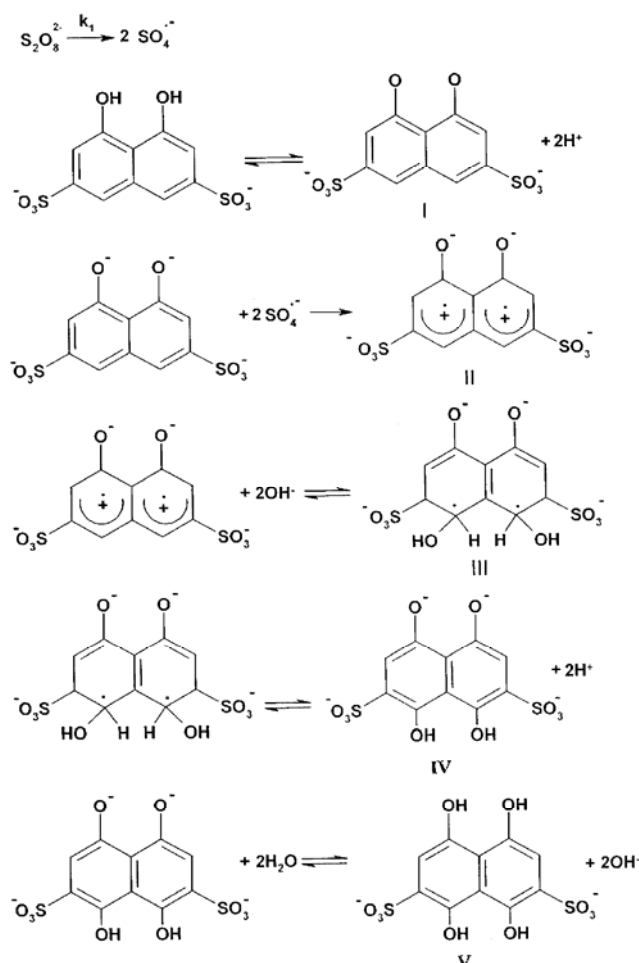
The oxidation kinetics of ANS by  $S_2O_8^{2-}$  were studied over 0.015-0.025  $[OH^-]$  range, at 25-45°C over a range of organic compound and potassium peroxodisulphate concentration.

Plots of  $\ln(A_\infty - A_t)$  versus time were linear up to 80% of the reaction where  $A_t$  and  $A_\infty$  are absorbance at time  $t$  and infinity, respectively. Pseudo-first order rate constant,  $k_{obs}$ , obtained from the slopes of these plots, are given in Table 3. These results show that  $k_{obs}$  was unaffected when [ANS] was varied at constant  $[S_2O_8^{2-}]$ , indicating first order dependence of [ANS]. Thus, the rate at fixed  $[S_2O_8^{2-}]$  is given by:

$$d[\text{product}]/dt = k_{obs}[\text{ANS}] \quad \dots (3)$$



Scheme 1



At constant  $[\text{OH}^-]$ ,  $k_{\text{obs}}$  varies linearly with  $[\text{S}_2\text{O}_8^{2-}]$  at different temperatures as shown in Table 3. These results lead to Eq. (4).

$$k_{\text{obs}} = k_1 [\text{S}_2\text{O}_8^{2-}] \quad \dots (4)$$

The rate law can be given as:

$$d[\text{product}]/dt = k_1 [\text{S}_2\text{O}_8^{2-}] [\text{ANS}] \quad \dots (5)$$

Enthalpy  $\Delta H^*$  and entropy  $\Delta S^*$  of activation associated with  $k_1$  were obtained as  $40.64 \text{ kJ mol}^{-1}$  and  $-139.22 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. Table 3 shows the independence of reaction rate on  $[\text{OH}^-]$ .

Kinetic studies on the hydroxylation of ANS by  $[\text{S}_2\text{O}_8^{2-}]$  were studied in different water-methanol mixtures with different wt% MeOH in the range of 10.2-18.8 under constant concentrations of  $\text{S}_2\text{O}_8^{2-}$  and ANS. Table 4 shows that the overall rate of hydroxylation decreases with increasing the wt% of methanol in the reaction medium.

Table 3 — Dependence of rate on  $[\text{S}_2\text{O}_8^{2-}]$ ,  $[\text{ANS}]^a$ ,  $[\text{OH}^-]^b$  and temperatures at  $I = 0.3 \text{ mol dm}^{-3}$

$10^2 [\text{S}_2\text{O}_8^{2-}]$ , $\text{mol dm}^{-3}$	$10^4 k_{\text{obs}}, \text{s}^{-1}$				
	T = 25°C	T = 30°C	T = 35°C	T = 40°C	T = 45°C
5.0	12.69	16.55	26.58	30.54	35.35
4.5	11.39	14.76	23.36	27.45	31.69
4.0	9.78	13.12	20.76	24.40	29.87
3.5	8.60	11.48	18.17	21.35	25.08
3.0	7.41	9.84	15.57	18.52	23.04
2.5	6.45	8.18	12.98	15.25	18.85
2.0	5.04	6.46	10.38	12.26	15.28
1.5	3.74	4.92	7.79	9.15	10.01
1.0	2.58	3.28	5.19	6.09	6.81
0.5	1.05	1.77	2.905	3.01	3.09

$[\text{ANS}]^a = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $10^4 k_{\text{obs}} = 9.88, 9.83$ , and  $9.87 \text{ s}^{-1}$  at  $10^4 [\text{CTA}]$  of 3, 7,  $10 \text{ mol dm}^{-3}$ , respectively, at  $30^\circ\text{C}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 0.03 \text{ mol dm}^{-3}$ .

$[\text{OH}^-]^b = 0.015 \text{ mol dm}^{-3}$ ,  $10^4 k_{\text{obs}} = 5.21, 5.17, 5.20$  and  $5.19 \text{ s}^{-1}$  at  $10^2 [\text{OH}^-]$  of 1.25, 1.75, 2.00, and  $2.50 \text{ mol dm}^{-3}$  respectively, at  $35^\circ\text{C}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 0.01 \text{ mol dm}^{-3}$ .

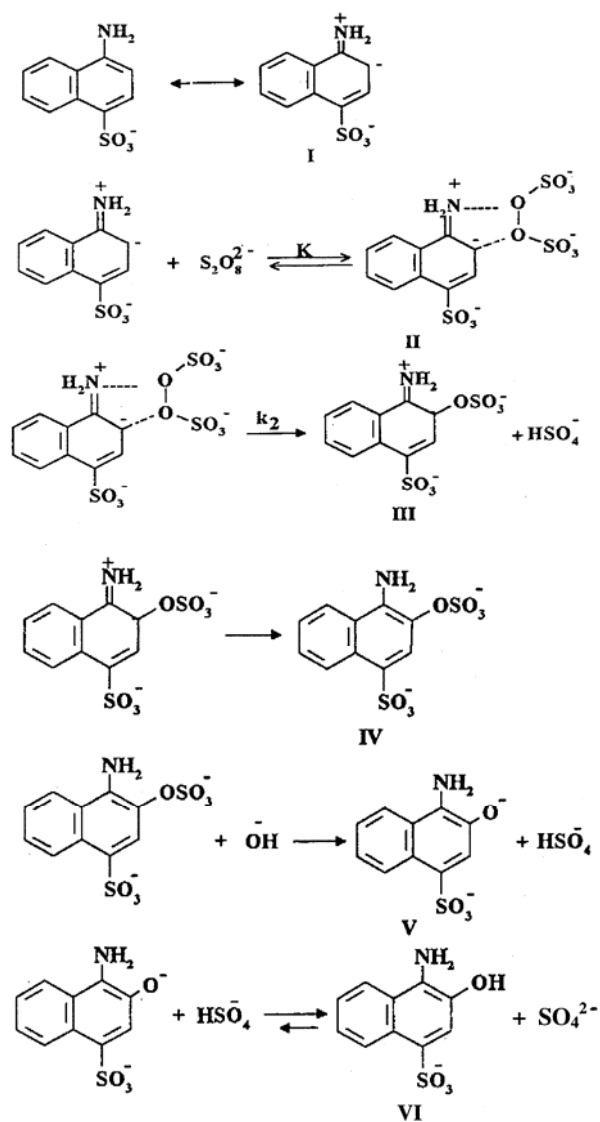
Table 4 — Dependence of rate of oxidation on solvent at  $[\text{S}_2\text{O}_8^{2-}] = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{ANS}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{OH}^-] = 0.015 \text{ mol dm}^{-3}$ ,  $I = 0.3 \text{ mol dm}^{-3}$  and  $T = 35^\circ\text{C}$

MeOH, wt%	$10^4 k_{\text{obs}}, \text{s}^{-1}$
0.00	5.19
10.2	1.34
14.4	1.12
18.8	1.02

The fact that the rate of oxidation of ANS by  $[\text{S}_2\text{O}_8^{2-}]$  is independent of  $[\text{OH}^-]$ , seems to suggest that the hydroxide ion does not participate in the rate-determining step. Also, the acrylonitrile is not polymerized when added to the reaction mixture indicating the absence of free radical.

Peroxodisulphate ion is known to be a mild electrophilic reagent capable of substituting activated aromatic compounds. Present results suggest that the reaction proceeds through an electrophilic attack of the oxidant at the nucleophilic cite (ANS) by a mechanism involving nucleophilic displacement of peroxide oxygen or sulphate ion<sup>22-24</sup> as shown in Scheme 3.

The resonance structure (I) may be the most reactive species. The formation of the hypothetical cyclic transition state (II) results from the electrophilic attack of the peroxide oxygen of  $[\text{S}_2\text{O}_8^{2-}]$  on the positive amino-nitrogen. Intramolecular electron-transfer, takes place in the formation of (III) in which  $-\text{SO}_4$  is introduced at ortho position to  $-\text{NH}_2$ . Bond rearrangement in (III) takes place leading to the formation of (IV), which reacts with the



Scheme 3

hydroxide ion causing abstraction of  $-\text{SO}_3$  from  $-\text{SO}_4$  forming (V) and  $\text{HSO}_4^-$ . Then protonation of (V) at the oxygen in the ortho position takes place by  $\text{H}^+$  from  $\text{HSO}_4^-$  with the formation of 1-amino-2-hydroxynaphthalene-3-sulfonate (VI). On acidification, the final product 1-amino-2-hydroxynaphthalene-3-sulphonic acid is formed. In fact, there is evidence for the involvement of a similar cyclic intermediate in the oxidation of some aromatic compounds by peroxodisulphate<sup>25,26</sup>. Based on the above mechanism, the rate of the reaction is given by,

$$d[\text{product}]/dt = k_2[\text{ANS} \cdot \text{S}_2\text{O}_8^{2-}] \quad \dots (5)$$

$$d[\text{product}]/dt = k_2K[\text{ANS}][\text{S}_2\text{O}_8^{2-}] \quad \dots (6)$$

If  $[\text{ANS}]$  represents the total concentration of amino-naphthalene sulphonate species, then

$$[\text{ANS}]_T = [\text{ANS}] + [\text{ANS} \cdot \text{S}_2\text{O}_8^{2-}] \quad \dots (7)$$

$$[\text{ANS}]_T = \{1 + K[\text{S}_2\text{O}_8^{2-}]\}[\text{ANS}] \quad \dots (8)$$

Substitution for  $[\text{ANS}]$  from Eq. (8) into Eq. (6) gives,

$$d[\text{product}]/dt = \{k_2K[\text{ANS}]_T[\text{S}_2\text{O}_8^{2-}]\} / \{1 + K[\text{S}_2\text{O}_8^{2-}]\} \quad \dots (9)$$

Assuming that  $K[\text{S}_2\text{O}_8^{2-}] \lll 1$ , the rate law Eq. (10), which is consistent with the experimental results, is derived.

$$d[\text{product}]/dt = k_2K[\text{ANS}]_T[\text{S}_2\text{O}_8^{2-}] \quad \dots (10)$$

Hence,

$$k_{\text{obs}} = k_2K[\text{S}_2\text{O}_8^{2-}] \quad \dots (11)$$

A comparison of Eq. (11) and Eq. (4) shows that

$$k_1 = k_2K \quad \dots (12)$$

The negative  $\Delta S^*$  values for the oxidation of both CTA and ANS by  $\text{S}_2\text{O}_8^{2-}$  in aqueous solutions suggest that solvent participation is more pronounced in the transition state. The reactant ions are of like sign, so they form an activated complex of higher charge that exerts more electrostriction on the surrounding  $\text{H}_2\text{O}$  molecules. This electrostriction leads to entropy loss resulting in negative entropy of activation.

Enthalpy of activation,  $\Delta H^*$ , reported for both CTA and ANS are composite values. The relatively lowering of enthalpy of activation for ANS reaction, is probably, due to the formation of cyclic intermediate being a fast exothermic step. The intramolecular electron-transfer step, probably, is endothermic. For CTA reaction the hemolytic fission of  $\text{S}_2\text{O}_8^{2-}$ , may be, endothermic process followed by probably a fast step, in which substitution of  $\text{SO}_4^-$  in the two benzene rings takes place. Hence, the contributions of  $\Delta H^*$  and  $\Delta S^*$  to the rate constant seem to compensate each other.

The decrease in the rate of oxidation of both CTA and ANS with increasing methanol content in the solvent mixtures can be explained in the light of oxidation mechanism. This observation may be due to

the polarity of the solvent mixture. Formation of  $\text{SO}_4^{\cdot-}$  in case of oxidation of CTA and the cyclic transition state in case of ANS is facilitated by increase the polarity of the solvent mixture and vice versa.

### Conclusion

It can be concluded, that, the oxidation of 1,8-dihydroxynaphthalene-3,6-disulphonic acid (CTA) and 1-amino-4-naphthalenesulphonic acid (ANS) by  $\text{S}_2\text{O}_8^{2-}$  leads to hydroxylation of these organic compounds. The homolytic fission of  $\text{S}_2\text{O}_8^{2-}$  is the determining step in the oxidation of CTA, whereas, the intramolecular electron transfer in the precursor compounds is the rate determining step in the mechanism of oxidation of ANS. Hydroxylation takes place at para position of benzene ring in CTA and ortho position in ANS is blocked. Rate of oxidation of CTA is slower than ANS, because the rate of fission of  $-\text{O}-\text{O}-$  in  $\text{S}_2\text{O}_8^{2-}$  is slower than rate of intramolecular electron transfer in the intermediate compound, as confirmed by the higher value of  $\Delta H^*$  in case of CTA than ANS.

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