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Research Article

Rapid Bromination of some Regioisomers of Dimethylphenol by Molecular Bromine in Aqueous Solution: Kinetic Verification of Reactivities

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ABSTRACT

Kinetics of bromination of 2,3-dimethylphenol, 2,4-dimethylphenol, and 2,5-dimethylphenol by molecular bromine in aqueous solution at pH 7.0 have been studied. The Kinetic data obtained conclusively enlightened the relative reactivities of these isomers quantitatively. All three reaction studies were found to be rapid and hence needed a special technique to follow the kinetics. In the present study, a rotating platinum electrode is used and yielded specific reaction rates ranging from 1.32×10^3 $M^{-1}S^{-1}$ to 2.34×10^3 $M^{-1}S^{-1}$, activation energies from 30.8 KJ $mole^{-1}$ to 49.1 KJ $mole^{-1}$ and frequency factor from 5.85×10^8 $M^{-1}S^{-1}$ to 5.32×10^{11} $M^{-1}S^{-1}$ at 25°C and 7.0 pH. Stereochemical principles justifies this observed reactivities of three isomers under study. Thus, the speculated stereochemistry of these isomers was quantitatively verified using Kinetic as a tool.

Key words: Bromination, Dimethylphenols, Kinetics, Molecular bromine, Rotating platinum electrode, Stereochemistry.

1. INTRODUCTION

Bromination of organic compounds are important and fundamental reactions inorganic chemistry. Brominated compounds are of considerable commercial use. These compounds are offer used in the preparation of organometallic reagents [1,2] and coupling reactions, such as King *et al*. [3], Suzuki [4], Sonogashira [5], Tamao *et al*. [6], Tokuyama *et al*. [7] etc. Introduction of halogen atom in organic compound induces medicinal properties in these compounds. They can also be used as intermediates in the preparation of agrochemicals, pharmaceuticals, herbicides, pesticides, and flame retardants [8-15]. It is well known that halogenation of organic compounds are electrophilic aromatic substitution reactions [16]. Among these, brominations are well known to organic chemists. These reactions are rapid as compared to iodinations [17]. In aqueous solution, bromination is rapid and necessitates special technique for quantitative study [18].

In the present study, kinetics of bromination of 2,3-dimethylphenol, 2,4-dimethylphenol and 2,5-dimethylphenol by molecular bromine in aqueous solution [Scheme 1] have been studied. Since the reactions are two rapid to be studied by conventional techniques, the study is carried out using a rotating platinum electrode [19-22]. Molecular bromine gives diffusion current proportional to its concentration at rotating platinum electrode, whereas neither any isomer of dimethylphenol nor the product yields any diffusion current. Hence, the course of reaction can be followed by measuring the diffusion current at intervals of time. The technique is accurate and reproducible [23,24]. Under the studied conditions, the reaction rates completely depend on the nucleophilicities of the isomers and the electrophilicity of the bromine reagent. The relative reactivities of the isomers are determine in quantitative manner from the observed Kinetic data.

2. MATERIALS AND METHODS

2.1. Chemicals

All the chemicals were of analytical grade and purchased from local sources and used as supplied. Stock solution of 1.0×10^{-5} M 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, bromine, and 1.0×10^{-2} M potassium chloride were prepared in doubly distilled water. Sodium dihydrogen phosphate and disodium hydrogen phosphate, 0.1 M each was prepared for the phosphate buffer solution. These stock solutions were used to get required concentration in the reaction system.

2.2. Methods

Rotating platinum electrode is used to study the kinetics of the bromination of 2,3-dimethylphenol,2,4-dimethylphenol, and 2,5-dimethylphenol in aqueous medium at pH 7.0. Rotating platinum electrode is a negative electrode, rotating at a speed of 600 rpm. Saturated calomel electrode is a positive electrode.

Calibration of diffusion current, among the bromination of 2,3-dimethylphenol reaction studied, is described.

Calomel electrodes dipped in 100 cm^3 of potassium chloride (1×10^{-2} M), which is a supporting electrolyte. A potential of +0.1 volt versus the saturated calomel electrode is applied at the rotating platinum electrode. Then, zero deflection is adjusted on the scale of galvanometer using shunt. Potassium chloride solution is then replaced by 5.0×10^{-6} M bromine solution containing a hundred-fold concentration of supporting electrolyte. The galvanometer deflection is then adjusted to maximum on the scale. The diffusion current in terms of galvanometer deflection is recorded for different

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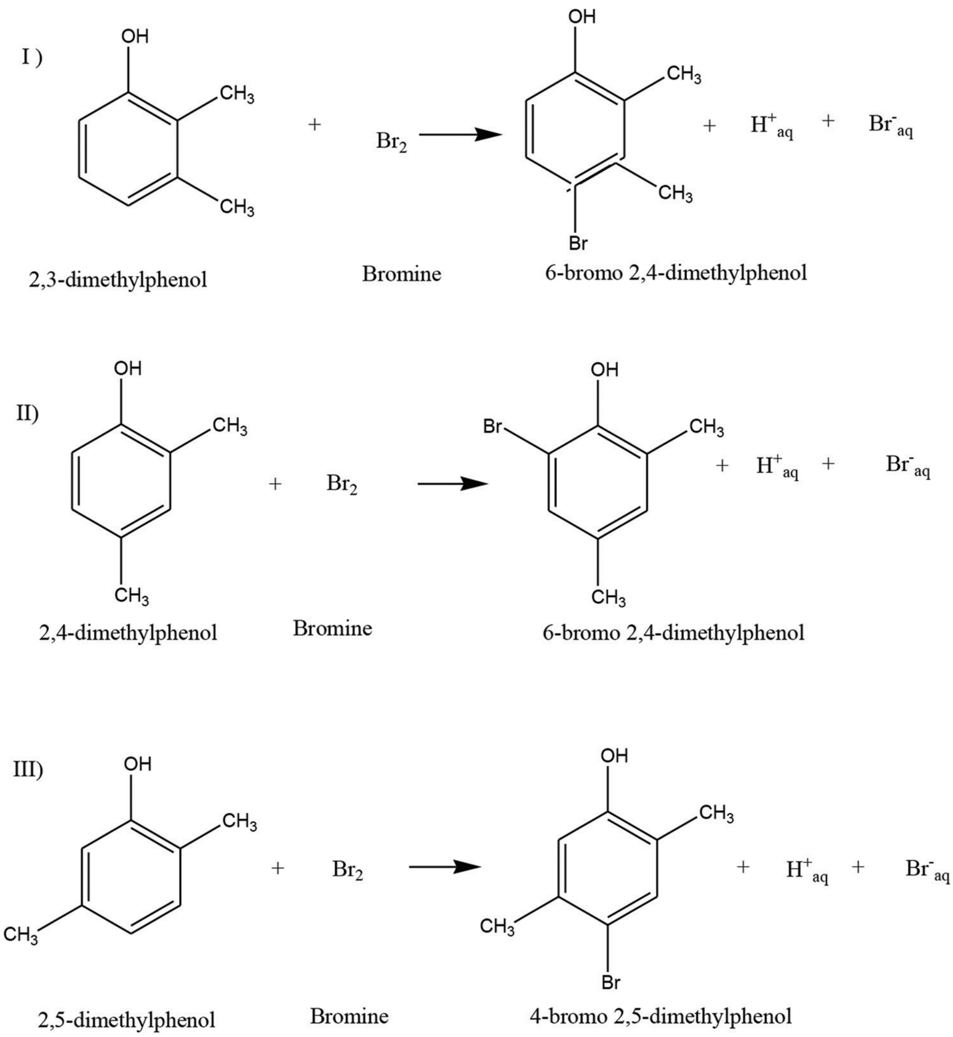

Scheme 1: Bromination reactions of various compounds.

bromine concentrations. A plot of diffusion current versus bromine concentrations were linear. Calibration is carried out at five different temperatures [Table 1 and Figure 1].

2.3. Kinetic Measurements

50 cm³ of 1.0×10^{-5} M bromine continue 5.0×10^{-4} M potassium chloride and 50 cm³ cube of 1.0×10^{-5} M dimethylphenol containing $5.0 \text{ M} \times 10^{-4}$ M potassium chloride, and the required buffer components are kept in a thermostat at a required temperature. Then the reactants are mixed in a container in which a rotating platinum electrode is rotating and saturated is dipped. A stopwatch is started as soon as the reactants are mixed. A diffusion current decreases steadily as the reaction proceeds.

Diffusion current was recorded at every 10 s in terms of galvanometer deflection of the reaction under study was completed. The final initial concentrations of the reactants after mixing are indicated [Table 2].

As the equal concentration of the reactant was used, the plot of $[BR_2]^{-1}$ versus time was linear and the reaction was of the second order. The slope of the plot was the specific reaction rate, K_2 of the bromination of 2,3-dimethylphenol. The Kinetic run for the other two reactions for similarly carried out.

The calibration and kinetic measurements were repeatedly checked for reproducibility of the galvanometer measurements, and the error was found to be within the limit of ± 0.2 cm. The error in the measurement of diffusion current was <1%, while in weighing chemicals was <0.25%.

Similar studies were carried out at different temperature from which the energy of activation, Ea and frequency factor, A were evaluated.

Table 1: Calibration of the diffusion current of bromine concentration at various temperatures for the bromination of 2,3-dimethylphenol in aqueous solution at pH 7.0.

[Bromine]×10^{-6} M	Diffusion current/ηA				
	10°C	15°C	20°C	25°C	30°C
1.0	7.0	7.2	8.0	8.5	9.2
2.0	14.0	14.7	16.0	17.2	18.5
3.0	21.0	22.0	24.0	25.7	27.7
4.0	28.0	29.5	32.0	34.5	36.7
5.0	35.0	37.0	40.0	43.0	46.0

3. RESULTS AND DISCUSSION

A plot of $[Br_2]^{-1}$ versus time is satisfactory linear in each case. It indicates that all the reactions are of second order. In a typical case

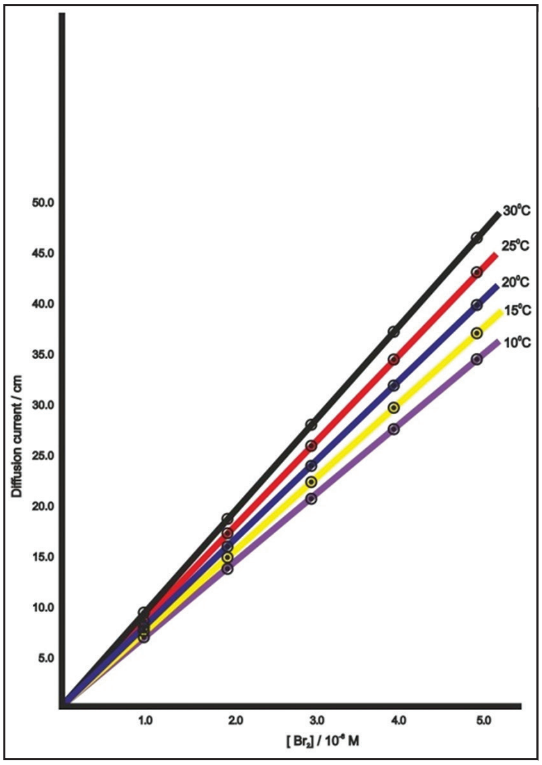

Figure 1: Calibration of the diffusion current of bromine concentration at various temperatures for the bromination of 2,3-dimethylphenol in aqueous solution at pH 7.0.

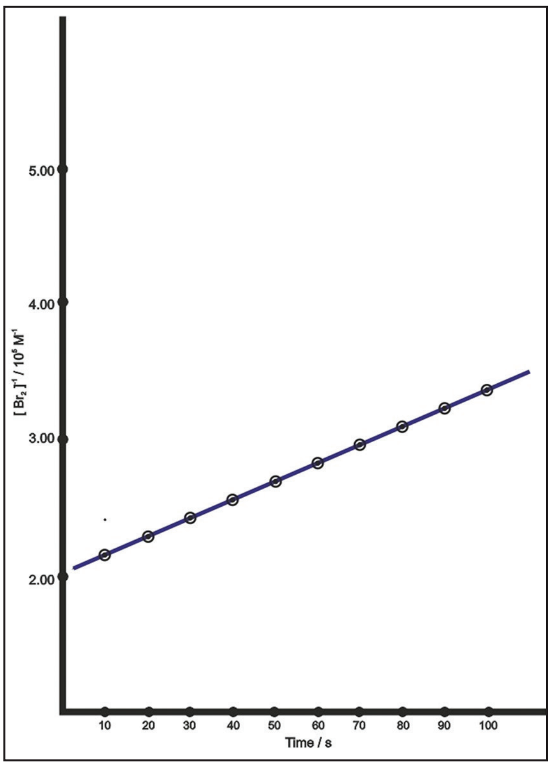

Figure 2: Kinetics of bromination of 2,3- dimethylphenol by molecular bromine in aqueous solution at pH 7.0.

of 2,3-dimethylphenol, the slope of the plot gives the specific reaction rate of 1.32×10^{3} $M^{-1}S^{-1}$ at 25°C [Table 3 and Figure 2]. Similar kinetic investigation of the reaction was carried out at five different temperatures to determine the energy of activation from an Arrhenius

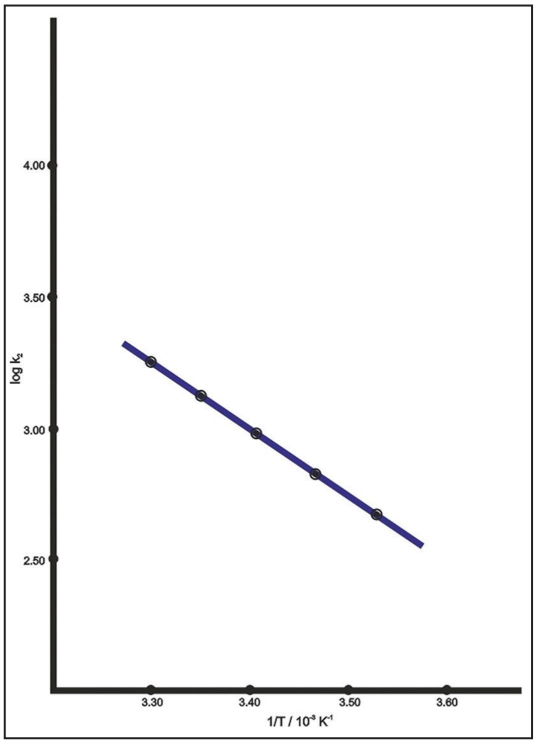

Figure 3: Kinetics of bromination of 2,3- dimethylphenol by molecular bromine in aqueous solution at pH 7.0: Energy of activation.

Table 2: Reaction parameters at all temperatures at pH 7.0.

Parameters	Value
Concentration of 2,3-dimethylphenol	5.0×10^{-6} M
Concentration of bromine	5.0×10^{-6} M
Concentration of potassium chloride	5.0×10^{-4} M
Concentration of disodium hydrogen phosphate	0.0125 M
Concentration of sodium dihydrogen phosphate	0.0125 M
Total volume of the reaction mixture	100 cm^3
Potential applied at a rotating platinum electrode	+0.1 volt

plot using the relation, Ea = 2.303 × R × slope of the plot log K versus time [Table 4 and Figure 3].

The order of energy of activation [Table 5] is 2,5-dimethylphenol <2,4-dimethylphenol <2,3-dimethylphenol.

Bromine in aqueous solution extensively hydrolysed according to equation;

$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$$

Although, HOBr is brominating agent, it is well weak electrolyte as compared to bromine [18,25,26]. Hence molecular bromine is a sole brominating agent in these reactions.

The reactivity order can be explained on the basis of the structure of the regioisomers under study and steric hindrance exerted by the incoming bromo-groups. In these isomers phenolic -OH group is ortho and para directing. Hence, the incoming bromonium ion (electrophile) substitutes to either ortho or para position on the basis of steric hindrance and intermolecular hydrogen bonding of bromine with hydrogen or phenolic group.

Table 3: Kinetics of bromination of 2,3- dimethylphenol by molecular bromine in aqueous solution at pH 7.0.

Time/s	Diffusion current/cm	Unreacted $[Br_2]/10^{-6}$ M	$[Br_2]^{-1}/10^5$ M^{-1}
10	41.3	4.69	2.13
20	38.9	4.42	2.26
30	36.7	4.17	2.40
40	34.8	3.95	2.53
50	33.1	3.76	2.66
60	31.5	3.58	2.79
70	30.1	3.42	2.92
80	28.8	3.27	3.06
90	27.5	3.13	3.19
100	26.5	3.01	3.32

concentration of 2,3-dimethylphenol: 5.0×10^{-6} M, concentration of bromine: 5.0×10^{-6} M, concentration of potassium chloride: 5.0×10^{-4} M, Temperature: 25°C, pH: 7.0, Specific reaction rate, $k_2=1.32\times10^3$ $M^{-1}S^{-1}$

Table 4: Kinetics of bromination of 2,3- dimethylphenol by molecular bromine in aqueous solution at pH 7.0: Energy of activation.

Temperature		$1/T/10^{-3}$ K^{-1}	Specific reaction rate, $K^2/M^{-1}S^{-1}$	LOG k_2
t/°C	T/K			
10	283	3.53	4.60×10^2	2.66
15	288	3.47	6.50×10^2	2.81
20	293	3.41	9.30×10^2	2.97
25	298	3.35	1.32×10^3	3.12
30	303	3.30	1.78×10^3	3.25

Energy of activation, Ea=2.303×R × slope=49.1 $KJ/mole^{-1}$

Table 5: Summary of kinetic parameters for bromination of regioisomers of dimethylphenol by molecular bromine in aqueous solution at pH 7.0.

Isomer of dimethylphenol	Specific reaction rate, $k_2/M^{-1}S^{-1}$	Energy of activation, $Ea/KJmole^{-1}$	Frequency factor, $A/M^{-1}S^{-1}$
2,3- dimethylphenol	1.32×10^3	49.1	5.32×10^{11}
2,4- dimethylphenol	2.14×10^3	34.9	2.80×10^9
2,5- dimethylphenol	2.34×10^3	30.8	5.85×10^8

In 2,5-dimethylphenol, the hydroxyl phenolic group and methyl group are both ortho and para directing. There is unison effect of the hydroxyl methyl group, which direct the incoming bromo group at para position to hydroxyl group and ortho to methyl group. This is responsible to highest specific reaction rate of bromination of 2,5-dimethylphenol.

In case of 2,4-dimethylphenol para position to the hydroxyl group is blocked by the methyl group. Also, there is steric conjuction of groups with methyl group and incoming bromo group. Hence, the specific reaction rate of 2,4-dimethylphenol is lower than that of 2,5-dimethylphenol.

In 2,3-dimethylphenol, two methyl groups are in close proximity due to this combined para directing effect of hydroxyl group and ortho directing effect of methyl group is weakened to large extent, and hence, the reduced specific reaction rate of 2,3-dimethylphenol than 2,5-dimethylphenol and 2,4-dimethylphenol.

4. CONCLUSION

The relative reactivities of bromination of 2,3-dimethylphenol, 2,4-dimethylphenol, and 2,5-dimethylphenol are considered in these reactions. The reactivities are speculated quantitatively on the basis of stereochemical principles. Such verification is provided by studying this rapid bromination reaction. As these reactions cannot be studied by conventional methods, the rotating platinum electrode technique has been used to evaluate specific reaction rates of these rapid reactions.

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6. CONFLICT OF INTEREST

The Author declares that there is no conflict of interest.

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