Kinetics and mechanism of bromination of phenols by sodium bromate-sodium bisulphite reagent in water-acetonitrile mixture

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Kinetics of bromination of phenols with HOBr produced in situ from sodium bromate-sodium bisulphite reagent has been studied in water-acetonitrile mixture iodometrically. The order of the reaction is found to be unity in [HOBr] and fractional in [phenol]. HOBr has been established as the effective brominating species. A mechanism involving a six-membered cyclic adduct between phenol and HOBr, which decomposes in a slow step, has been proposed. Thermodynamic parameters for the formation of adduct and the activation parameters for the first order decomposition of the adduct have been evaluated and discussed. The influence of the substituents on the first order decomposition rate constant (k/s⁻¹) of the adduct has been discussed. The sole reaction product has been identified as the corresponding o-bromophenol.

Considerable work has been reported using N-bromoacetamide (NBA)¹⁻⁶ as oxidizing or brominating agent. The kinetics of bromination of phenols by NBA in aqueous acetonitrile medium has been reported⁶ and it is seen that HOBr is generated by hydrolysis of NBA, which later reacts with the substrate. However, hypobromous acid (HOBr) was found to be easily generated in situ from NaBrO₃ in the presence of appropriate reducing agent such as NaHSO₃ and was successfully used in the synthesis of several organic compounds.¹¹ Recently the kinetic and mechanistic study of oxidation of DMSO¹² and bromohydroxylation of cinnamic acids¹³ by the same reagent has also been reported. It was very easy to handle this reagent in aqueous solution as compared to those of several N-halo compounds. A systematic kinetic investigation of the bromination of phenols by sodium bromate-sodium bisulfite reagent has not been reported in literature hitherto. Hence it was thought worthwhile to undertake the investigation.

Experimental

All the chemicals used were of AnalAR grade. Sodium bromate and sodium bisulphite used in this study were BDH grade. All the phenols (BDH) used were distilled or recrystallized before use. The solvent acetonitrile used was of AnalAR grade from E. Merck and used as such. All the aqueous solutions were prepared in doubly distilled water.

The reaction between phenols and sodium bromate-sodium bisulphite reagent was studied in water-acetonitrile (50:50 v/v) mixture. In this study, aqueous solutions of NaBrO₃ and NaHSO₃ were allowed to react first together for about two hours to generate HOBr completely and then kinetic runs were started with phenols. The kinetics of the reaction was studied in dark coloured reaction vessels by estimating the un-reacted HOBr iodometrically at regular time intervals. To see the effect of dissolved oxygen on the rates, nitrogen gas was bubbled through the reaction mixture to expel the dissolved oxygen and the reaction was studied. It was found that there was no effect of oxygen on rates.

The product of the reaction (taking 4-nitrophenol as a representative phenol) was identified as 2-bromo-4-nitrophenol by its m.p. 113°C (lit. m.p. 114°C). Stoichiometry of the reaction was carried out for 45 min. under the conditions [HOBr] >> [phenol]. The stoichiometry was found to be 1:1 (phenol : HOBr) in accordance with Eqn.(1).

\[ \text{OH} + \text{HOBr} \rightarrow \text{Br-Br} \quad \text{(1)} \]

The reason for restricting the time factor to 45 min was to avoid any other side reactions.

Results and discussion

Under pseudo-first order conditions [HOBr] << [phenol], the plot of log [HOBr] versus time was found to be linear indicating unit order dependence in [HOBr]. From the slopes of such plots, pseudo-first order rate constants (kₕₒₒᵢ/d/s⁻¹) have been evaluated
under varying initial [phenol]. Double logarithmic plot of log \( k_{\text{obsd}} \) versus log [phenol] was found to be linear with a slope of 0.27 indicating the order in [phenol] to be fractional. This indicates the formation of a six-membered cyclic adduct between phenol and HOBr. This fact was further supported by linearity in double reciprocal plots of 1/\( k_{\text{obsd}} \) versus 1/[phenol] with finite intercepts. This adduct is supposed to decompose in the rate-determining step to yield the products i.e. o-bromo phenols. Formation of adduct is not uncommon in literature.\(^{14}\) The formation of dienone intermediate (Step 4) from the adduct is also a frequently observed phenomenon. Flow NMR technique\(^{15}\) has been used in the bromination of phenols in aqueous acetic acid solutions to detect the dienone intermediate. Also such dienone intermediate has been isolated when 2,6-di-t-butyl phenol was reacted with bromine.\(^{16}\) Fractional order dependence in [phenol] in the reaction with N-halo compounds are also very common in literature.\(^{17,18}\) Addition of acrylonitrile to the reaction mixture did not show any polymerization, thereby ruling out the possibility of a free radical mechanism.

The rates were found to be unaffected on adding Na\(_2\)SO\(_4\) salt indicating that the reaction may be between two dipoles i.e. phenol and HOBr. In this study HOBr has been well established to be the only effective brominating species.\(^{6-10,16-18}\) Based on the foregoing discussion, product analysis and stoichiometry, a plausible mechanism for the bromination of phenols has been proposed as below.

\[
2\text{NaBrO}_3 + 2\text{NaHSO}_3 \rightarrow 2\text{HOBr} + 2\text{Na}_2\text{SO}_4 + \text{O}_2 \uparrow \quad (2)
\]

\[
\text{Scheme 1}
\]

\[
\text{Scheme 1 leads to rate law (6)}
\]

\[
\text{Rate} = \frac{kK[\text{phenol}][\text{HOBr}]}{1 + K[\text{phenol}]} \quad \ldots (6)
\]

\[
\text{or} \quad -2.303 \frac{d \log [\text{HOBr}]}{dt} = \frac{kK[\text{phenol}]}{1 + K[\text{phenol}]} \quad \ldots (7)
\]

where \( k_{\text{obsd}} \) is the observed pseudo-first order rate constant, \( k \) the first order rate constant for the decomposition of the adduct, and \( K \) the formation constant of the adduct. Equation (6) accounts for the first order dependence of rate in [HOBr] and fractional order dependence in [phenol]. Taking reciprocal of Eq.(7) at constant [phenol], we get,

\[
\frac{1}{k_{\text{obsd}}} = \frac{1}{kK[\text{phenol}]} + \frac{1}{k} \quad \ldots (8)
\]

Double reciprocal plot of 1/\( k_{\text{obsd}} \) versus 1/[phenol] is found to be linear, the slope of which is equal to \( 1/kK \) and intercept equal to \( 1/k \). The ratio of intercept to slope gives the value of \( K \) and the reciprocal of intercept gives the value of \( k \).

The values of \( K \) and \( k \) were found to increase with increase in temperature. Thermodynamic parameters for the formation of adduct (step 3) and the activation parameters for the decomposition of the adduct (step 4) were evaluated from Eyring plots of \( \log K/T \) or \( \log k/T \) versus 1/T (Table 1). The \( \Delta S^e \) values for the formation of adduct are found to be negative. This is because of bulky cyclic adduct, which accounts for decrease in number of molecules in going from reactants to the intermediate adduct state, may be sufficiently polar to be solvated.

Since free water molecule is generated in step 4 of Scheme 1, the \( \Delta S^e \) values are expected to be positive. The actual values observed in the present study are largely negative. These values can be interpreted in terms of loss in entropy due to solvation of developing 2-bromocyclohexadiene -1-one (step 4). The \( \Delta S^e \) values are highly negative and are comparable with that of hydration of proton transfer to solvent (\(-105 \text{ J mol}^{-1} \text{ K}^{-1}\))\(^{19}\). On analogy, the hydration of 2-H, which undergoes intramolecular migration to oxo group to give 2-bromophenol is suggested.

\textbf{Structure-reactivity relationships}

Effect of substituents on rate constants can be
explained with the help of Hammett's equation, log 
\( \frac{k}{k_0} = \rho^\prime \sigma^p \) where \( k, k_0 \) are the rate constants for substituted and unsubstituted substrates, \( \rho^\prime \) is the reaction constant and \( \sigma^p \) is the substituent constant. The order of reactivity of various phenols was found to be as follows: 3-methylphenol > 4-methylphenol > phenol > 4-chlorophenol > 3-chlorophenol > 4-nitrophenol > 3-nitrophenol. From Table 1, it is clear that the values of the formation constants \( (K) \) do not vary much for phenols and do not follow any sequence. Hence no attempt is made to give a qualitative interpretation to those values. But the values of first order decomposition rate constant \( (k) \) for the adduct vary systematically. Assuming bromination at carbon atom ortho to -OH group of phenol, the Hammett's plot of log \( k \) versus \( \sigma^p \) was found to be linear with reaction constant, \( \rho^\prime = -0.42 \) at 303K \( (r = 0.93) \) taking \( \sigma^p \) values of meta substituents as para and vice versa. The negative \( \rho^\prime \) value supports the electrophilic aromatic substitution.

### Acknowledgement

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### References


### Table 1: Effect of substituents on \( K, k \) thermodynamic and activation parameters

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \sigma^p ) ( (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) )</th>
<th>( \Delta H ) ( \text{kJ mol}^{-1} )</th>
<th>( \Delta S ) ( \text{J mol}^{-1} \text{K}^{-1} )</th>
<th>( k \times 10^6 ) ( \text{s}^{-1} )</th>
<th>( \Delta H^+ \text{c} ) ( \text{kJ mol}^{-1} )</th>
<th>( \Delta S^+ ) ( \text{J mol}^{-1} \text{K}^{-1} )</th>
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<td>3-NO(_2)</td>
<td>0.790</td>
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