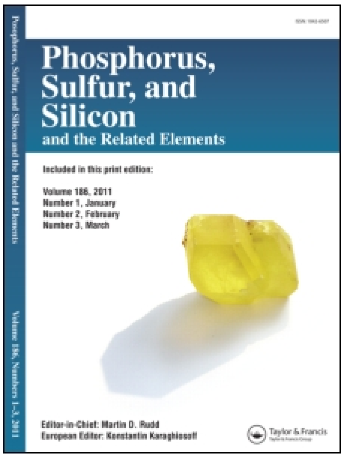

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KINETICS AND MECHANISM OF THE OXIDATION OF 1-PROPANETHIOL AND 2-PROPANETHIOL BY 2,6-DICHLOROPHENOLINDOPHENOL IN METHANOL-WATER MEDIUM

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KINETICS AND MECHANISM OF THE OXIDATION OF 1-PROPANETHIOL AND 2-PROPANETHIOL BY 2,6-DICHLOROPHENOLINDOPHENOL IN METHANOL-WATER MEDIUM

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The oxidative cleavage of 1-propanethiol and 2-propanethiol (1-PT and 2-PT respectively) by 2,6-dichlorophenolindophenol have been studied in methanol-water medium and the thiol-disulphide conversion has been studied kinetically in presence of hydroxyl ion at 30°C. The reaction follows a second order kinetics in indophenol in both cases. The order of reaction is one in 1-propanethiol while in 2-propanethiol, the order shows a transition from zero to one at higher concentrations of alkali. The rate constant shows a direct proportionality with [OH^-] in case of 1-propanethiol but in the oxidation of 2-propanethiol, an inverse linear proportionality has been noticed. Again in the oxidation of 2-PT, the rate is indifferent to [OH^-] at higher concentrations of sodium hydroxide (ca. $>2.5 \times 10^{-4}$M). The rate of oxidation of 1-PT increases on increasing the dielectric constant of the medium while a decrease in the rate of oxidation of 2-PT has been observed in these studies. Variation of ionic strength and the addition of reaction products do not influence the rate in both the cases. The reaction has been studied at different temperatures and activation parameters have been evaluated. Mechanisms consistent with kinetic data have been proposed and the diversity in kinetic results has been interpreted in terms of the difference in the mode of addition of thiol molecule to indophenol dimer.

The mechanistic studies on the oxidation of thiols have evoked considerable interest in recent years owing to their involvement in cellular activities. The oxidation of sulphydryl compounds by a host of oxidants has been reported in the literature. 2,6-Dichlorophenolindophenol, a well known reagent[1] for the determination of vitamin C, was also used for this purpose by Basford and Huennekens[2] and later by Overberger and coworkers[3] and by Hadler *et al.*[4] Its interaction with thiols has been exploited in the determination of membrane SH group[5] in biochemical studies. Recently, its involvement in the binding of flavines has also been reported.[6] Looking to such a wide involvement of this oxidant, we started detailed kinetic investigations, perhaps for the first time, on the oxidation of a variety of sulphydryl compounds[7–14] and this communication describes the kinetics and mechanism of the oxidation of 1-propanethiol and 2-propanethiol in alkaline medium.

EXPERIMENTAL

Reagents and Procedure

The solutions of 1-propanethiol and 2-propanethiol (obtained from Fluka A. G., Chemische Fabrick, Buchs S. G., Switzerland and denoted later as 1-PT and 2-PT respectively) were prepared by diluting the

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* For correspondence.

sample in methanol (E. Merck, G. R.). Back iodometric titration[15] procedure was followed for determining the concentration of thiol solution. The solution of indophenol was prepared and standardised as described previously.[7] The stock solution of thiols were stored under a nitrogen atmosphere. The disulphide was prepared by oxidizing the corresponding thiol with iodine.[16] All other details are the same as described earlier.[11]

RESULTS

Both analytical and spectrophotometric methods were employed to determine the stoichiometry of the reaction.[17,11] Both the methods gave a stoichiometry of 2 : 1. Thus,

$$2\mathrm{RSH} + \mathrm{In} \longrightarrow \mathrm{RSSR} + \mathrm{H_2In}$$

(Here In and H_2In denote indophenol and leucodye respectively).

The reaction between the referred thiols and indophenol follows a second order kinetics in indophenol. The order in the oxidant was determined by Ostwald's isolation and van't Hoff's differential method. The runs were made with ten to seventy fold excess of thiol over indophenol (ca. 4.5×10^{-5}M) keeping all other variables fixed (Table I). It may be added here that the runs were made at a fixed composition of aqueous methanol (70% v/v in case of 1-PT and 40% v/v in case of 2-PT) because the runs are kinetically smooth at these compositions. The results shown in Table I suggest a first order kinetics in 1-propanethiol as revealed by the near constant values obtained for the relation 'k_2/[1-PT]'. Further, in case of 2-propanethiol, there is no variation in rate constant on varying [RSH] which indicates a zero order dependence on the substrate in these studies.

In the next series of experiments, [In] was varied keeping other variables unchanged. The rate decreases on increasing [In]. The results, summarised in Table II, reveal a diversity in the relation of rate with the initial concentration of indophenol.

The hydroxyl ion concentration wields a diagonally opposite influence on the rate of oxidation of the steric isomers. The rate increases linearly on increasing [OH^-] in case of 1-PT (Table III). In case of 2-PT, however, the rate shows an inverse linear proportionality with [OH^-] at lower concentrations of alkali (ca. $<2.5 \times 10^{-4}$M). Above 2.50×10^{-4}M, the rate is found to be indifferent towards [OH^-] (Table IV).

TABLE I

Rate constants at different [RSH]

[1-PT] × 10^4M	k_2, litre $\mathrm{mole^{-1}\,sec^{-1}}$	$\frac{k_2}{[1\text{-PT}]} \times 10^{-4}$	[2-PT] × 10^4M	k_2, litre $\mathrm{mole^{-1}\,sec^{-1}}$
4.50	10.58	2.351	4.50	16.21
9.00	20.94	2.326	9.00	16.52
13.50	30.16	2.239	13.50	15.71
18.00	41.46	2.303	18.00	15.54
22.50	54.00	2.400	22.50	15.80
31.50	74.58	2.367	31.50	15.93

4.50×10^{-5}M—Indophenol
5.00×10^{-4}M-Sodium hydroxide
Methanol—70% (v/v)
Ionic strength—5×10^{-4}M,
temp.—30°

4.50×10^{-5}M—Indophenol
1.00×10^{-4}M—Sodium hydroxide
Methanol—40% (v/v)
Ionic strength—1×10^{-4}M
temp.—30°

TABLE II

Rate constants at different [In]

[In] × 10^5M	k_2, litre mole^{-1} sec^{-1} (1-PT)	k_2 × [In] × 10^5	k_2, litre mole^{-1} sec^{-1} (2-PT)	k_2 × $[\mathrm{In}]^2$ × 10^8
4.50	10.58	47.61	16.21	3.280
4.00	11.91	47.64	18.59	2.970
3.50	14.05	49.17	26.39	3.230
3.00	15.73	47.19	32.26	2.900
2.50	20.69	51.60	51.82	3.230
2.00	24.33	48.66	73.78	2.950

4.50 × 10^{-4}M—1-PT;
5.00 × 10^{-4}M—Sodium hydroxide
Methanol—70% (v/v)
Ionic strength—5 × 10^{-4}M
temp.—30°

4.50 × 10^{-4}M—2-PT
1 × 10^{-4}M—Sodium hydroxide
Methanol—40% (v/v)
Ionic strength—1 × 10^{-4}M
temp.—30°

TABLE III

Rate constants at different [OH$^-$] obtained for the oxidation of 1-propanethiol

[OH$^-$] × 10^4M	k_2, litre mole^{-1} sec^{-1}	(k_2/[OH$^-$]) × 10^{-4}
0.50	0.9266	1.853
1.00	2.355	2.355
5.00	10.58	2.116
10.00	23.16	2.316
15.00	31.30	2.086
25.00	52.13	2.085
40.00	83.93	2.090

4.5 × 10^{-4}M—1-PT;
4.5 × 10^{-5}M—Indophenol

Methanol—70% (v/v)
temp.—30°

TABLE IV

Rate constants at different [OH$^-$] obtained for the oxidation of 2-propanethiol

[OH$^-$] × 10^4M	k_2, litre mole^{-1} sec^{-1}	(k_2 × [OH$^-$]) × 10^4M
0.25	68.23	17.05
0.50	30.16	15.08
1.00	16.21	16.21
1.50	12.11	18.16
2.00	7.713	15.42
2.50	6.041	15.05
2.75	6.195	—
3.00	6.287	—
3.50	6.390	—
4.50	5.989	—
6.00	5.990	—

4.5 × 10^{-4}M—2-PT
4.5 × 10^{-5}M—Indophenol

Methanol—40% (v/v)
temp.—30°

TABLE V

Rate data at different [2-PT] at higher [OH⁻]

[2-PT] × 10^4M	k_2, litre mole^{-1} sec^{-1}	(k_2/[2-PT]) × 10^{-3}
4.50	5.989	13.29
9.00	12.39	13.71
13.50	18.90	14.00
18.00	24.42	13.56
22.50	29.83	13.25
31.50	43.47	13.80

4.50 × 10^{-5}M—Indophenol
4.50 × 10^{-4}M—Sodium hydroxide

Methanol—40% (v/v)
temp.—30°

It may be added here that the pH dependence of the reactions of thiols are generally found to be of baffling nature.[17] The variation in sodium hydroxide concentration exerts a peculiar influence on the kinetic features of the oxidation of 2-propanethiol. A glance at Table 1 reveals a zero order dependence of rate in 2-PT but this is true in the lower concentration range of alkali (ca. $<2.5 \times 10^{-4}$M). At higher concentrations, however, the order in thiol increases from zero to unity. The results obtained for the runs having different [RSH] in the higher concentration range of hydroxyl ion (ca. 4.50×10^{-4}M) are summarised in Table V.

The rate increases on increasing the dielectric constant of the medium in case of 1-PT while in case of 2-PT, an opposite effect is observed.

The rate is not influenced on increasing the ionic strength of the system as well as on the addition of reaction products. The ionic strength could be varied by adding uni-univalent electrolytes only because in alkaline medium, higher valent cations are precipitated.

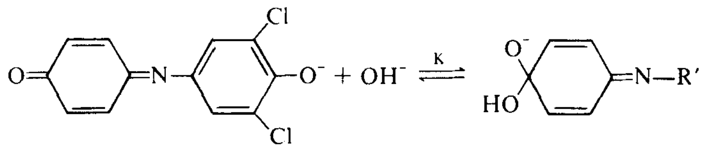
The runs were made at different temperatures ranging between 20°C to 40°C. Obedience to the Arrhenius equation was observed in both the cases. Activation parameters determined with the aid of usual expressions are given below:

		1-PT	2-PT
ΔH^*	(kcal mole^{-1})	6.10	4.57
ΔS^*	(e.u.)	−34.55	−38.77
ΔF^*	(kcal mole^{-1})	16.40	16.13

MECHANISM

As reported, the experimental findings suggest a first order kinetics in 1-propanethiol and a second order kinetics in indophenol. The rate, in this case, is directly proportional to [OH⁻]. These results can be explained by assuming the formation of an adduct (II) between indophenol and hydroxyl ion as shown in Scheme I.

Scheme I

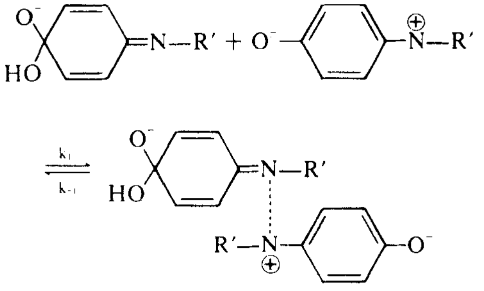


(1)

(I, In) (II)

(here R′ represents the remaining part of the molecule)

A similar adduct as represented by structure (II) has also been reported to be formed in case of quinones.[18] This is further shown to react with the mesomeric form of indophenol molecule forming a dimer (D) as shown below:



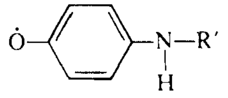
(2)

(III, D)

The dimer (D) would be obviously transient owing to steric crowding and on interaction with a thiol molecule, may facilitate the formation of various reactive intermediates (C*).

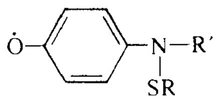
$$D + RSH \xrightarrow{k_2} C^* + OH^- \tag{3}$$

'C*' as given in step (3) includes free radicals such as 'HIn$^{\bullet}$' and 'RSIn$^{\bullet}$'.[9] It can be admitted here that the actual path traversed by the system en route the formation of these free radicals could not be chalked out authentically and is very much of a suggestive nature. It would, however, be judicious to add that the reactions of thiols have been generally explained on the basis of free radical mechanism.[19–21] Incidentally, the formation of half-reduced indophenol (HIn$^{\bullet}$) has been proposed earlier also in the reaction of this oxidant with N-methyl acridan[22] and has been assigned the following structure:



(IV)

Similarly, the species like 'RSIn$^{\bullet}$' has been proposed to be formed in case of quinones[23] and may be represented by the structure:



(V)

Thus,

$$D + RSH \xrightarrow{k_2} RSIn^{\bullet} + HIn^{\bullet} + OH^- \tag{4}$$

These free radicals may combine with substrate molecules in a sequence of fast steps and establish a stoichiometry of 2 : 1 (Thiol:In).

$$\mathrm{RSIn^{\bullet} + RSH \xrightarrow{fast} RSSR + HIn^{\bullet}} \tag{5}$$

$$\mathrm{HIn^{\bullet} + RSH \xrightarrow{fast} RS^{\bullet} + H_2In} \tag{6}$$

$$\mathrm{2\,RS^{\bullet} \xrightarrow{fast} RSSR} \tag{7}$$

Incidentally, the participation of free radicals in these reactions is qualitatively demonstrated by the capability of the system to polymerise vinyl acetate.[24]

The rate of reaction for the above scheme would be given by

$$-\frac{d\,[\mathrm{In}]}{dt} = k_1\,[\mathrm{InOH^-}]\,[\mathrm{In}] - k_{-1}\,[\mathrm{D}] \tag{8}$$

On assuming steady-state for 'D'

$$[\mathrm{D}] = \frac{k_1\,[\mathrm{InOH^-}]\,[\mathrm{In}]}{k_{-1} + k_2\,[\mathrm{RSH}]} \tag{9}$$

On substituting the value of [D] and $[\mathrm{InOH^-}] = K\,[\mathrm{In}]\,[\mathrm{OH^-}]$ in Eq. (8), the rate expression would be

$$-\frac{d\,[\mathrm{In}]}{dt} = \frac{k_1 k_2 K\,[\mathrm{In}]^2\,[\mathrm{RSH}]\,[\mathrm{OH^-}]}{k_{-1} + k_2\,[\mathrm{RSH}]} \tag{10}$$

if $k_{-1} >> k_2$ [RSH], Eq. (10) is further simplified to

$$-\frac{d\,[\mathrm{In}]}{dt} = \frac{k_1 k_2 k}{k_1}\,[\mathrm{In}]^2\,[\mathrm{RSH}]\,[\mathrm{OH^-}] \tag{11}$$

Equation (11) explains the principal kinetic features of the reaction except the retarding influence of [In]. This has been explained in terms of the formation of dye conjugate in such reactions.[4,11] The assumption $k_{-1} >> k_2$ [RSH] has been further verified by plotting '$1/k_{\mathrm{obs}}$' against '1/[RSH]' (Figure 1). From Eq. (10), it follows that

$$k_{\mathrm{obs}} = \frac{k_1 k_2 K\,[\mathrm{RSH}]\,[\mathrm{OH^-}]}{k_{-1} + k_2\,[\mathrm{RSH}]} \tag{12}$$

(where k_{obs} is the observed second order rate constant)

or,
$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-1}}{k_1 k_2 K\,[\mathrm{RSH}]\,[\mathrm{OH^-}]} + \frac{1}{k_1 K\,[\mathrm{OH^-}]} \tag{13}$$

From Figure 1, intercept = 0.15×10^{-2} and slope = 4.3×10^{-5}

In the light of this, the assumption made in Eq. (11) seems justified.

The kinetic observations for 2-propanethiol can be explained vis-a-vis the interaction of indophenol with $\mathrm{OH^-}$ ion in the higher concentration range of alkali (pH 8.2) and with $\mathrm{H^+}$ ion in the lower concentration range (pH 7.1). Schemes II and III give a tentative account of the course of reaction. In Scheme II, indophenol dimer (D) is presumed to be formed as a consequence of the interaction of protonated indophenol ($\mathrm{HIn^+}$) with the mesomeric form of indophenol.

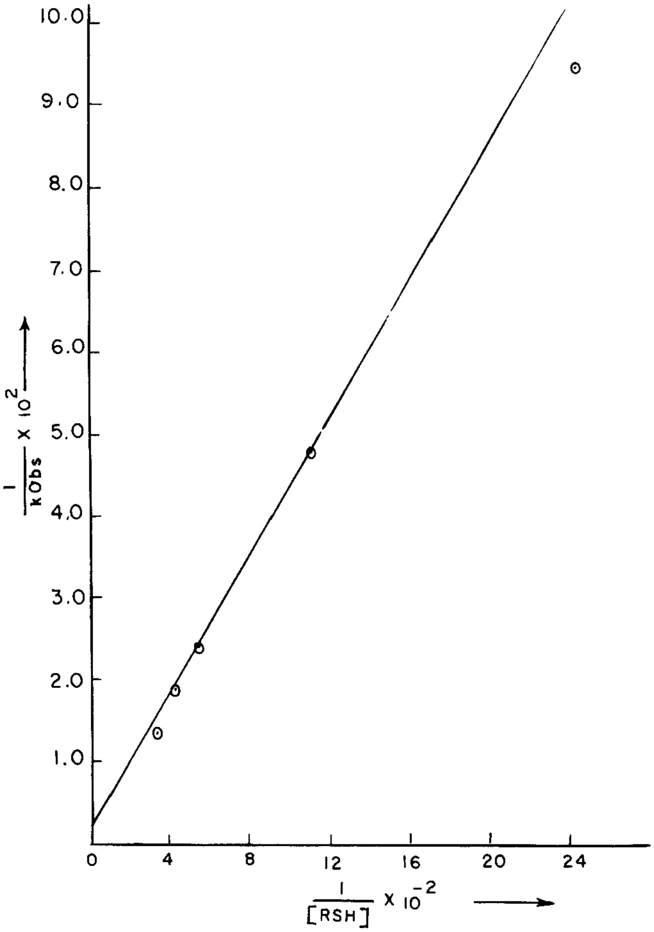
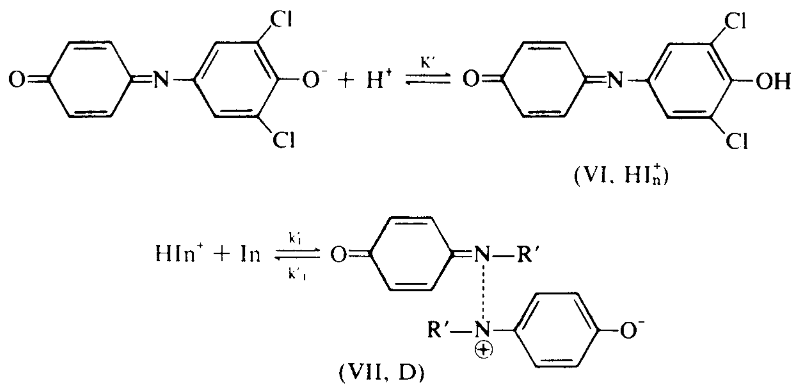


FIGURE 1 (In] = 4.5 × 10^{-5}M; [NaOH] = 5.0 × 10^{-4}M; CH_3OH = 70% (V/V); I = 5 × 10^{-4}M; TEMP = 30°

Scheme II

(Oxidation of 2-PT at lower [OH^-])



(14)

(VI, HI_n^+)

(15)

(VII, D)

The dimeric species may further react with a thiol molecule producing the free radicals—'RSIn$^{\cdot}$' and 'HIn$^{\cdot}$' as given in Scheme I. Thus,

$$D + RSH \xrightarrow{k_2'} C^* + H^+ \qquad (16)$$

'C*' would react with thiol molecules in a series of fast steps as shown in steps (5–7).

On assuming steady-state for 'D' and substituting $[HIn^+] = K' [In] [H^+]$; the rate of reaction would be given by the expression

$$-\frac{d\,[In]}{dt} = \frac{k_1'k_2'K' \,[In]^2\,[RSH]\,[H^+]}{k_{-1}' + k_2'\,[RSH]} \qquad (17)$$

If $k_2' \times [RSH] \gg k_{-1}'$; then

$$-\frac{d\,[In]}{dt} = k_1'K'\,[In]^2\,[H^+]$$

or

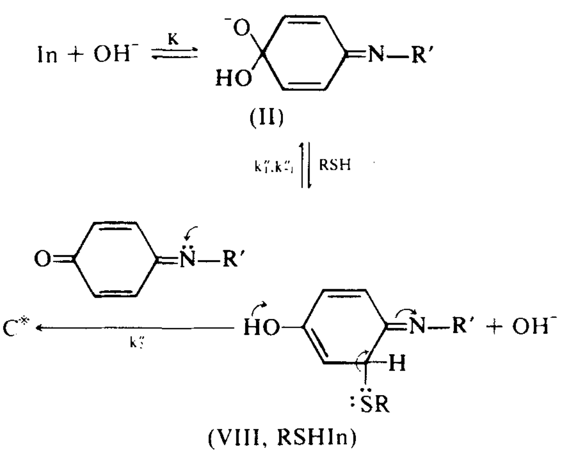
$$-\frac{d\,[In]}{dt} = \frac{k_1'K'Kw\,[In]^2}{[OH^-]} \qquad (18)$$

Eq. (18) explains the second order kinetics in indophenol and an inverse linear relation with $[OH^-]$ observed under these conditions. Moreover, the rate of reaction under these circumstances should not be influenced by [RSH] which has actually been observed. The validity of the proposed mechanism has been further checked by plotting '$1/k_{obs}$' against '$[OH^-]$', which gives a straight line passing through the origin (Figure 2) which is in conformity with the relation

$$k_{obs} = \frac{k_1'K'Kw}{[OH^-]} \qquad (19)$$

At higher $[OH^-]$, the possibility of the formation of the adduct 'HIn$^+$' would be remote and thus, the adduct 'InOH$^-$' is presumed to react as shown in Scheme III.

Scheme III
(Oxidation of 2-PT at higher $[OH^-]$)



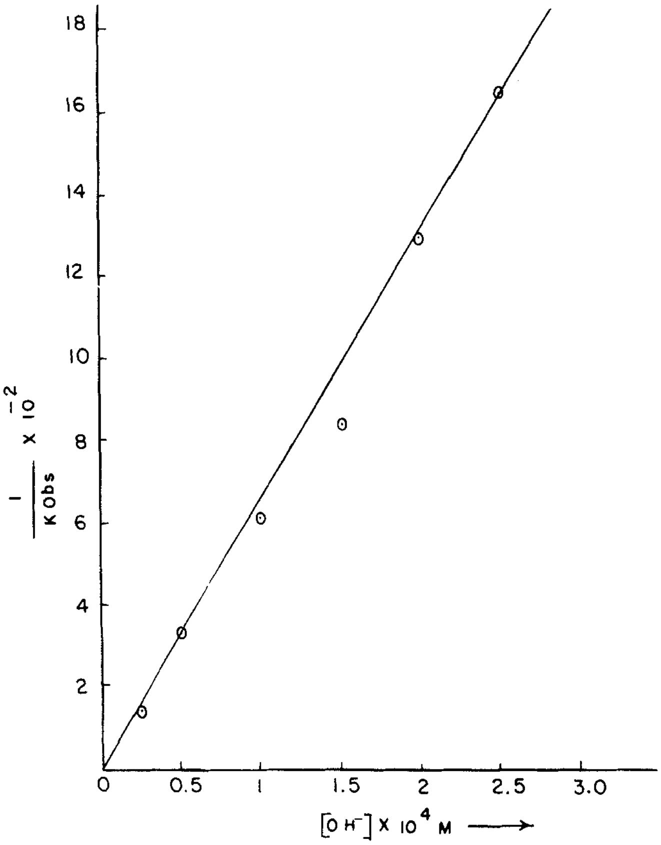
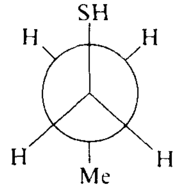
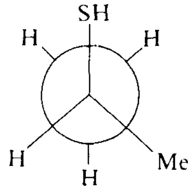


FIGURE 2 $[2\text{-PT}] = 4.50 \times 10^{-4}$M; $[In] = 4.50 \times 10^{-5}$M; CH_3OH = 40% (V/V); TEMP = 30°C

A glimpse at Schemes I and III would reveal that kinetic results obtained for 2-PT are best explained by assuming the formation and subsequent participation of a 1,4-addition product (species VIII) as suggested by Hadler *et al.*[4] and Mishra *et al.*[13] in such cases. This can be explained by comparing the conformations of thiol, 1-propane and 2-propane.



1-Propanethiol



2-Propanethiol

The electron donating methyl group in 2-PT would tend to stabilize the carbonium ion and thus, electron density on sulphur atom would be more in this molecule as compared to 1-PT. This seems further justified because the two isomers represent typical examples of primary and secondary thiols and the former should be more acidic owing to a comparatively more destabilized sulphonium ion. Incidentally, the steric influence on the oxidation of primary and secondary alcohols is well established.

Again, on applying a steady state treatment for 'RSHIn' and on substituting $[InOH^-] = K[In][OH^-]$, the rate is given by

$$-\frac{d[In]}{dt} = \frac{k_1''k_2''K[RSH][In]^2[OH^-]}{k_{-1}''[OH^-] + k_2''[In]} \tag{20}$$

Since $[OH^-] \gg [In]$ and a large negative entropy of activation has been noticed for the reaction; $k_{-1}''[OH^-]$ would be appreciably larger. Under these circumstances,

$$-\frac{d[In]}{dt} = \frac{k_1''k_2''K}{k_{-1}''}[RSH][In]^2 \tag{21}$$

Eq. (21) explains a first order behaviour in thiol and a zero order dependence on hydroxyl ion concentration in this region.

The mechanisms given above are largely circumstantial but explain succinctly the observed kinetic features of the reactions. Moreover, one would notice a striking similarity in Schemes I and II except for the participation of hydrogen and hydroxyl ions in case of the two isomers. It concludes, therefore, that in acidic medium, the two compounds should behave in an exactly similar manner which has actually been observed.[25] In the light of this, the proposed schemes seem logical on theoretical grounds.

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