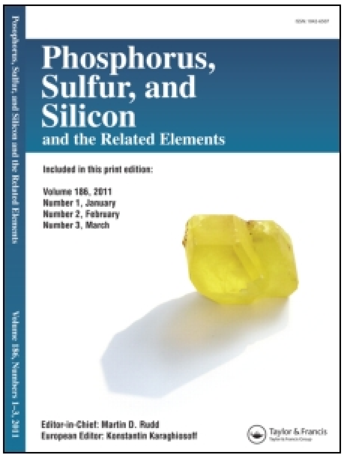

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OXIDATION OF SOME THIO ACIDS BY 2,6-DICHLOROPHENOL INDOPHENOL IN NEUTRAL AND ALKALINE MEDIUM BY SPECTROPHOTOMETRIC STOPPED FLOW TECHNIQUE

H. S. Singh[a]; P. K. Tandon[a]; S. K. Singh[a]; A. K. Jaiswal[a]
[a] Chemical Laboratories, University of Allahabad, Allahabad, India

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OXIDATION OF SOME THIO ACIDS BY 2,6-DICHLOROPHENOL INDOPHENOL IN NEUTRAL AND ALKALINE MEDIUM BY SPECTROPHOTOMETRIC STOPPED FLOW TECHNIQUE

H. S. SINGH, P. K. TANDON, S. K. SINGH and A. K. JAISWAL
Chemical Laboratories, University of Allahabad, Allahabad - 211002 India

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Using spectrophotometric stopped flow technique, the oxidation of thiolactic acid, thioglycollic acid, 3-mercaptopropionic acid and thiobenzoic acid by the dye, 2,6-dichlorophenol indophenol, has been investigated. The reaction shows first order kinetics with respect to thioacids and 2,6-dichlorophenol indophenol concentrations while zero order kinetics with respect to hydroxide ion concentrations. Neither of the reaction products viz. the disulfide or the leuco-dye, affects the rate. Similarly, the addition of neutral electrolyte also does not influence the rate. The data suggest the formation of an activated complex between thioacids and the oxidant which in turn slowly decomposes into the intermediate product.

Key words: Stopped flow technique; thioacids; 2,6-dichlorophenol indophenol; disulphide; leuco-dye.

INTRODUCTION

The oxidation kinetics of thio acids[1–5] has been described in acidic as well as in alkaline medium by one electron transfer oxidants. It has been reported that the thiol group is very sensitive towards reaction with oxygen.[6] The oxidation of thiol to its disulfide is a process of fundamental importance in biochemistry. The redox property of 2,6-dichlorophenol indophenol has been used as a mild oxidant[7] having redox potential +0.22 volts at pH 7. The redox reactions of thio acids with 2,6-dichlorophenol indophenol have yet not been studied by stopped flow technique. This prompted us to study the oxidation of thiolactic acid (TLA), thioglycollic acid (TGA), 3-mercaptopropionic acid (3-MPA) and thiobenzoic acid (TBA) by 2,6-dichlorophenol indophenol (denoted as In and referred hereafter as indophenol) in neutral as well as in alkaline medium by spectrometric stopped flow technique.

RESULTS AND DISCUSSION

The kinetic data for the oxidation of thiolactic acid, thioglycollic acid, 3-mercaptopropionic acid and thiobenzoic acid were studied in alkaline medium as well as in the absence of hydroxide ion. The results obtained are given in the Tables I–V and Figures 1–4.

The reaction velocity shows first order kinetics with respect to 2,6-dichlorophenol indophenol to the completion of the reaction. Tables I–V clearly indicate that the

TABLE I

Rate data for the oxidation of thioglycollic acid (μ = .075M, λ_{max} = 620 mμ, temp. = 35 ± 0.1°C, 2 mm cell)

[2,6-dichlorophenol indophenol] x 10^5M	[TGA] x10^3M	[OH]x10^2M	k_1'x10^2sec^{-1}	k_ψ x10^{-1} mole^{-1} sec^{-1}
10.00	5.00	4.00	26.06	5.21
6.25	5.00	4.00	25.96	5.19
5.00	5.00	4.00	24.84	4.97
2.50	5.00	4.00	25.65	5.13
1.25	5.00	4.00	25.55	5.11
10.00	5.00	4.00	26.06	5.21
10.00	10.00	4.00	57.19	5.12
10.00	20.00	4.00	118.40	5.92
10.00	30.00	4.00	155.20	5.17
10.00	50.00	4.00	261.20	5.22
10.00	5.00	1.00	25.15	5.03
10.00	5.00	3.00	25.86	5.17
10.00	5.00	4.00	26.06	5.21
10.00	5.00	5.00	25.17	5.03
10.00	5.00	6.00	25.00	5.1
10.00	5.00	7.00	26.22	5.24

Where k_ψ = k_1'/[TGA] and k_1' is the first order velocity constant.

k_1' values are practically constant in case of indophenol variation indicating first order kinetics with respect to oxidant i.e., 2,6-dichlorophenol indophenol.

The values of k_ψ calculated for molar concentration of the thioacids are fairly constant for about ten fold variation, so it is concluded that the order with respect to each thioacid is unity.

The experimental results clearly indicate that the reaction proceeds even in the absence of hydroxide ions i.e., indophenol reacts directly with thio acids. The addition of hydroxide ion in the reaction mixture only enhances the reaction velocity. This clearly shows that hydroxide ion only facilitates the formation of the sodium salt of acid. Due to this reason the reaction of catalyzed as well as uncat-

TABLE II

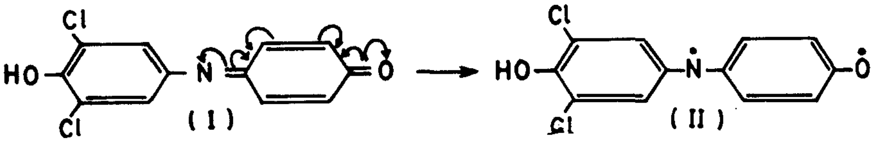
Rate data for the oxidation of thiobenzoic acid (μ = 0.25 M, λ_{max} = 620 mμ, temp. = 30°C ± 0.1°C, 2 mm cell)

[2,6-Dichlorophenol Indophenol] M x 10^5	[TBA] x10^2M	[OH^-] x10^2M	k'_1 sec^{-1}	k_ψ x10^{-1} mol e^{-1} sec^{-1}
10.00	5.00	2.50	3.367	6.73
5.00	5.00	2.50	2.987	5.97
2.50	5.00	2.50	3.384	6.77
1.66	5.00	2.50	3.385	6.77
1.25	5.00	2.50	3.450	6.90
1.00	5.00	2.50	2.930	5.86
2.50	1.00	2.50	0.663	6.63
2.50	1.50	2.50	0.952	6.34
2.50	2.00	2.50	1.397	6.98
2.50	3.00	2.50	1.932	6.44
2.50	5.00	2.50	3.384	6.77
2.50	5.00	5.00	3.058	6.11
2.50	5.00	10.00	3.384	6.77
2.50	5.00	15.00	3.259	6.51
2.50	5.00	20.00	3.398	6.79

Where $k_\psi = k'_1/[TBA]$ and k'_1 is the first order velocity constant.

alyzed passes through the same reaction mechanism. It has already been reported that the dissociation of sulfydryl group is very small (K = 1.995×10^{-11} at 25°C).[14] Constancy of k_ψ values (second order velocity constant) clearly confirms the validity of the proposed reaction mechanism.

It is well known[13] that 2,6-dichlorophenol indophenol in solution exists in the mixed form (i.e., in structures I & II).



On the basis of these results the following rate law might be proposed

$$-\frac{d[In]}{dt} = k[In][RSH] \qquad (1)$$

TABLE III

Rate data for the oxidation of thiolactic acid (μ = 0.075 M, λ_{max} = 620 mμ, temp. = 35°C ± 0.1°C, 2 mm cell)

[2.6 Dichlorophenol Indophenol] $\times 10^5$ M	[TLA] $\times 10^2$ M	$[OH^-] \times 10^2$ M	$k'_1 \times 10$ Sec^{-1}	$k_\psi \times 10$ mole^{-1} sec^{-1}
2.00	2.50	2.00	9.05	3.62
2.50	2.50	2.00	8.83	3.53
5.00	2.50	2.00	9.70	3.88
10.00	2.50	2.00	7.57	3.03
20.00	2.50	2.00	8.28	3.31
10.00	1.25	2.00	2.81	2.25
10.00	2.00	2.00	5.71	2.85
10.00	2.50	2.00	8.37	3.35
10.00	5.00	2.00	17.04	3.41
10.00	10.00	2.00	27.40	2.74
10.00	2.50	0.50	11.12	4.45
10.00	2.50	0.625	10.19	4.08
10.00	2.50	1.25	10.45	4.18
10.00	2.50	2.50	8.34	3.34
10.00	2.50	5.00	8.34	3.34
10.00	2.50	5.00	8.70	3.48

Where $k_\psi = k'_1/[TLA]$ and k'_1 is the first order velocity constant.

where [In] = 2,6-dichlorophenol indophenol and [RSH] is substrate.

The kinetic data for the oxidation of TLA, TGA, 3-MPA and TBA were also collected in the absence of hydroxide ion. Table V clearly indicates first order kinetics with respect to 2,6-dichlorophenol indophenol and TLA each. The similar results were obtained with TGA, 3-MPA and TBA also.

To study the effect of the reduced form of 2,6-dichlorophenol indophenol (leuco-dye) a number of runs were made in which different concentrations of the reduced form were added initially. Such addition does not produce any significant effect on the value of the rate coefficients. This clearly shows that the reduced dye is not involved in any reversible step of the reaction scheme. Since the velocity constant

TABLE IV

Rate data for the oxidation of 3-mercaptopropionic acid (μ = 0.25 M, λ_{max} = 620 mμ, temp. = 35°C ± 0.1°C, 2 mm cell)

[2,6-Dichlorophenol Indophenol.] $M \times 10^5$	[3-MPA] $\times 10^2 M$	$[OH^-] \times 10^2$	$k'_1 \times 10$ sec^{-1}	$k_\psi \times 10^{-1}$ $mole^{-1}\ sec^{-1}$
5.00	5.00	2.00	7.87	1.57
6.25	5.00	2.00	7.75	1.55
10.00	5.00	2.00	7.95	1.59
12.50	5.00	2.00	7.43	1.48
25.00	5.00	2.00	8.52	1.70
10.00	2.00	2.00	2.32	1.16
10.00	2.50	2.00	3.41	1.76
10.00	4.00	2.00	5.66	1.41
10.00	5.00	2.00	7.94	1.59
10.00	10.00	2.00	12.67	1.26
10.00	5.00	0.50	5.99	1.19
10.00	5.00	0.62	5.89	1.18
10.00	5.00	1.00	6.75	1.35
10.00	5.00	1.25	5.90	1.18
10.00	5.00	2.50	6.47	1.29

Where $k_\psi = k'_1/[3\text{-MPA}]$ and k'_1 is the first order velocity constant.

values remain the same, they have not been included in the tables. For these results also the rate law similar to Equation (1) might be given.

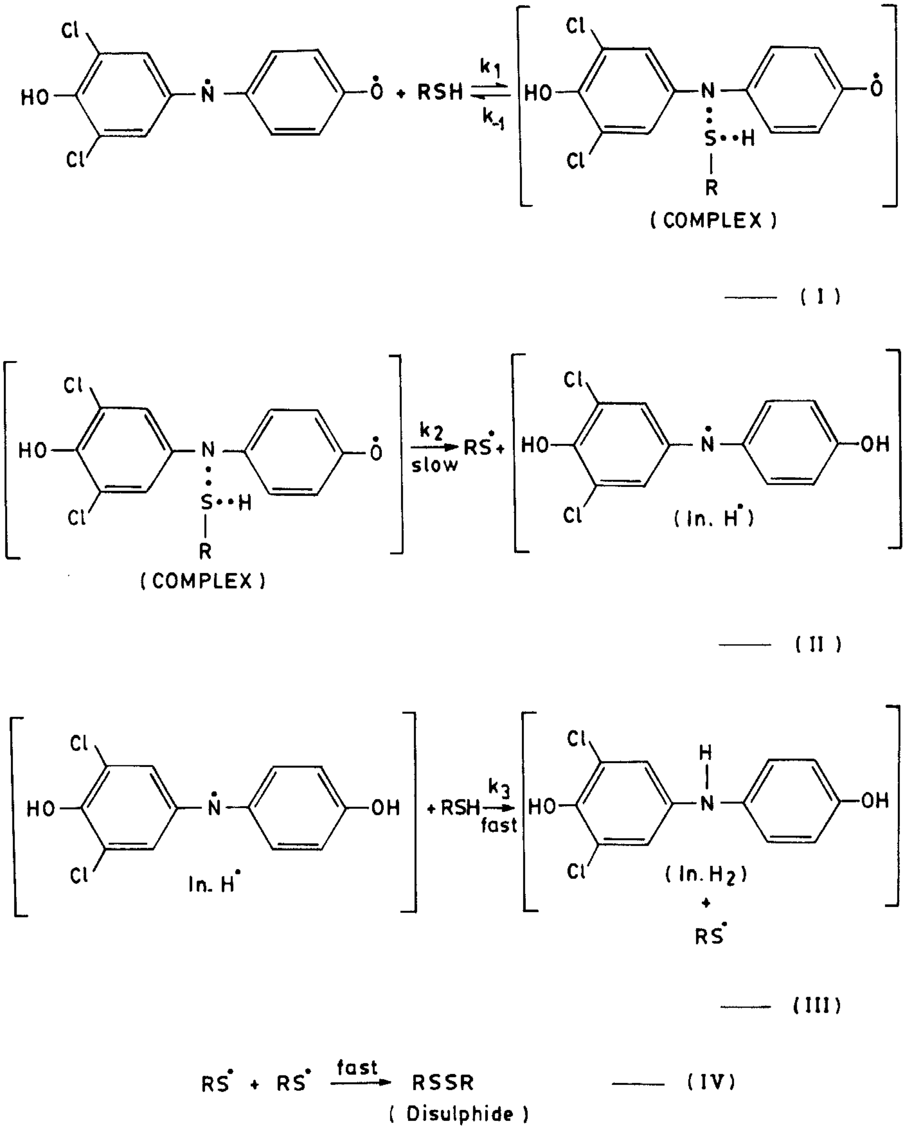
On the basis of the above results, i.e., first order dependence of the reaction rate with respect to thio acids and 2,6-dichlorophenol indophenol concentrations and zero order kinetics with respect to hydroxide ion concentration, the following mechanistic steps might be proposed. In these steps:

$$R = \text{—}CH_2COOH(TGA), \qquad R = CH_3.CHCOOH(TLA)$$

$$R = \text{—}CH_2CH_2COOH\ (MPA),\ R = C_6H_5CO\text{—}(TBA)$$

On the basis of the results the substrate combines with indophenol to give the complex In.RSH[10–13] which slowly decomposes in the next step. This also appears justified in the view of the low dissociation of sulfydryl group.[14]

MECHANISTIC STEPS INVOLVED FOR THE OXIDATION OF THIO ACIDS



At steady state condition the concentration of the complex can be given as

$$[\mathrm{In.RSH}] = \frac{k_1[\mathrm{In}][\mathrm{RSH}]}{k_{-1} + k_2} \tag{2}$$

Thus the rate equation would result as

$$-\frac{d[\mathrm{In}]}{dt} = \frac{k_1 k_2[\mathrm{In}][\mathrm{RSH}]}{k_{-1} + k_2} = k'[\mathrm{In}][\mathrm{RSH}] \tag{3}$$

TABLE V

Rate data for the oxidation of thiolactic acid in the absence of hydroxide ion (λ_{max} = 620 mμ, temp. = 35°C ± 0.1°C, 2 mm cell)

[2,6-Dichlorophenol Indophenol] $\times 10^5$ M	[TLA] $\times 10^2$ M	$k'_1 \times 10$ sec^{-1}	k_ψ $\times 10^{-1}$ mole^{-1} sec^{-1}
5.00	5.0	15.85	3.17
6.25	5.0	17.07	3.41
10.00	5.0	17.22	3.44
12.50	5.0	15.70	3.14
25.00	5.0	18.57	3.71
50.00	5.0	18.43	3.68
10.00	2.0	7.56	3.78
10.00	2.5	88.91	3.57
10.00	3.3	13.15	3.95
10.00	5.0	17.23	3.44
10.00	10.0	32.95	3.29

Where $k_\psi = k'_1/[\text{TLA}]$ and k'_1 is the first order velocity constant.

where

$$k' = \frac{k_1 k_2}{k_{-1} + k_2}$$

Now

$$-\frac{d[\text{In}]}{dt} \Big/ [\text{In}] = k'[\text{RSH}] = k'_1 \qquad (4)$$

where k'_1 is the first order velocity constant.

The rate law Equation (4) clearly explains first order kinetics with respect to indophenol and thio acids, as well as zero order kinetics with respect to hydroxide ion.

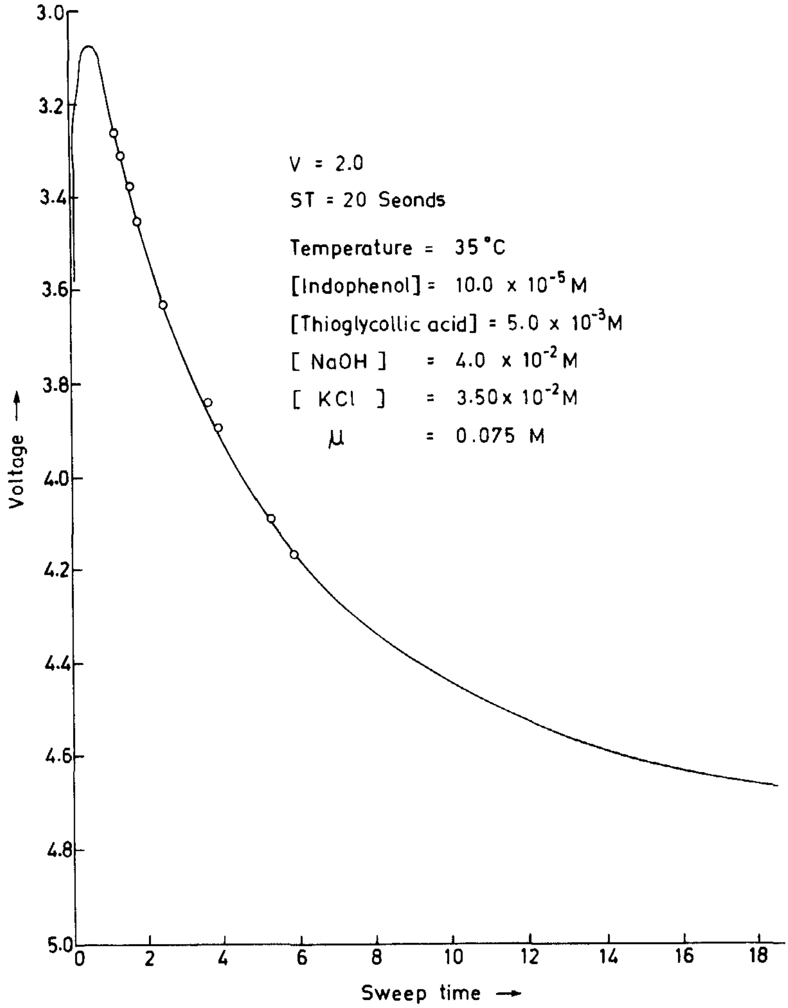


FIGURE 1 Curve obtained on oscilloscope between time and voltage.

EXPERIMENTAL

The solution of 2,6-dichlorophenol indophenol was prepared daily in double distilled water and purified nitrogen was passed through the solution in order to remove the dissolved oxygen from water. The disulfide was prepared by oxidizing the thioacids with ferric alum.[8] The leuco-dye was prepared by bleaching indophenol on passing SO_2 gas through the solution and later boiling the solution to remove the excess SO_2 gas. All these solutions were stored in a N_2 atmosphere. All other chemicals used were either Analar or chemically pure grade.

Because of the short reaction time the rates were determined by following spectrometrically the disappearance of 2,6-dichlorophenol indophenol (620 nm) in a stopped flow reactor.[9]

The stopped flow apparatus is designed so that the storage and reacting solutions can be thermostated. The apparatus provides the reaction cell with the volume of 2 mls. The reactants contained in the cell were in 1:1 ratio. In the simple absorption detection mode, a transmitted light of intensity I, as a

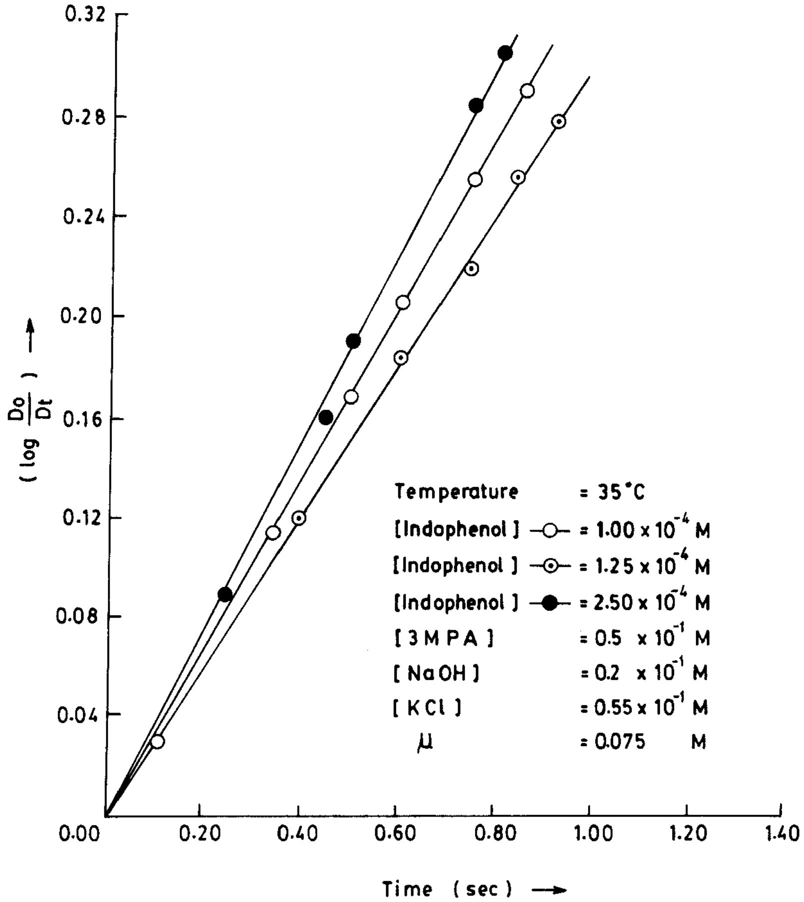


FIGURE 2 Effect of variation of [Indophenol] on the Reaction Rate in case of 3 MPA.

function of time is obtained. This is readily transformed in optical density (Dt) by means of logarithmic amplifier. The control unit passes the output signal to an oscilloscope, which is fitted with a digital memory as well as a pen recorder. The curve obtained on the oscilloscope screen in time versus voltage is traced by a pen recorder (Figure 1).

All studies were performed under pseudo-first order conditions and the rates were followed until the reactions were 100% complete. The rate constants were obtained from the plots of log (Do/Dt) vs. time (Figure 2). The rate constants given in the tables are the average of two or more runs. pH of the solution were 12.45 ± 0.15 except in hydroxide ion variation itself.

The stoichiometry of reaction was determined analytically as well as spectrophotometrically. In the former case, the amount of indophenol consumed by thioacid was determined while in the latter the amount of disulfide formed was determined by 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 the following equation.

$$2\,\mathrm{RSH} + \mathrm{In} \rightarrow \mathrm{RSSR} + \mathrm{H_2In} \qquad (5)$$

The formation of the disulfide, when stoichiometry is 2:1 has also been suggested by Basford & Huennekens.[10]

The ultraviolet absorption spectra of an ether abstract of the product disulfide and thio acids were measured with a recording spectrophotometer and the results clearly indicate the formation of disulfide of the corresponding acid.

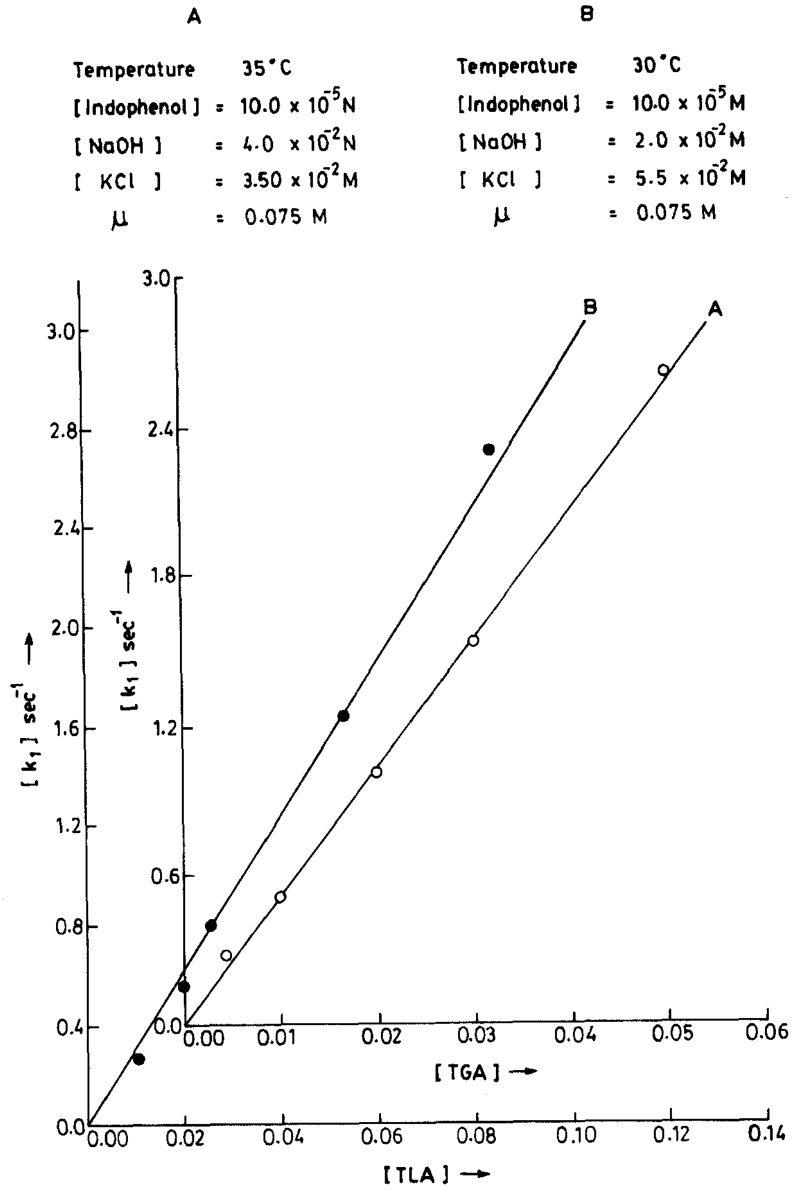


FIGURE 3 Effect of variation of [TGA] and [TIA] on the Reaction Rate.

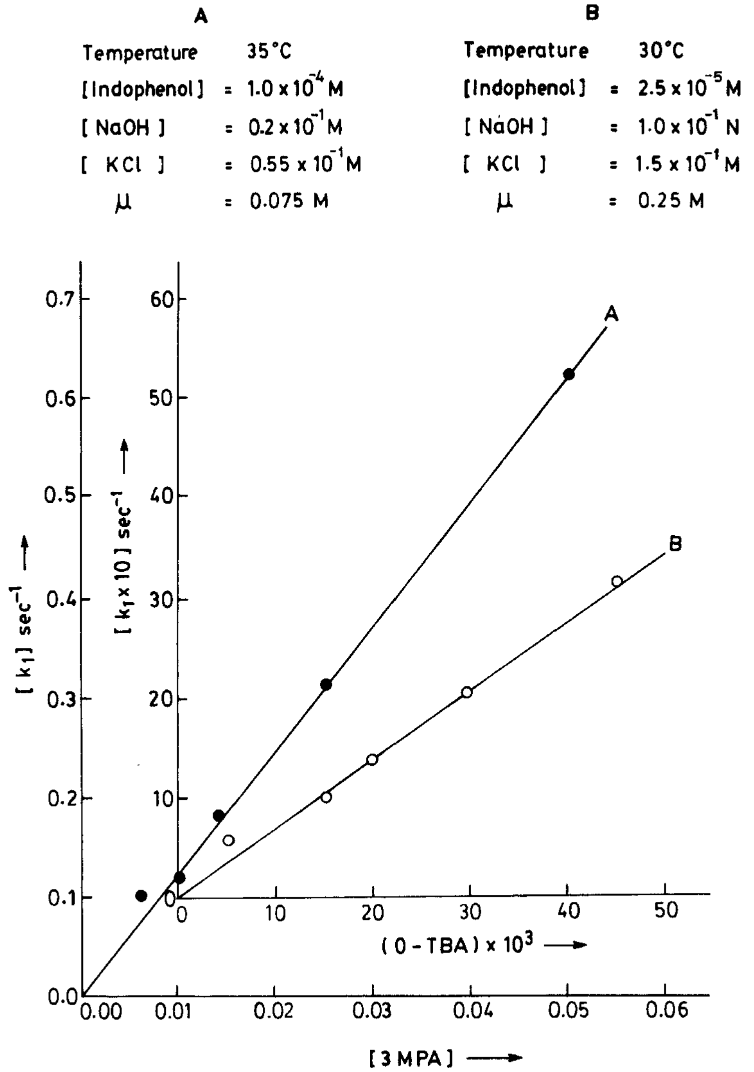


FIGURE 4 Effect of variation of [O-TBA] and [3 MPA] on the Reaction Rate.

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