# Kinetic Aspects of the Oxidation of Perfumery Phenols by *n*-Bromosuccinimide in Alkaline Medium, Potassium Bromate and Potassium Iodate in Acidic Medium†

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The isomeric phenols eugenol and isoeugenol are used in the formulation of perfumes. Not much work has been reported on the kinetic and thermodynamic aspects of the oxidation of these perfumery phenols. The kinetic studies of the oxidation of phenols to *o*-quinones have been carried out using (1) *N*-bromosuccinimide in alkaline medium and (2) inorganic oxidants KBrO₃ and KIO₃ in acidic medium. The oxidation was carried out using pseudo first order kinetics with respect to the oxidizing agent. The effects of phenol and oxidant concentrations, ionic strength and temperature (303-318 K) on the oxidation rate have been studied in detail. For all the oxidizing agents under study, the oxidation rates of phenols follow the sequence isoeugenol > eugenol which has been explained on the basis of structures, steric factors and isomeric characteristics of the phenols. Suitable reaction mechanisms have been suggested for the oxidation of the phenols to *o*-quinones.

**Key Words: Perfumery phenols, Oxidation, Rate determining step, Halic acid, Energy of activation, Thermodynamic activation parameters.**

## INTRODUCTION

In our laboratory, the kinetic aspects of the oxidation of perfumery phenols, using chloramine-T in alkaline medium has been carried out[1]. This paper deals with the kinetics of the oxidation of the perfumery phenols eugenol and isoeugenol using (1) *N*-bromosuccinimide (NBS) in alkaline medium; (2) KBrO₃ in acidic medium and (3) KIO₃ in acidic medium.

The oxidation was studied in the temperature range (303-318 K) to determine thermodynamic activation parameters. The effect of ionic strength on the rate of the reaction was determined using K₂SO₄ in dilute solution.

## EXPERIMENTAL

High purity eugenol and isoeugenol were used: Yasho Industries Pvt. Ltd. Mumbai. All other chemicals used were of A.R. grade: N-Bromosuccinimide (NBS)-Sisco Research Industries, Mumbai. KBrO₃ and KIO₃ : BDH and K₂SO₄ : SD Fine Chemicals

The oxidation of phenols to *o*-quinones was studied using pseudo first order kinetics with respect to the oxidizing agent. The progress of the reaction was monitored by the iodometric estimation of the unreacted oxidant at regular intervals and the pseudo first order rate constants were determined from the linear plots of log (a-x) *versus* time.

From the effect of temperature (303-318 K) on the oxidation rate, the energy of activation and other thermodynamic parameters were determined. K₂SO₄ was used to determine the effect of ionic strength on the oxidation rate in the range, $\mu$ = 5 to 25 × 10⁻² mol dm⁻³.

## RESULTS AND DISCUSSION

**N-Bromosuccinimide in NaOH:** The perfumery phenols, eugenol and isoeugenol were oxidized to the corresponding *o*-quinones by *N*-bromosuccinimide in alkaline medium.

**Effect of phenol concentration and oxidant concentration on oxidation rate:** the rate concentration increases with phenol concentration as expected, but decreases with [NBS] for the phenols under study (Table-1).

**Reaction mechanism of the oxidation of phenols by NBS in alkaline medium:** In alkaline medium, the oxidation proceeds *via* the formation of a complex between the active species of the oxidant and the substrate followed by the decomposition of the complex in a slow rate determining step to yield the *o*-quinones (**Scheme-I**).

The oxidation rates for the perfumery phenols follow the sequence isoeugenol > eugenol (Table-1, Fig. 1). In isoeugenol, conjugation extends outside the aromatic ring but in eugenol there is no such extended conjugation. The product obtained

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on oxidation of isoeugenol, *i.e.* o-quinone is more stable hence rate of oxidation is higher. Whereas in case of eugenol, the o-quinone obtained is less stable therefore rate of oxidation is lower[2].
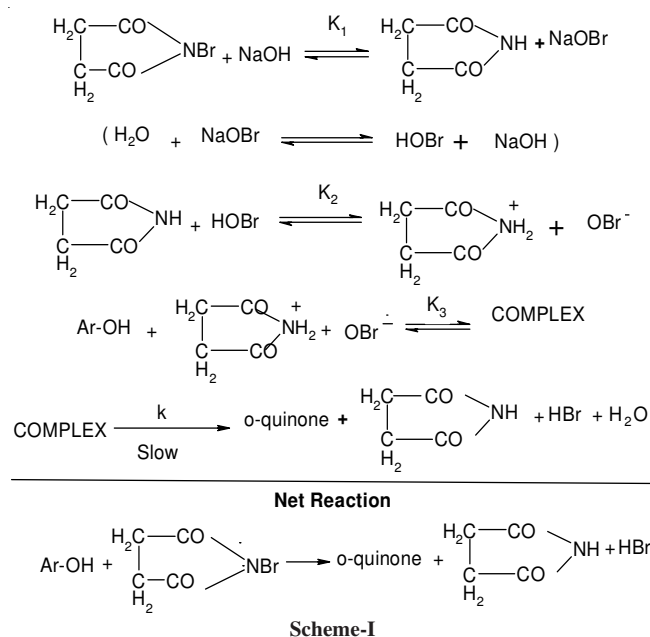


**Scheme-I**

**TABLE-1**
RATE CONSTANT DATA FOR THE OXIDATION OF PERFUMERY PHENOLS BY N-BROMOSUCCINIMIDE (IN NaOH) [NaOH] = $5 \times 10^{-2}$ M Temperature = 303 K

| [Phenol] × 10¹ (mol dm⁻³) | [NBS] × 10³ (mol dm⁻³) | Eugenol (k × 10³s⁻¹) | Isoeugenol (k × 10³s⁻¹) |
|---|---|---|---|
| 1.00 | 2.50 | 0.72 | 3.57 |
| 1.00 | 5.00 | 0.63 | 3.29 |
| 1.00 | 10.00 | 0.51 | 2.84 |
| 1.00 | 15.00 | 0.52 | 2.29 |
| 1.00 | 20.00 | 0.50 | 2.17 |
| 1.00 | 25.00 | 0.47 | 1.97 |
| 0.25 | 5.00 | 0.35 | 1.90 |
| 0.50 | 5.00 | 0.41 | 2.21 |
| 0.63 | 5.00 | 0.44 | 2.39 |
| 0.75 | 5.00 | 0.48 | 2.45 |
| 0.88 | 5.00 | 0.53 | 2.78 |
| 1.00 | 5.00 | 0.63 | 3.28 |



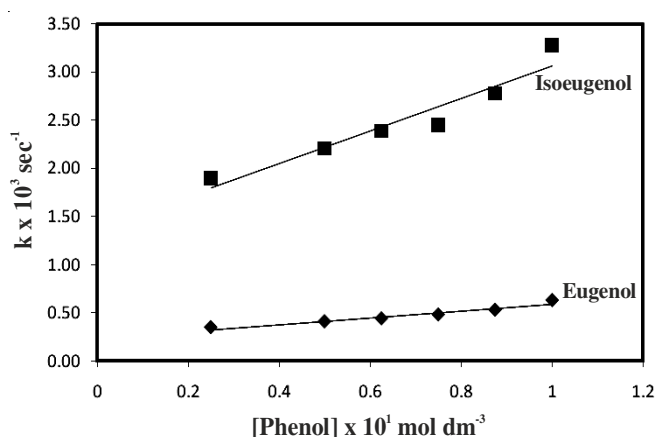Fig. 1.  Variation of the rate constant of oxidation of perfumery phenols with [phenol] (NBS as oxidant)

**Effect of ionic strength on oxidation rate:** The effect of ionic strength on oxidation rate was studied in dilute solution using $K_2SO_4$ in the range, $\mu = 5$ to $25 \times 10^{-2}$ mol dm⁻³ at 313 K (Table-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 suggested for the oxidation reaction.

**TABLE-2**
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES OF PERFUMERY PHENOLS BY USING N-BROMOSUCCINIMIDE IN NaOH. [phenol] = 0.1 M, [NaOH] = $2.5 \times 10^{-2}$ M, [NBS] = $2.5 \times 10^{-2}$ M, Temp. = 313 K

| $\mu \times 10^2$ mol dm⁻³ | Eugenol | Isoeugenol |
|---|---|---|
|  | k × 10⁴ s⁻¹ | |
| 0 | 4.12 | 25.47 |
| 5.00 | 4.04 | 25.78 |
| 10.00 | 4.09 | 25.32 |
| 15.00 | 4.00 | 29.48 |
| 20.00 | 4.14 | 25.00 |
| 25.00 | 4.09 | 25.71 |

**Effect of temperature and thermodynamic activation parameters:** The reaction was carried out in the temperature range 303-318 K and the thermodynamic parameters were evaluated (Table-3).

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

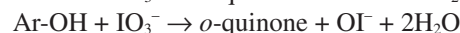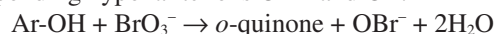| Phenol | $E_a$ (kJ mol⁻¹) | $\Delta H^*$ (kJ mol⁻¹) | $\Delta G^*$ (kJ mol⁻¹) | $\Delta S^*$ (kJ K⁻¹mol⁻¹) |
|---|---|---|---|---|
| Eugenol | 32.91 | 30.39 | 93.53 | -0.2084 |
| Isoeugenol | 23.01 | 20.49 | 89.81 | -0.2288 |

The negative values of entropy of activation indicate an extensive re-orientation of water molecules as a result of the formation of a rigid activation complex[3] and can be explained by a model in which the solvent molecules are tightly held to the phenolic -OH bond, which is the site of oxidation of phenols.

**$KBrO_3$ and $KIO_3$ in $H_2SO_4$:** The perfumery phenols, eugenol and isoeugenol were oxidized to the corresponding o-quinones using the inorganic oxidants $KBrO_3$ and $KIO_3$ in acidic medium.

**Effect of phenol concentration and oxidant concentration on the rate of oxidation:** The rate concentration increases with phenol concentration but decreases as the concentration of the inorganic oxidant increases [Tables 4a and 4b].

**Reaction mechanism of oxidation of phenols by $KBrO_3$/ $KIO_3$ in acidic medium:** In acidic medium, the inorganic oxidants $KBrO_3$ and $KIO_3$ quickly form the halic acids $HBrO_3$ and $HIO_3$ respectively[4], which are strong acids as well as strong oxidizing agents[5].

The oxidation of phenol results in the formation of the corresponding hypohalite ions $OBr^-$ and $OI^-$.

$$Ar\text{-}OH + BrO_3^- \rightarrow o\text{-quinone} + OBr^- + 2H_2O$$
$$Ar\text{-}OH + IO_3^- \rightarrow o\text{-quinone} + OI^- + 2H_2O$$

The unreacted $KBrO_3$/$KIO_3$ was estimated iodometrically:

$$BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Br^- + 3H_2O$$
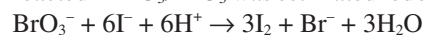$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

TABLE-4a
RATE CONSTANT DATA FOR THE OXIDATION OF
PERFUMERY PHENOLS BY $KBrO_3$ IN ACIDIC MEDIUM
$[H_2SO_4]$ = 1M; Temperature = 303 K

| [Phenol] × 10$^1$ (mol dm$^{-3}$) | [KBrO$_3$] × 10$^3$ (mol dm$^{-3}$) | Eugenol (k × 10$^3$ s$^{-1}$) | Isoeugenol k × 10$^3$ s$^{-1}$ |
|---|---|---|---|
| 1.00 | 2.50 | 2.30 | 5.60 |
| 1.00 | 5.00 | 2.15 | 5.16 |
| 1.00 | 10.00 | 2.12 | 4.81 |
| 1.00 | 15.00 | 1.91 | 3.87 |
| 1.00 | 20.00 | 1.56 | 3.66 |
| 1.00 | 25.00 | 1.43 | 3.39 |
| 0.25 | 5.00 | 1.35 | 3.71 |
| 0.50 | 5.00 | 1.48 | 3.88 |
| 0.63 | 5.00 | 1.62 | 4.31 |
| 0.75 | 5.00 | 1.74 | 4.62 |
| 0.88 | 5.00 | 2.03 | 4.99 |
| 1.00 | 5.00 | 2.16 | 5.20 |

TABLE-4b
RATE CONSTANT DATA FOR THE OXIDATION OF
PERFUMERY PHENOLS BY $KIO_3$ IN ACIDIC MEDIUM
$[H_2SO_4]$ = 1 M; Temperature = 303 K

| [Phenol] × 10$^1$ (mol dm$^{-3}$) | [KIO$_3$] × 10$^3$ (mol dm$^{-3}$) | Eugenol (k × 10$^4$ s$^{-1}$) | Isoeugenol (k × 10$^4$ s$^{-1}$) |
|---|---|---|---|
| 1.00 | 2.50 | 5.18 | 15.53 |
| 1.00 | 5.00 | 1.97 | 11.62 |
| 1.00 | 10.00 | 1.79 | 10.05 |
| 1.00 | 15.00 | 1.55 | 7.56 |
| 1.00 | 20.00 | 1.34 | 6.83 |
| 1.00 | 25.00 | 1.13 | 5.13 |
| 0.25 | 5.00 | 1.16 | 7.54 |
| 0.50 | 5.00 | 1.36 | 7.91 |
| 0.63 | 5.00 | 1.36 | 8.58 |
| 0.75 | 5.00 | 1.37 | 8.83 |
| 0.88 | 5.00 | 1.75 | 9.85 |
| 1.00 | 5.00 | 1.88 | 11.62 |

The liberated iodine was titrated against standard $Na_2S_2O_3$ using starch as an indicator.

The oxidation rates for perfumery phenols follow the sequence isoeugenol > eugenol for both the inorganic oxidants (Tables 4a and 4b) (Figs. 2a and 2b). In isoeugenol, conjugation extends outside the aromatic ring but in eugenol there is no such extended conjugation. The product obtained on oxidation of isoeugenol, *i.e. o*-quinone is more stable hence rate of oxidation is higher. Whereas in case of eugenol, the *o*-quinone obtained is less stable therefore rate of oxidation is lower[2].
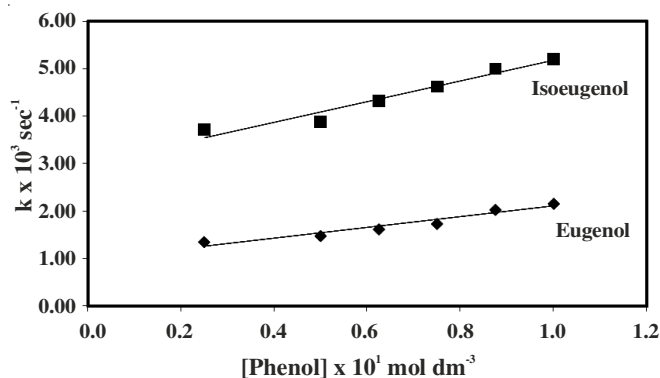


Fig. 2a. Variation of the rate constant of oxidation of perfumery phenols with [phenol] (KBrO$_3$ as oxidant)
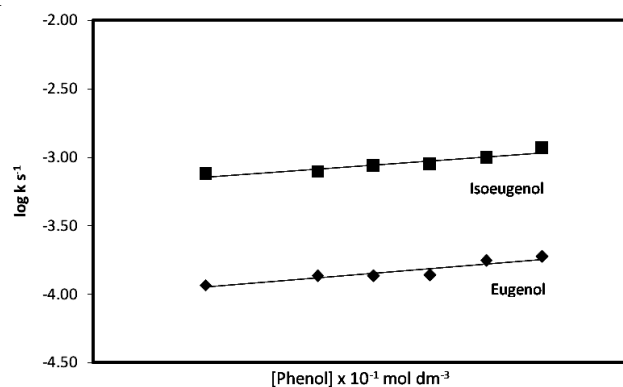


Fig. 2b. Variation of the rate constant of oxidation of perfumery phenols with [phenol] (KIO$_3$ as oxidant)

**Effect of ionic strength on the oxidation rate:** The effect of ionic strength on the oxidation rate was studied in dilute solution using $K_2SO_4$ in the range, $\mu$ = 5 to 25 × 10$^{-2}$ mol dm$^{-3}$ at 313 K (Tables 5a and 5b).

TABLE-5a
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES
OF PERFUMERY PHENOLS BY $KBrO_3$ IN ACIDIC MEDIUM
[Phenol] = 0.1 M, [KBrO$_3$] = 2.5 x10$^{-2}$ M, Temp. = 313 K

| $\mu$ × 10$^2$ (mol dm$^{-3}$) | Eugenol (k ×10$^3$ s$^{-1}$) | Isoeugenol (k ×10$^3$ s$^{-1}$) |
|---|---|---|
| 0 | 2.16 | 6.21 |
| 5 | 2.08 | 6.01 |
| 10 | 2.04 | 6.19 |
| 15 | 2.00 | 6.12 |
| 20 | 2.25 | 6.06 |
| 25 | 2.01 | 6.15 |

TABLE 5b
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES OF
PERFUMERY PHENOLS BY $KIO_3$ IN ACIDIC MEDIUM
[Phenol] = 0.1 M, [KIO$_3$] = 2.5 × 10$^{-2}$ M, Temperature = 313 K

| $\mu$ × 10$^2$ mol dm$^{-3}$ | Eugenol (k × 10$^4$s$^{-1}$) | Isoeugenol (k × 10$^4$s$^{-1}$) |
|---|---|---|
| 0 | 2.07 | 7.91 |
| 5 | 1.88 | 7.66 |
| 10 | 1.94 | 7.65 |
| 15 | 1.87 | 7.98 |
| 20 | 1.95 | 7.67 |
| 25 | 1.85 | 7.62 |

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. The reaction mechanism of oxidation of phenols under study supports this observation.

**Effect of temperature and thermodynamic activation parameters:** The oxidation was carried out in the temperature range 303-318 K and the thermodynamic activation parameters were evaluated from the Arrhenius plots of log k *vs.* T$^{-1}$ (Tables 6a and 6b).

TABLE-6a
THERMODYNAMIC ACTIVATION PARAMETERS
FOR THE OXIDATION OF PERFUMERY PHENOLS
BY $KBrO_3$ IN ACIDIC MEDIUM

| Phenol | E act (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $\Delta G^*$ (kJ mol$^{-1}$) | $\Delta S^*$ (kJ K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|
| Eugenol | 18.96 | 16.44 | 89.73 | -0.2419 |
| Isoeugenol | 17.20 | 14.68 | 87.06 | -0.2389 |

| TABLE-6b THERMODYNAMIC ACTIVATION PARAMETERS FOR THE OXIDATION OF PERFUMERY PHENOLS BY $KIO_3$ IN ACIDIC MEDIUM | | | |
|---|---|---|---|
| Phenol | E act (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $\Delta G^*$ (kJ mol$^{-1}$) | $\Delta S^*$ (kJ K$^{-1}$ mol$^{-1}$) |
| Eugenol | 75.04 | 72.52 | 95.87 | -0.0771 |
| Isoeugenol | 47.19 | 44.67 | 91.30 | -0.1539 |

Negative values of $\Delta S^*$ indicate orientation of water molecules around the activated complex[3] leading to decrease in the disorder of the reaction system.

**Conclusion**

For all the oxidizing agents used, the oxidation rates of the perfumery phenols follow the sequence: isoeugenol > eugenol. The oxidation rates increase with phenol concentration but decrease with increasing oxidant concentration. The oxidation reaction is independent of ionic strength in dilute solution.

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