



## Kinetic and Thermodynamic Studies of the Oxidation of Eugenol and Isoeugenol by Sodium *N*-Chlorobenzene-*p*-Sulphonamide in NaOH

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Eugeneol and isoeugenol are used in the perfume and fragrance industry. The oxidation of these alcohols has been carried out using sodium *N*-chlorobenzene-*p*-sulphonamide in NaOH medium. The oxidation was studied using pseudo first order kinetics with respect to the *N*-haloamine oxidant. Aliquots of the reaction mixture were withdrawn at regular time intervals, the reaction was quenched and the unreacted oxidant was estimated iodometrically. The pseudo first order rate constants were determined from the straight line graphs of  $\log(a-x)$  versus time. The variation of oxidation rate with substrate and oxidant concentrations and ionic strength was studied. Potassium sulfate was used to study the effect of ionic strength ( $\mu$ ) on oxidation rate in accordance with the Bronsted-Bjerrum equation,  $\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$ . The oxidation rate was found to be independent of ionic strength. From the temperature dependence of reaction rate, the energy of activation and other thermodynamic activation parameters were evaluated. The rate determining step of the oxidation process has been identified and suitable reaction mechanisms and rate laws have been discussed. The oxidation rates follow the sequence: isoeugenol > eugenol, which has been explained on the basis of the structures and steric factors of the substrates under investigation.

**Key Words:** Perfumery phenols, Oxidation, Rate determining step, Energy of activation, Entropy of activation.

### INTRODUCTION

In our laboratory, the kinetic investigations of a variety of alcohols using various oxidizing agents have been carried out<sup>1-5</sup>. This paper deals with the kinetics of oxidation of some phenols *i.e.*, eugenol and isoeugenol, which are extensively used in the manufacture of perfumes and fragrances. The phenols were oxidized using sodium-*N*-chlorobenzene-*p*-sulphonamide (chloramine T) in NaOH. Potassium sulfate was used to determine the effect of ionic strength on the oxidation rate. The oxidation rate was carried out in the temperature range 303-318 K to determine thermodynamic activation parameter.

### EXPERIMENTAL

High purity perfumery phenols were used (Yasho Industries Pvt. Ltd., Mumbai). All other chemicals used were of A.R. grade: sodium-*N*-chlorobenzene-*p*-sulphonamide (Fluka Chemicals) and K<sub>2</sub>SO<sub>4</sub> (S.D. Fine Chemicals, Mumbai).

The oxidation of phenols to *o*-quinones was studied with respect to the oxidant. The progress of the reaction was monitored by iodometric titration of the unreacted oxidant at regular time intervals. The pseudo first order rate constants were determined from the linear plots of  $\log(a-x)$  vs. time. The reaction was studied in the temperature range 303-318 K and the energy of activation and other thermodynamic parameters

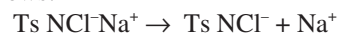
were determined from the Arrhenius plot of  $\log k$  vs.  $T^{-1}$ . The effect of ionic strength ( $\mu$ ) on the oxidation rate was determined in the range  $\mu = 5$  to  $25 \times 10^{-2}$  mol dm<sup>-3</sup> using K<sub>2</sub>SO<sub>4</sub> in accordance with the Bronsted Bjerrum equation,  $\log k = \log k_0 + 1.02 Z_A \cdot Z_B \cdot \sqrt{\mu}$ .

### RESULTS AND DISCUSSION

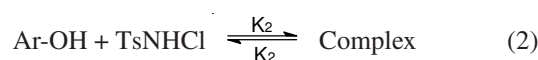
The phenols were oxidized to the corresponding *o*-quinones by sodium *N*-chlorobenzene-*p*-sulphonamide (chloramine T) in NaOH medium.

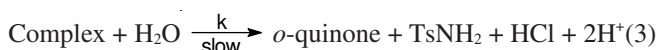
**Effect of alcohol concentration and oxidant concentration on the oxidation rate:** The rate constant increases with phenol concentration as expected, but decreases with increase in concentration of chloramine T for all the alcohols under study (Table-1).

**Reaction Mechanism of oxidation and rate law equation:** In aqueous medium, chloramine-T (Ts NCl<sup>-</sup>Na<sup>+</sup>) where the tosyl group Ts = H<sub>3</sub>C-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>- acts as a strong electrolyte and ionizes as follows:



In alkaline medium, the mechanism suggested is as follows:





Applying steady state treatment to steps 1, 2 and 3, we get,

$$[\text{TsNHCl}] = \frac{K_1[\text{TsNCl}^-]}{[\text{OH}^-]}$$

$$\begin{aligned} \text{and } [\text{Complex}] &= \frac{k_2[\text{Phenol}][\text{TsNHCl}]}{[k_2 + k]} \\ &= \frac{K_1 k_2 [\text{Phenol}][\text{TsNCl}^-]}{[k_2 + k][\text{OH}^-]} \end{aligned}$$

Step 3 determines the rate of oxidation hence the rate law equation is as follows:

$$\begin{aligned} \frac{d}{dt}[\text{Complexes}] &= k[\text{Complex}] \\ &= \frac{kK_1 k_2 [\text{Phenol}][\text{TsNCl}^-]}{[k_2 + k][\text{OH}^-]} \\ &= \frac{k'[\text{Phenol}][\text{TsNCl}^-]}{[\text{OH}^-]} \end{aligned}$$

$$\text{where } k' = \frac{k'K_1 k_2}{[K_{-2} + k]}$$

The rate law equation indicates a first order dependence on phenol and oxidizing agent and inverse first order dependence with respect to  $\text{OH}^-$  ions. A retarding influence of  $\text{OH}^-$  ions on the oxidation rate has been observed<sup>6</sup> in many reactions involving chloramine T. This is attributed to the formation of the conjugate acid;  $\text{TsNCl}^-$ . The inverse dependence of oxidation rate on  $[\text{OH}^-]$  indicates that  $\text{TsNHCl}$  is the predominant oxidizing species in alkaline medium<sup>7</sup>. This explains the decrease of oxidation rate with increase in chloramine-T concentration.

The oxidation rates follow the sequences for perfumery phenols: isoeugenol > eugeneol (Table-1, Fig. 1).

| [Phenol] $\times 10^1$<br>mol dm <sup>-3</sup> | [CAT] $\times 10^3$<br>mol dm <sup>-3</sup> | $k \times 10^4 \text{ s}^{-1}$ |            |
|--|---|--------------------------------|------------|
|  |   | Eugenol                        | Isoeugenol |
| 1.00   | 2.50  | 4.74                           | 6.46       |
| 1.00   | 5.00  | 4.69                           | 6.18       |
| 1.00   | 10.00                                       | 4.21                           | 5.88       |
| 1.00   | 15.00                                       | 4.06                           | 5.50       |
| 1.00   | 20.00                                       | 4.17                           | 5.76       |
| 1.00   | 25.00                                       | 3.60                           | 5.32       |
| 0.25   | 5.00  | 3.48                           | 4.17       |
| 0.50   | 5.00  | 3.54                           | 4.93       |
| 0.625  | 5.00  | 3.83                           | 5.65       |
| 0.75   | 5.00  | 4.007                          | 5.80       |
| 0.875  | 5.00  | 4.31                           | 6.09       |
| 1.00   | 5.00  | 4.72                           | 6.24       |

In eugenol, the dearomatization extends outside the aromatic ring. This stabilizes the substrate making it less susceptible to oxidation. In isoeugenol, the aromatization is confined within the ring making it more susceptible to oxidation<sup>8</sup>.

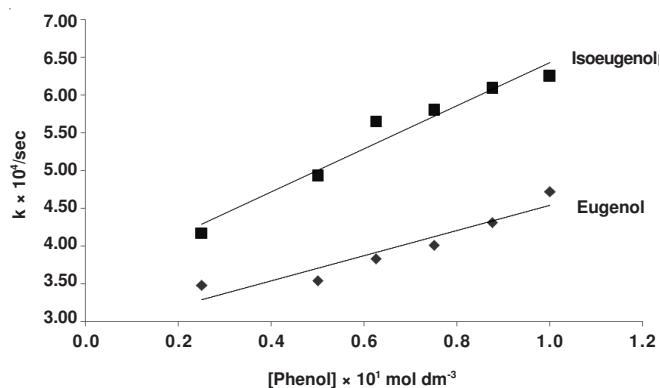


Fig. 1. Variation of rate constant of oxidation of perfumery phenols with [Phenol].

**Effect of ionic strength on oxidation rate:** The effect of ionic strength on the oxidation rate was studied in dilute solution using  $\text{K}_2\text{SO}_4$  in the range  $\mu = 5$  to  $25 \times 10^{-2}$  mol dm<sup>-3</sup> at 313 K (Table-2, Fig. 2). The graphs of  $\log k$  vs.  $\sqrt{\mu}$  were found to be straight lines parallel to the  $\sqrt{\mu}$  axis indicating that the oxidation rate is independent of ionic strength. This observation is supported by the reaction mechanism and rate laws suggested for the oxidation reaction.

| $\mu \times 10^2$ (mol dm <sup>-3</sup> ) | $k \times 10^4 \text{ s}^{-1}$ |            |
|---|--------------------------------|------------|
|   | Eugenol                        | Isoeugenol |
| Zero                                      | 4.21                           | 5.87       |
| 05.00                                     | 4.15                           | 5.78       |
| 10.00                                     | 4.02                           | 5.29       |
| 15.00                                     | 3.96                           | 5.76       |
| 20.00                                     | 4.15                           | 5.68       |
| 25.00                                     | 4.00                           | 6.36       |
| 30.00                                     | 4.13                           | 5.48       |

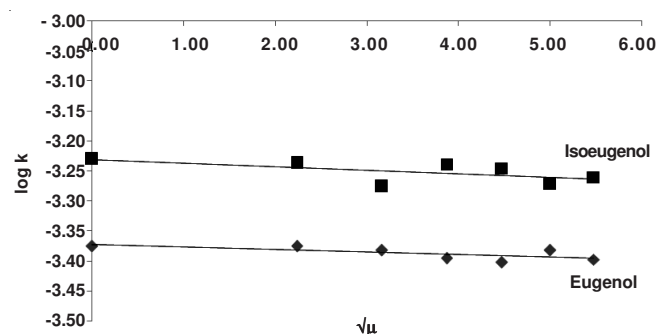


Fig. 2. Variation of rate constant of oxidation of perfumery phenols with ionic strength [ $\text{K}_2\text{SO}_4$ ]

**Effect of temperature and thermodynamic activation parameters:** The reaction was carried out in the temperature range 303 to 318 K and the thermodynamic activation parameters were evaluated (Table-3). The negative values of  $\Delta S^\ddagger$  indicate an extensive reorientation of water molecules as a result of the formation of a rigid activated complex<sup>9</sup> and can be explained by a model in which the solvent molecules are tightly held to the  $-\text{OH}$  bond which is the site of oxidation of phenols.

TABLE-3  
THERMODYNAMIC ACTIVATION PARAMETERS FOR  
THE OXIDATION OF PERFUMERY PHENOLS BY  
CHLORAMINE-T (IN NaOH) AT 303 K

| Thermodynamic activation parameters                     | Eugenol | Isoeugenol |
|---|---------|------------|
| E (kJ mol <sup>-1</sup> )                               | 17.44   | 24.63      |
| K* × 10 <sup>17</sup>                                   | 5.51    | 2.50       |
| ΔG <sup>*</sup> (kJ mol <sup>-1</sup> )                 | 94.33   | 96.31      |
| ΔH <sup>*</sup> (kJ mol <sup>-1</sup> )                 | 19.95   | 27.15      |
| ΔS <sup>*</sup> (kJ K <sup>-1</sup> mol <sup>-1</sup> ) | -0.3772 | -0.4075    |

### Conclusion

The oxidation rates of the perfumery phenols follow the sequence: isoeugenol > eugeneol. The oxidation rates increase with phenol concentration but decrease with oxidant concentration. Ionic strength has no effect on the oxidation rates of the eugenol and isoeugenol under study.

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