Kinetics of Oxidation of 2-Mercaptoethylamine Hydrochloride by 2,6-Dichlorophenolindophenol in Methanol-Water Medium

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The kinetics of oxidation of 2-mercaptoethylamine hydrochloride by 2,6-dichlorophenol-indophenol have been investigated in methanol-water medium (88% v/v), and in the presence of alkali. The reaction shows zero order in thiol hydrochloride and second order with respect to 2,6-dichlorophenolindophenol. The rate increases linearly with the [alkali] in the range investigated. Neither of the reaction products, viz. the disulphide or the leuco-dye, affects the rate. Similarly, the addition of neutral electrolytes also does not influence the rate. Activation parameters have been determined and a plausible reaction scheme has been suggested.

TO follow the course of many biochemical redox reactions 2,6-dichlorophenolindophenol, a well-known oxidation-reduction indicator, has often been used. The redox properties of this dye have been studied extensively[1]. Basford and Huennekens[2] also employed this compound in the assay of a number of thiols with quite reliable results. This paper deals with the kinetics of oxidation of 2-mercaptoethylamine hydrochloride with this oxidant and also suggests the tentative course of the reaction. However, it would be relevant to add that like ferricyanide[3-11] ion used earlier for the oxidation of a variety of thiols including the present one, this chromophoric compound too possesses several advantages and the kinetics of oxidation can be followed colorimetrically in a convenient manner.

Materials and Methods

2-Mercaptoethylamine hydrochloride (designated as RSH) of 99% purity was obtained as a gift from M/s Evans Chemetics, USA. Its solution was prepared in doubly distilled water, standardized against iodine solution[12] and stored under N_2 atmosphere. The solution of 2,6-dichlorophenolindophenol (denoted as 'In' and referred hereafter as indophenol) was prepared in redistilled methanol (BDH, LR). The solution was prepared afresh for each run, since the light and temperature both affect the stability[13]. The disulphide was prepared by oxidizing the thiol hydrochloride with ferric alum[14]. The leuco-dye was prepared by bleaching indophenol by passing SO_2 gas[15] and later boiling-off the solution to remove excess SO_2. This solution was also stored under N_2 atmosphere. All other reagents were either of BDH (analar) or E. Merck's (GR) grade.

The reaction was studied colorimetrically by measuring the depletion in the concentration of 2,6-dichlorophenolindophenol with time. For this purpose, a Klett-Summerson photoelectric colorimeter fitted with filter No. 59 (spectral range 565-630 nm) was employed. The use of this filter

is justified as indophenol has maximum absorbance at 620 nm (ϵ_{max} 2×10^4 cm^2 $mole^{-1}$) while the disulphide and the leuco-dye respectively show maximum absorbance at 240 and 284 nm. These spectra were recorded on a Unicam spectrophotometer SP 500 using silica cells with a light path of 1 cm. As the Beer's law is obeyed in the entire concentration range of indophenol under investigation, the concentration of indophenol was read from a calibration curve. The runs were made under N_2 atmosphere though it was observed that for the duration of the experiments described, its absence did not affect the rate.

Results and Discussion

The stoichiometry was determined analytically as well as spectrophotometrically. In the former case, the amount of indophenol consumed by thiol hydrochloride was determined while in the latter, the amount of disulphide formed was determined employing the relationship $D = \epsilon ct$ at the wavelength of its maximum absorbance. These experiments lead to a stoichiometry of 2:1 in accordance with Eq. (1)

$$2RSH + In \rightarrow RSSR + H_2In \qquad \ldots(1)$$
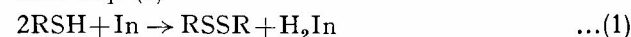
The formation of the disulphide, when stoichiometry is 2:1 has also been suggested by Basford and Huennekens[2].

The order of the reaction with respect to oxidant was first determined by Ostwald's isolation method. As stated earlier, all the runs were made in 88% (v/v) methanol-water medium. It may also be added that the runs followed at this composition of the system showed good reproducibility. These runs gave a second order dependence in indophenol, which was evident from second order plots shown in Fig. 1. This was further confirmed by van't Hoff's differential method (Fig. 2). It would, however, be seen from Fig. 1 that the magnitude of rate coefficients depends upon the initial [indophenol]. It was found that the index of inverse proportionality is 1·5. Incidentally, this observation
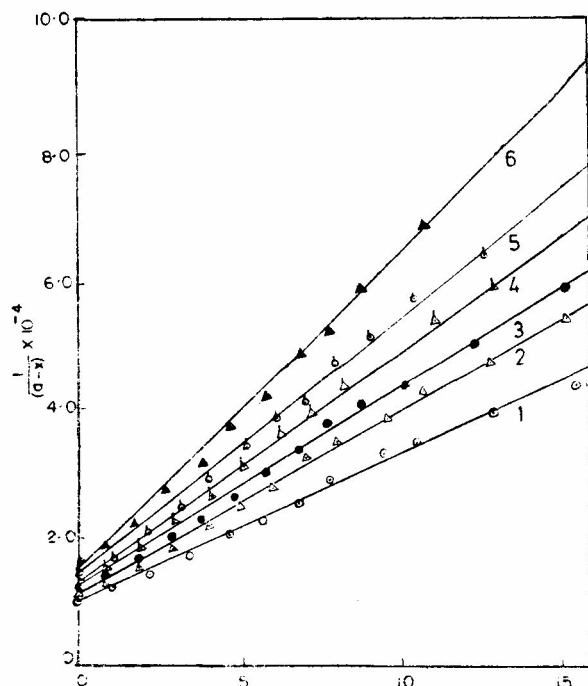
Fig. 1 — Second order plots in the oxidation of 2-mercapto-ethylamine hydrochloride (RSH) by 2,6-dichlorophenol indophenol at different initial [oxidant] {[RSH] = 1·5 ×10⁻³M; [NaOH] = 2×10⁻²M; [oxidant]₀ = 10×10⁻⁵ (curve 1), 9·33×10⁻⁵ (curve 2), 8·67×10⁻⁵ (curve 3), 8×10⁻⁵ (curve 4), 7·33×10⁻⁵ (curve 5) and 6·67×10⁻⁵M (curve 6); CH₃OH = 88% (v/v); and temp.= 25°}
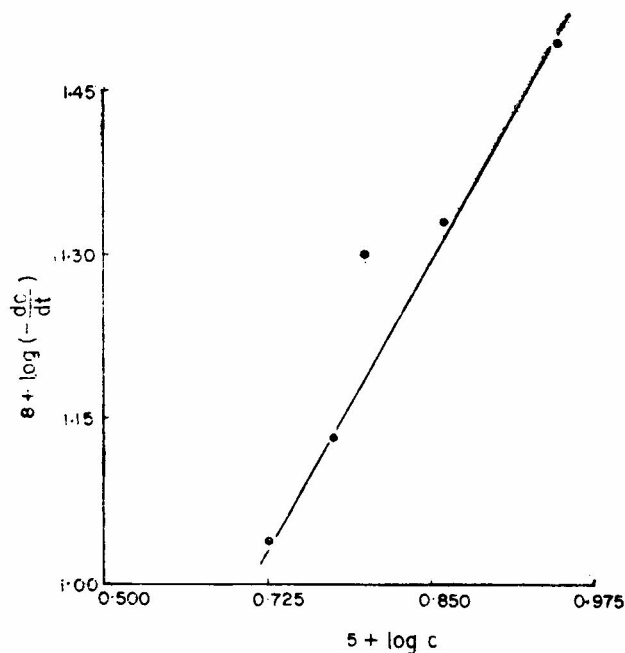
is similar to that made earlier by Shrivastava[15] while using this oxidant in the oxidation of some other thiols. In the next series of experiments, the concentration of thiol hydrochloride was increased from ten to forty-folds in excess over indophenol, while keeping [indophenol] $\approx$ $(1 \times 10^{-4}M)$ and other variables unchanged. The rate was found to be independent of [thiol] (Table 1) which suggests zero order in this reactant. Keeping in view the fast nature of the reaction, the values of k_2 given in Table 1 may be taken to be reasonably constant.

The reaction rate is found to exhibit a linear dependence on the [alkali] as revealed by the linear plot of log k_2 versus log [OH⁻] with a slope of unity. As the addition of neutral electrolytes did not produce any change in the rate over a wide concentration range (0·020 to 0·053M), it was not deemed necessary to maintain the ionic strength of the reaction system at any constant value in these runs.

The reaction products, viz. 2,2'-diaminoethyl-disulphide dihydrochloride (the disulphide) and the leuco-dye also did not influence the rate when added externally in a series of runs (Table 2). This implies that these products are not involved in the mass law term.

Arrhenius equation was found to be applicable and the slope of the Arrhenius plot gave the value of energy of activation as 13·86 kcal/mole. The entropy of activation was calculated employing Eyring's equation and found to be −4·41 e.u.

Mechanism — In the light of the results obtained above, the tentative reaction Scheme 1 is suggested.

$$In + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} InOH^- \qquad ...(2)$$

$$InOH^- + In \overset{k_2}{\rightarrow} C \text{ (reactive intermediate)} \qquad ...(3)$$

$$C + RSH \overset{fast}{\longrightarrow} reaction products \qquad ...(4)$$

Scheme 1

TABLE 1 — RATE DATA FOR THE OXIDATION OF 2-MERCAPTOETHYLAMINE HYDROCHLORIDE BY INDOPHENOL

{[In]=1·00×10⁻⁴M; [NaOH]=2·00×10⁻²M; CH₃OH=88% (v/v); μ = 0·020M; temp.= 25°}

[RSH]×10³M	k_2, litre mole⁻¹ sec⁻¹	[RSH]×10³M	k_2, litre mole⁻¹ sec⁻¹
1·50	37·38	3·00	36·72
2·00	38·49	4·00	39·54
2·50	37·14	—	—

TABLE 2 — RATE DATA IN PRESENCE OF REACTION PRODUCTS

{[RSH] = 1·5×10⁻³M; [In] = 1·0×10⁻⁴M; [NaOH] = 2·0 ×10⁻²M; CH₃OH = 88% (v/v); μ = 0·020M; temp.= 25°}

[H₂In]×10⁵M	2	4	6	8
k_2, litre mole⁻¹ sec⁻¹	39·90	38·72	38·38	37·89

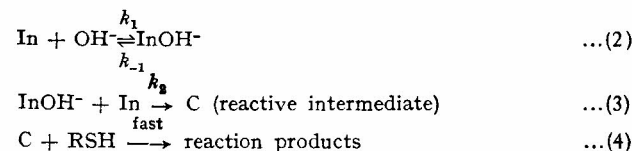| [RSSR]×10⁴M	1	2	3	4	5
k_2, litre mole⁻¹ sec⁻¹	41·59	40·14	40·21	41·76	42·19

Fig. 2 — Confirmation of second order dependence on [oxidant] by van't Hoff's differential method

In Scheme 1 formation of InOH$^-$ has been presumed in one of the rate determining steps. This presumption is similar to that made by Amis and La-Mer[16] in the case of alkaline fading of certain phthalein and sulphophthaleine dyes. Further, 2-mercaptoethylamine hydrochloride (HS.CH$_2$.CH$_2$.NH$_2$.HCl) molecule has been presumed to participate in the reaction as HS.CH$_2$.CH$_2$.NH$_2$ and is represented as RSH. This also appears justified in view of the nature of the medium and the fact that the dissociation of sulphydryl (—SH) group is reported to be very small ($K = 1 \cdot 995 \times 10^{-11}$ at 25°)[17]. Since as per stoichiometry step (4) cannot alone give the reaction products it appears probable that this in turn produces other reaction intermediates which through a sequence of fast steps lead finally to the reaction products, viz. the disulphide and the leuco-dye. The participation of one such reaction intermediate is at least partly demonstrated by the capability of this system to initiate the polymerization of vinyl acetate.

For deriving the rate law on the basis of reaction Scheme 1 if one applies the steady-state treatment to InOH$^-$, its concentration would be given by Eq. (5):

$$[InOH^-] = \frac{k_1[In][OH^-]}{k_{-1}+k_2[In]} \qquad ...(5)$$

On this basis the rate of reaction would be given by Eq. (6):

$$-\frac{d[In]}{dt} = \frac{2k_1k_2[In]^2[OH^-]}{k_{-1}+k_2[In]} \qquad ...(6)$$

On dividing Eq. (5) by 'k_{-1}', we get

$$-\frac{d[In]}{dt} = \frac{2k_2K[In]^2[OH^-]}{1+\dfrac{k_2}{k_{-1}}[In]} \qquad ...(7)$$

where $K = (k_1/k_{-1})$ and is the equilibrium constant of step (2).

Under the condition when $k_2 [In]/k_{-1} \ll 1$, Eq. (7) becomes Eq. (8).

$$-\frac{d[In]}{dt} = 2k_2K[In]^2[OH^-] \qquad ...(8)$$

or

$$-\frac{d[In]}{dt} = k'[In]^2[OH^-]$$

where $k' = 2k_2K$. At a constant [OH$^-$] Eq. (8) can be further simplified to Eq. (9)

$$-\frac{d[In]}{dt} = k''[In]^2 \qquad ...(9)$$

where $k'' = k'[OH^-]$ and is the observed pseudo-second order rate coefficient. The assumption that $(k_2/k_{-1})[In] \ll 1$ appears reasonable, firstly because [In] is fairly small ($\sim 10^{-4}M$) and secondly, under the conditions described k_2/k_{-1} is also expected to be

less than unity. The proposed mechanism satisfactorily explains all the observed kinetic features excepting the inverse proportionality between the rate and the initial [indophenol]. In this context a mention of the addition reactions of quinones[18-20] would be useful as this may at least qualitatively account for this effect. According to Hadler et al.[21] thiols undergo addition reactions with 2,6-dichlorophenolindophenol and form 1,4-addition product (II) (species II). This product may again react with an another indophenol molecule and result in a conjugate of the dye (III) and the leuco-dye.

A species of the type III is expected to be relatively inert as compared to indophenol as was also suggested by Hadler et al.[21]. Consequently, on increasing the initial [indophenol] the side reaction leading to the formation of III may become prominent, and this would consequently produce the retardation in rate.

Acknowledgement

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