Spectrophotometric Determination of Metal ions with Modified reagents :

General Procedure :

Adjust the pH of the metal ion solution containing 6 to 70 μg (see Table 1 and 2 for effective range) to the required pH (Tables 1 and 2). Add 2 ml of $1 \times 10^{-3} M$ modified reagent solution of the same pH (The modified reagents are prepared by adding about four fold excess of CTAB solution to reagent solutions and keeping them for atleast 15-20 minutes for complete micelle formation). Make up the volume to 25 ml with distilled water. Measure the absorbance at suitable wave length (Tables 1 and 2) against modified reagent as blank. The results obtained should be compared with a calibration curve prepared according to the same procedure.

The reproducibility of the reaction was found to be excellent with ECAB, PCV and SCR.

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Kinetics of the Oxidation of Methyl Phenyl Sulphoxide by Chloramine-T in Acid Medium : Effect of Low Acid Concentrations

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IN a previous communication the authors[1] have reported on the kinetics and mechanism of oxidation of methyl phenyl sulphoxide in the presence of hydrochloric acid (0.04-0.08 M) and sodium chloride (0.40 to 0.70 M) at 10°. The rate of disappearance of chloramine-T showed first order dependence on [chloramine-T], [H+] and [Cl-] and it was independent of the substrate concentration. In the present communication we have examined the kinetic behaviour of oxidation with [H+] less than 0.035 M.

Experimental

Chloramine-T used was of AnalaR grade (M & B). Methyl phenyl sulphoxide was prepared by a known method. All solutions were prepared in doubly distilled water. The kinetics of the reaction was followed by iodometric estimation of chloramine-T in a measured aliquot of the reaction mixture at various time intervals. Methyl phenyl sulphone was found to be the oxidation product of substrate[1] even under these conditions.

Results and Discussion

The kinetics of the oxidation of methyl phenyl sulphoxide by chloramine-T has been studied at several initial concentrations of the reactants (Table 1). When methyl phenyl sulphoxide is in excess plots of log (titre) versus time are found to be linear. The first order constants in chloramine-T calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration.

TABLE 1—EFFECT OF REACTANT CONCENTRATIONS

Temp. = 20°   [H+]=2.0×10⁻³M   [Cl-]=0.42 M   I=0.42

10^4[Chloramine-T] M	10^3[$C_6H_5SOCH_3$] M	$k_{obs} \times 10^4$ sec⁻¹
8.0	20.0	8.46
14.0	20.0	8.34
20.0	20.0	8.72
20.0	8.0	8.17
20.0	14.0	8.31

Effect of Variation of Acid Concentration :

The kinetic runs were carried out at 20° keeping the concentrations of methyl phenyl sulphoxide and chloramine-T constant at varied concentrations of hydrochloric acid (Table 2). A plot of log k against log [H+] gave a straight line with slope slightly higher than 0.5.

TABLE 2—DEPENDENCE OF RATE ON [H+]

Temp.=20°   [$C_6H_5SOCH_3$]=2.0×10⁻²M
[Chloramine-T]=2.0×10⁻³M,   [Cl-]=0.42M,   I=0.42

10^3[H+] M	$k_{obs} \times 10^4$ sec⁻¹
1.4	7.78
2.0	8.72
2.4	10.04
3.0	11.19
3.5	12.49

Effect of Variation of Chloride Ion Concentration :

The kinetic runs were carried out at 20° with varying concentrations of chloride ions (Table 3). A plot of log k versus log [Cl-] gave a straight line with slope nearly 1.

TABLE 3—DEPENDENCE OF RATE ON [Cl⁻]

Temp.=20° $[C_6H_5SOCH_3]=2.0\times10^{-3}M$
$[\text{Chloramine-T}]=2.0\times10^{-3}M$, $[H^+]=2.0\times10^{-3}M$

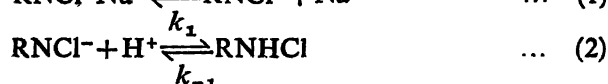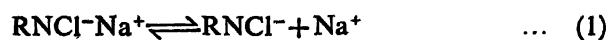| $10\,[Cl^-]$ M	$k_{obs}\times10^4$ sec^{-1}
4.2	8.72
5.2	10.12
6.2	12.09
7.2	13.00

Effect of Neutral Salt :

The reaction has been studied with varying concentrations of $NaClO_4$. The results indicate that the ionic strength has no effect on the rate constant.
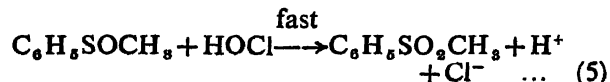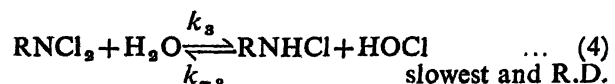
Effect of Temperature :

The kinetic runs were made in the temperature range of 10-25°. The energy of activation and the entropy of activation of the reaction have been computed as 64.5 KJ mole⁻¹ and −92.87 JK⁻¹ respectively.

Chloramine-T, being a strong electrolyte, dissociates in aqueous solution to its anion (p-$CH_3C_6H_4SO_2\overline{N}Cl$) which can be protonated by mineral acid.
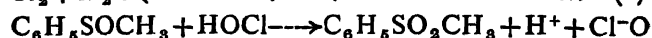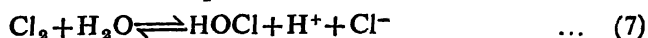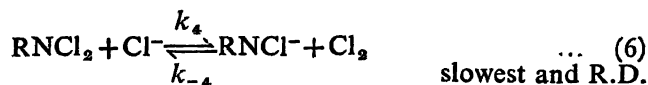
$$RNCl^-Na^+ \rightleftharpoons RNCl^- + Na^+ \qquad \ldots (1)$$
$$\underset{k_{-1}}{\overset{k_1}{RNCl^- + H^+ \rightleftharpoons RNHCl}} \qquad \ldots (2)$$

$$R = p\text{-}CH_3C_6H_4SO_2$$

The free acid has not been isolated. In the absence of added chloride the following mechanism has been proposed.

$$\underset{k_{-2}}{\overset{k_2}{RNHCl + RNCl^- \rightleftharpoons RNCl_2 + RNH^-}} \qquad \begin{array}{l}\ldots (3)\\ \text{slow}\end{array}$$

$$\underset{k_{-3}}{\overset{k_3}{RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl}} \qquad \begin{array}{l}\ldots (4)\\ \text{slowest and R.D.}\end{array}$$

$$\overset{\text{fast}}{C_6H_5SOCH_3 + HOCl \longrightarrow C_6H_5SO_2CH_3 + H^+ + Cl^-} \qquad \ldots (5)$$

Pryde and Soper[2,3] have shown that the direct interaction of RNHCl with the substrate could be slow while HOCl formed by the hydrolysis of $RNCl_2$ would attack at a faster rate. The direct interaction of $RNCl_2$ with the substrate is expected to be negligible because of the faster rate of interaction of HOCl, produced by the hydrolysis of this species, with the substrate. This is supported by the fact that in the oxidation of some primary alcohols[4] and allyl alcohol[5] a mechanism involving HOCl as the oxidizing species has been proposed. The first order dependence on chloramine-T and fractional order on H⁺ concentration suggest that the slowest step could be the hydrolysis of $RNCl_2$ producing HOCl. Since the rate is independent of sulphoxide concentration, the disappearance of sulphoxide probably takes place by the fast reaction (5) with HOCl.

In the presence of added chloride, the oxidizing species will be either molecular chlorine or positive chlorine[6,7]. $RNCl_2$ reacts with chloride ions to form molecular chlorine which, in turn, reacts with water to produce hypochlorous acid. The rate of disappearance of chloramine-T is independent of the ionic strength of the medium. This observation along with the first order dependence on chloramine-T and positive effects of hydrogen ion concentration and chloride ion concentration suggests that the slowest step could be the reaction between $RNCl_2$ and chloride producing molecular chlorine. In this case also, the disappearance of sulphoxide takes place by the fast reaction with HOCl which is produced by the reaction between molecular chlorine and water.

$$\underset{k_{-4}}{\overset{k_4}{RNCl_2 + Cl^- \rightleftharpoons RNCl^- + Cl_2}} \qquad \begin{array}{l}\ldots (6)\\ \text{slowest and R.D.}\end{array}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad \ldots (7)$$
$$C_6H_5SOCH_3 + HOCl \longrightarrow C_6H_5SO_2CH_3 + H^+ + Cl^-O$$

Two mechanisms have been proposed by the authors[1] for the oxidation of methyl phenyl sulphoxide by assuming (i) direct attack by HOCl and (ii) the attack by protonated HOCl in acid medium.

The required rate laws can be derived by a considering steady states for RNHCl and $RNCL_2$ and assuming

$$k_{-1} \gg k_2\,[CAT],\ k_{-2} \gg k_3\frac{[H_2O]}{[DCT]}\ \text{and}\ k_{-2} \gg k_4\frac{[Cl^-]}{[DCT]}.$$

The derived rate expressions are $-d[CAT]/dt = k[CAT]\,[H^+]^{\frac{1}{2}}$, in the absence of added chloride and $-d[CAT]/dt = k[CAT][H^+]^{\frac{1}{2}}[Cl^-]$, in the presence of added chloride.

Acknowledgement

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