

## Kinetics of oxidation of alkyl phenyl sulphides by thallium(III)

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### ABSTRACT

The kinetics of oxidation of alkyl phenyl sulphides with thallium(III) in 65% (v/v) aqueous acetic acid was measured at 35°. The overall reaction follows a second order, first order each in substrate and reagent. A plot of  $\log k/k_{Me}$  versus Taft's polar substituent constants ( $\sigma^+$ ) gave a fair correlation. In the same way a plot of  $\log k/k_{Me}$  versus Taft's steric substituent constants gave an excellent correlation. The kinetic measurements are indicative of the fact that the reaction is sensitive to the steric congestion of the reaction centre.

**Key words:** Alkyl phenyl sulphides, oxidation, kinetics, thallium(III).

### INTRODUCTION

Several studies have been reported on the kinetics of oxidation of organosulphur compounds<sup>1-10</sup>. Mechanism and rate of oxidation of these compounds are largely affected by the nature of oxidant. In spite of extensive studies on the mechanism of the oxidation of sulphides to sulphoxides by several oxidants like peroxy disulphate<sup>11</sup>, peroxydiphosphate ion<sup>12</sup>, bromine<sup>5</sup>, hydrogen peroxide<sup>1,13</sup>, peroxy benzoic acid<sup>14</sup>, diacetoxyiodobenzene<sup>15</sup>, chloramines-T<sup>16</sup>, bromamine-T<sup>16</sup> and chlorine<sup>17</sup>, kinetics of oxidation by metal ion oxidants has received little attention. However, oxidation of aryl methyl sulphides by chromium(VI)<sup>18</sup>, vanadium(V)<sup>19</sup> and thallium(III)<sup>20</sup> were reported and suitable mechanisms were proposed. Oxidation kinetics of alkyl phenyl sulphides has not received much attention, The kinetics of oxidation of sulphides by pyridinium fluoro- and bromo-chromates<sup>21,22</sup> and recently the oxidation kinetics of organic sulphides by BPCC was reported by Vyas and Sharma<sup>23</sup>. In the present investigation the kinetics of oxidation of alkyl phenyl

sulphides with thallium(III) was reported. The results were analysed in the light of the Taft's polar energy-steric energy relationship.

### MATERIAL AND METHODS

#### Preparation and purification of compounds

All the alkyl phenyl sulphides (alkyl=methyl, ethyl, n-propyl, isopropyl, t-butyl) were prepared by modification of the method described by Vogel<sup>15</sup> and purified by distillation under reduced pressure. The melting and boiling points are uncorrected. The samples were dried in vacuum before use.

The acetic acid (A.R) supplied by S. Merck was refluxed with chromium trioxide for about 6h and fractionally distilled. The fraction collected at 117-118°C was used.

#### Other reagents

Thallic oxide (B.D.H), sulphuric acid (A.R.), potassium iodide (A.R.), sodium sulphate (A.R.) were used as such. Double distilled water was used for all purposes.

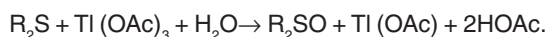
**Kinetic measurements:** Titrimetric procedure<sup>25</sup> was followed for all kinetic runs and measurements were made at 35°. The temperature was controlled by using a thermostat (accuracy  $\pm 0.1^\circ$ ). The thallium (III) solution was prepared by dissolving appropriate quantity of thallic oxide in the reaction medium containing required concentration of sulphuric acid. The sulphide solution was prepared by dissolving the appropriate quantity of the compound so that the concentration was always greater than the concentration of thallium(III). The reactant solutions were equilibrated by keeping them in the thermostat before mixing. The kinetics of the reactions were followed by quenching aliquots (5ml) of the reaction mixture at definite intervals of time.

### Product analysis

Methyl phenyl sulphide (0.01mol) was dissolved in 10ml of 65% acetic acid–water mixture (v/v) and treated with thallium(III) (0.02mol) solution containing 2M sulphuric acid. The reaction mixture was kept aside at room temperature for about two days. After that, all the acid was neutralized with a strong solution of sodium carbonate, the liberated compound was extracted with ether. The ether extract was dried over anhydrous sodium sulphate. The product was obtained after removing ether. The thin layer chromatography on a layer of silica gel showed identical behaviour of the oxidation product (methyl phenyl sulphoxide) and an authentic sample. Further, it was also supported by IR and 1H NMR spectra.

### Stoichiometry

A number of reaction mixtures containing excess of thallium(III) (at least twice the concentration of sulphide) were left in a thermostat at 35°. The estimation of the unreacted thallium(III) indicated that one mole of reagent was used for one mole of sulphide. The reaction can be written as.



The second order rate constants of the reaction were calculated by using the equation.

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

'a' and 'b' initial concentrations of sulphide and thallium(III) respectively 'x' is amount of thallium(III) reacted in time 't' seconds.

## RESULTS AND DISCUSSION

The second order rate constants for the oxidation of some alkyl phenyl sulphides with thallium(III) acetate in 65%[v/v] aqueous acetic acid were measured at 35°C. The oxidation of sulphides by thallium(III) is practically negligible in the absence of added mineral acid. On addition of suitable amount of sulphuric acid, the reaction proceeded smoothly. It was also found that increase in the concentration of added sulphuric acid increased rate of oxidation at a given temperature. For this the concentration of sulphuric acid in the reaction mixture was maintained constant when the comparison of the rates of reaction is of prime importance. The ionic strength was maintained constant by adding appropriate quantity of sodium sulphate.

For the determination of the order of the reaction, kinetic measurements were made at various concentrations of methyl phenyl sulphide and thallium(III). The second order rate constants were calculated and are given in Table 1 and 2.

The rate data clearly indicated that the variation in the concentration of either sulphide or thallium(III) has no appreciable effect on the calculated second order rate constants, indicating that the reaction follows total second order–first order each in sulphide and thallium(III).

Oxidation of the solvent under the experimental conditions is practically nil and the solutions of thallium(III) in aqueous acetic acid is very stable.

Almost all the runs were carried out under conditions of mutual check in order to ensure the constancy of the rate constants. These were believed to be accurate to  $\pm 3\%$  error and are reproducible within this limit.

The second order rate constants for the oxidation of alkyl phenyl sulphides by thallium(III) are given in Table 3.

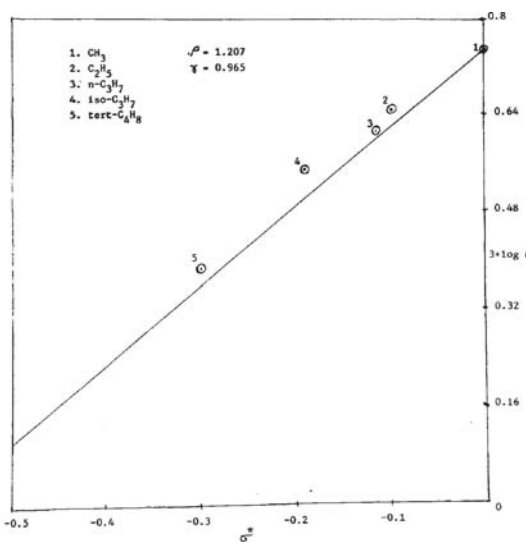


Fig. 1: Plot of log K vs  $\sigma^*$  for the oxidation of alkyl phenyl sulphides at 35°

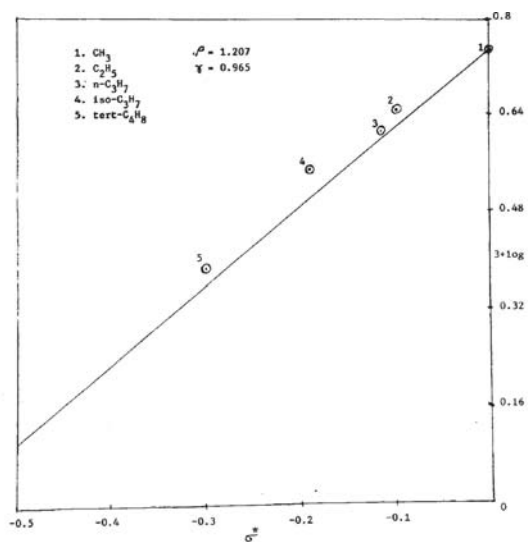


Fig. 2: Plot of log K vs  $E_s$  for the oxidation of alkyl phenyl sulphides at 35°

Table 1: Effect of  $[C_6H_5SCH_3]$  on oxidation with thallium (III)

$[C_6H_5SCH_3] \times 10^2$ moles/ dm <sup>3</sup>	Tl(III) x 10 <sup>3</sup> moles/ dm <sup>3</sup>	$K_2 \times 10^3$ dm <sup>3</sup> . mole <sup>-1</sup> sec <sup>-1</sup> at 40°
1.497	7.565	4.88
2.177	7.565	4.89
2.645	7.565	4.85
3.162	7.565	4.93

Table 2: of [Tl(III)] on oxidation of  $[C_6H_5SCH_3]$

$[C_6H_5SCH_3] \times 10^2$ moles/ dm <sup>3</sup>	Tl(III) x 10 <sup>3</sup> moles/ dm <sup>3</sup>	$K_2 \times 10^3$ dm <sup>3</sup> . mole <sup>-1</sup> sec <sup>-1</sup> at 40°
2.389	6.575	4.91
2.389	7.075	4.88
2.389	8.840	4.86
2.389	9.535	4.89

Table 3: Rate constants for the oxidation of different sulphides

Compound	$K_2 \times 10^3$ dm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup>
Ph-S-Me	5.56±0.12
Ph-S-Et	4.87±0.14
Ph-S-(n-pr)	4.49±0.05
Ph-S-(i-pr)	3.97±0.04
Ph-S-(t-Bu)	2.41±0.05

The observed second order rate constants for the oxidation of alkyl phenyl sulphides  $C_6H_5SR$ , where R=Me, Et, n-pr, i-pr and t-Bu by thallium (III) reveal that the rate decrease is in the order

Ph-S-Me > Ph-S-Et > Ph-S-n-pr > Ph-S-i-pr > Ph-S-t-Bu.

The same order has also been observed in the oxidation of these sulphides by peroxyanions<sup>26</sup>, diacetoxybenzene<sup>15</sup> and chromium(VI)<sup>27</sup>. If the contribution of the +I effect of the alkyl group predominates over the steric effect exerted by the increasing bulkiness of the alkyl groups, One would expect a reverse order in the rate.

A plot of  $\log k/k_{Me}$  versus Taft's polar Substituent constants ( $\sigma^*$ ) gave a fair correlation with  $r=0.96$  (Fig.1). However, an excellent correlation is obtained when  $\log k/k_{Me}$  is plotted against Es, Taft's steric Substituent constants (Fig. 2) (slope = 0.223) with  $r=0.991$ . These observations are indicative of the fact that the reaction is sensitive to the steric congestion of the reaction centre. Similar conclusions were reached in the oxidation of these sulphides by other oxidizing agents.

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