



## Kinetic Study of Some Para-Substituted Benzhydrols with Selenium Dioxide

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### ABSTRACT

This paper discusses  $\text{SeO}_2$  led kinetic studies of the oxidation of *p*-Br, *p*- $\text{CH}_3$ , and *p*- $\text{CH}_3\text{CH}_2$  benzhydrols in aqueous acetic acid medium. The study afforded a good yield of a series of variously *p*-substituted benzophenones as the oxidation products. The rate of reaction was found to vary as a first-power of concentration of oxidant, substrate and acid. The postulated  $\text{H}_2\text{SeO}_3^+$  reacting species participated in the reaction mechanism with stoichiometric mole ratio 1:2. The effect of changing dielectric constant of the medium on the rate indicates the reaction to be of dipole-dipole type. The activation parameters are computed for the slow step of the mechanism.

Keywords: *p*-bromobenzhydrol, *p*-methylbenzhydrol, *p*-ethylbenzhydrol, selenium dioxide, inductive effect.

### INTRODUCTION

$\text{SeO}_2$  is a selective and mild, non-hazardous oxidant used mostly in acidic medium producing  $\text{H}_2\text{SeO}_3^+$  or  $\text{AcH}_2\text{SeO}_3$  as reacting species.<sup>1</sup> Owing to presence of  $-\text{Br}$ ,  $-\text{CH}_3$  and  $-\text{CH}_3\text{CH}_2$  functional groups in para-position and  $-\text{OH}$  group which is linked directly to the secondary carbon atom of benzhydrol make its mechanism very interesting and reactive in addition to exhibition of electro negativity,  $-\text{I}$ ,  $+\text{I}$  effects and  $+\text{mesomeric}$  effect.

These substrates show a numerous chemical reactions with variety of oxidants viz. NBS,<sup>2</sup> NBP<sup>3</sup> halo oxidants  $\text{KMnO}_4$  etc.. The researcher have also been reported in their previous communication the results of  $\text{SeO}_2$ <sup>5</sup> oxidation of benzhydrol and *p*-chloro benzhydrol. A few reports are available for the possibility of using  $\text{SeO}_2$  in oxidizing ketones,<sup>6-8</sup> alcohol<sup>9</sup> and aldehydes<sup>10</sup> etc.

There is however, no reported information on the possible reaction mechanism or its selectivity. A kinetic study was undertaken to formulate a possible mechanism. For this purpose, after studying the overall reaction, we

### EXPERIMENTAL

All the chemicals used were of reagent grade and the solutions were prepared in double distilled water. The solution of  $\text{SeO}_2$  (Loba grade) was prepared and kept in safer dark and dry place so that it could not decompose even after long periods at  $50^\circ\text{C}$ .

The solutions of reagent grade of *p*-Br, *p*- $\text{CH}_3$  and *p*- $\text{CH}_3\text{CH}_2$  benzhydrols were prepared at the required concentrations by dilution and testing the stability under the same operating conditions. Other required standard solutions of appropriate concentrations of reagents were prepared related to study. The oxidation reactions were carried out in a 500 ml pyrex glass reaction vessel fitted with a variable speed stirrer and a jacket for the circulation of thermo regulating water. The temperature of the water was regulated with a precision of  $\pm 0.1^\circ$  by a thermostat. The volumes of  $\text{SeO}_2$  were determined by redox titration.<sup>11</sup>

### Kinetics

The kinetic study of the reaction was approached by the method of initial rates.

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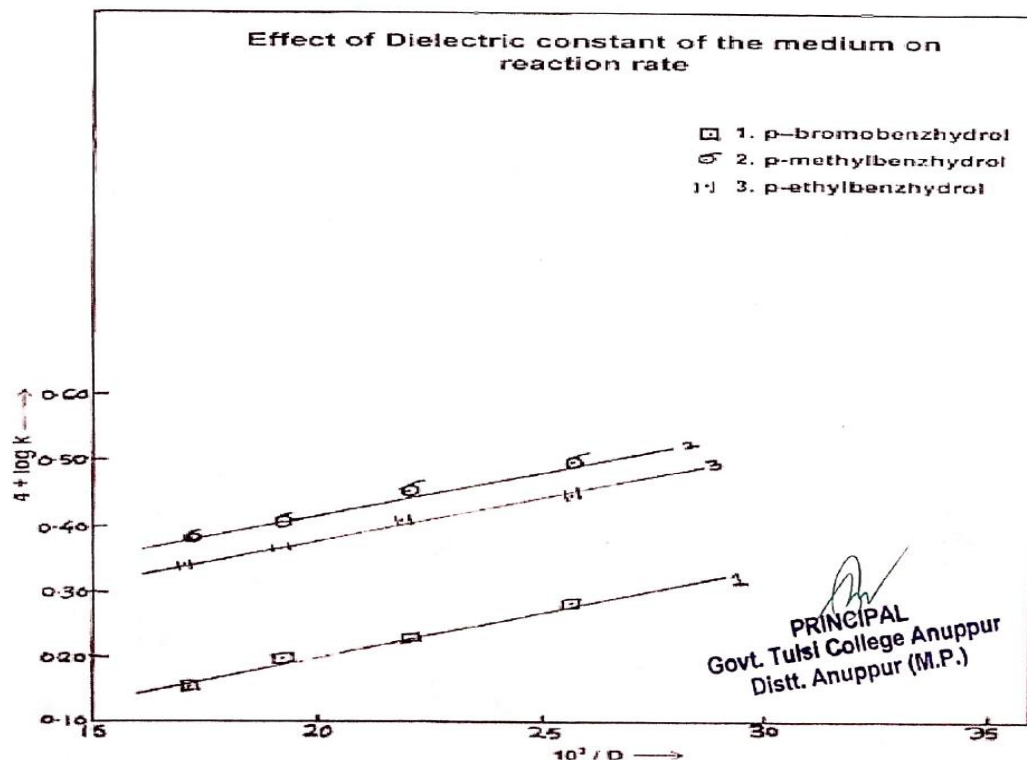
as to avoid having to physically control the reaction rate. The reduction reaction was followed by adding the substrates directly into the thermo regulated vessel containing the  $\text{SeO}_2$  solution. The determination of the concentrations of the oxidant  $\text{SeO}_2$  unreacted left was done iodometrically. The rate constant ( $k$ ) was computed by graphical and other methods that satisfied stoichiometry (1:2). p-Br, p- $\text{CH}_3$ , and p- $\text{CH}_2\text{CH}_2$  benzophenones were identified as the products of the reactions by forming their yellow 2,4-DNP derivatives, spectrophotometrically and also by determining their melting points compared with authenticated samples. The study rules out the presence of free radicals in the reaction mixtures when tested with acrylonitrile.

### RESULTS AND DISCUSSION

The effect of oxidant  $\text{SeO}_2$  was studied by keeping all other concentrations constant at fix temperature. The  $[\text{SeO}_2]$  was varied from  $1.25 \times 10^{-3}$  to  $5.0 \times 10^{-3}$  mol  $\text{dm}^{-1}$  and pseudo first-order rate constant ( $k_{\text{obs}}$ ), were found to be indicating the first-order dependence of the reaction on  $[\text{SeO}_2]$ . The pseudo first-order rate constants ( $k_{\text{obs}}$ ) were found to increase with

increase in concentration of p-bromo, p-methyl and p-ethyl benzhydrols varied between 0.02 to 1.0 mol  $\text{dm}^{-3}$  at constant concentrations of oxidant,  $\text{H}^+$ ,  $\text{CH}_3\text{COOH}$  etc. The plot of  $k_{\text{obs}}$  against  $[\text{p-substituted benzhydrol}]$  were also found to be linear ( $R^2 = > 0.9912$ ), indicating that rate of reaction is proportional to first-power of [substrate]. The  $\text{H}^+$  ion concentration in the reaction mixture was calculated using known equilibrium constants of  $\text{H}_2\text{SO}_4$  and orders in  $[\text{H}^+]$  were determined from  $\log [\text{H}^+]$  against  $\log k_{\text{obs}}$  plots. By examining the data obtained, it was found that  $k_{\text{obs}}$  is first-order (slope = 0.97) for each of the reagents.

The primary salts effects have been found negligible as rate of reaction remains almost unaltered by the addition of different concentrations of salt. The rate of oxidation was found to increase with increase in composition of  $\text{CH}_3\text{COOH}$ -water (v/v) (Table 1). By plotting the inverse of dielectric constant ( $D$ ) as a function of  $\log k$  and examining the data obtained (Fig.1) afforded positive slopes for each substrate clearly indicate that the positive ion dipole involved in the rate determining step.





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$[H^+] \times 10^3 \text{ (mol dm}^{-3}) = 1.50(1), 1.0(2), 0.30(3)$ ; Temperature  $K = 308(1), 303(2,3)$

Table 1. Effect of solvent polarity on reaction rate

$10^2 \times [\text{Substrate}] \text{ (mol dm}^{-3}) = 2.50 (1, 2), 2.0 (3)$ ;

$10^3 \times [\text{SeO}_2] \text{ (mol dm}^{-3}) = 2.50 (1, 2, 3)$ ;

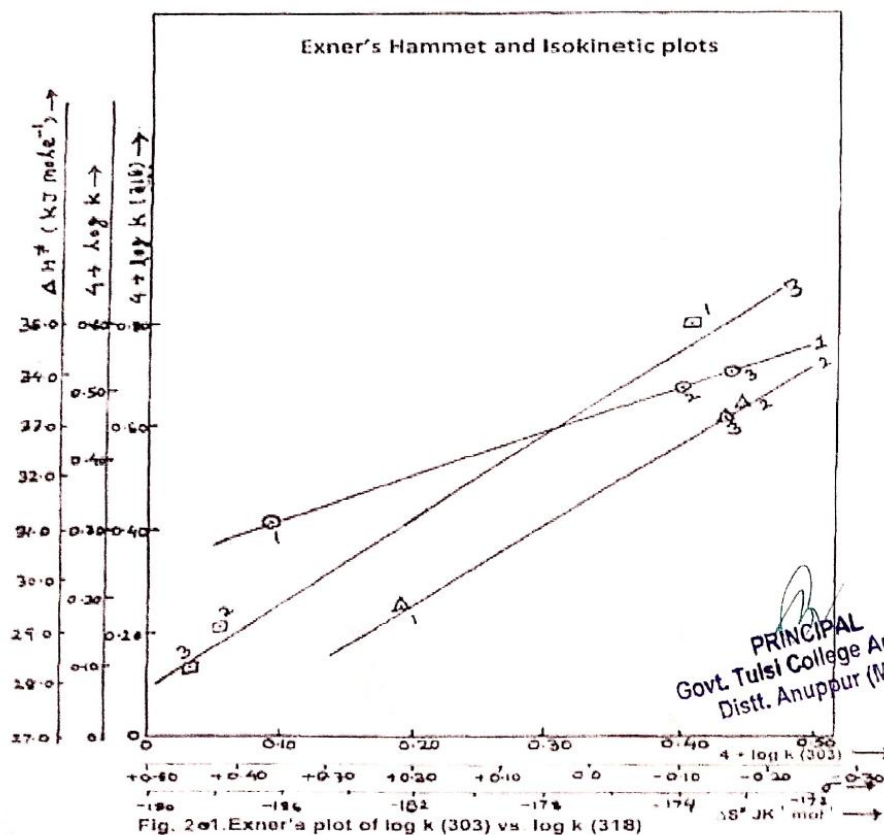
$10^3 \times [H^+] \text{ (mol dm}^{-3}) = 0.50 (3), 1.0 (2), 1.540 (1)$ ;

Temperature  $K = 308 (1), 303 (2, 3)$

S. No	CH <sub>3</sub> COOH-H <sub>2</sub> O, % (v/v)	10 <sup>3</sup> × 1/D	k × 10 <sup>4</sup> (s <sup>-1</sup> )		
			p-bromo benzhydrol (1)	p-methyl benzhydrol (2)	p-ethyl benzhydrol (3)
1.	20	17.17	1.41	2.39	2.18
2.	30	19.15	1.58	2.54	2.33
3.	40	21.98	1.74	2.83	2.59
4.	50	25.64	1.93	3.13	2.79

Table 2. Thermodynamic parameters for the reaction between p-substituted benzhydrols and oxidant SeO<sub>2</sub>

S. No	Activation parameters	para-substituted benzhydrols		
		p-bromo benzhydrol (1)	p-methyl benzhydrol (2)	p-ethyl benzhydrol (3)
1.	E <sub>a</sub> (kJ mol <sup>-1</sup> )	38.74	31.92	30.48
2.	A × 10 <sup>-2</sup> (s <sup>-1</sup> )	5.80	6.11	4.74
3.	ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	35.23	29.06	28.34
4.	ΔG <sup>‡</sup> (kJ mol <sup>-1</sup> )	89.23	86.42	85.98
5.	-ΔS <sup>‡</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	173.88	187.78	188.65



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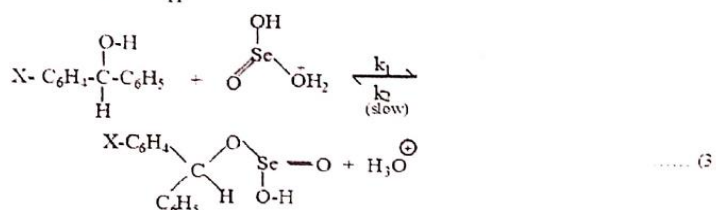
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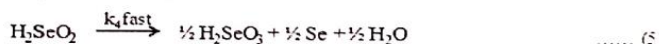
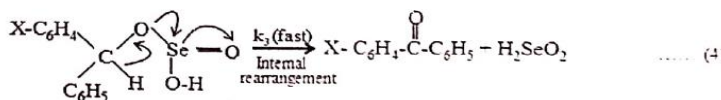
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where, X = -Br, -CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>2</sub> respectively.



### Reaction Mechanism

Mechanistically the reaction modes depicted by involving neutral form of substrates and H<sub>3</sub>SeO<sub>3</sub><sup>+</sup> prevailing reacting species in presence of mineral acid H<sub>2</sub>SO<sub>4</sub>. A plausible mechanism rationalizing the observed kinetic data is proposed. :

The rate law was derived in consistent with the observed kinetic data and thermodynamic parameters logically through postulated mechanism.

$$k_{\text{obs}} = k_1 [\text{p-substituted benzhydrol}] [\text{H}_2\text{SeO}_3] [\text{H}^+]$$

The following sequence of order of reactivity was observed:

p-ethylbenzhydrol > p-methylbenzhydrol > p-bromobenzhydrol

The substituents -CH<sub>2</sub>CH<sub>2</sub> and -CH<sub>3</sub> groups present in the para-position of benzhydrol exhibit +I inductive and hyperconjugative effect which is more pronounced in the substrates understudy. The reactivity of the compound p-bromo benzhydrol will be least reactive due to -I effect. The above order of reactivity is also supported by substituents effect, Hammett and isokinetic and Exner's plots (ΔH# vs. ΔS#, and log k 303 against log 318) (Fig.2). The linearity of Exner's plot<sup>12</sup> implies that all the substrates are oxidized by the same mechanism.

The isokinetic temperature 'β' (363.17 K) lies well above the experimental temperature. The value of energy of activation is measure of

The values of ΔG# and ΔS# execute important role in monitoring the rates of oxidation reactions through the enthalpy factor appear to be more predominating this lead that reactions are enthalpy controlled.

### CONCLUSION

The H<sub>3</sub>SeO<sub>3</sub><sup>+</sup> reaction species in presence of mineral acid postulated that lead the oxidation reactions with neutral species of substrate. The substituent's -CH<sub>2</sub>CH<sub>2</sub> and -CH<sub>3</sub> group in the para-position of benzhydrol exhibit +I, hyper conjugation, and +mesomeric effect which is more pronounced in the substrates. The order of reactivity was explained based activation parameter Isokinetic and Exner's plot was also discussed.

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