CHAPTER - I

Introduction
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INTRODUCTION

Kinetics is one of the fundamental tools to study the rate and mechanism of chemical reactions. This involves the tests for heterogeneity as well as the determination of the rate and order of a reaction in terms of concentration of reactant or reactants. The kinetic study involving the estimation of rate coefficient for a particular elementary reaction under the suitable conditions of pressure and temperature provides, in the first instance, Arrhenius parameters, which give valuable information about the nature of change. The parameters should be rationalised in terms of thermodynamics of the reversible process of reactants and products interconverting, and may finally lead to particular bond energies.

Kinetics is fundamentally concerned with the details of the process, whereby a system of the reactants changes from one state to another and it takes into account the time required for the transformation. Kinetics and stereochemical studies provide the most powerful methods of investigating detailed reaction mechanisms. However, it is generally observed that it is not possible to get the absolute information regarding reaction mechanism. The postulated mechanisms are essentially theories devised to
explain the facts observed experimentally. The proposed mechanisms are of the greatest use in understanding and systematising the study of chemistry.

The primary aim of a chemical kinetic study is to investigate the process whereby a system changes from one state to another and maintain the conditions required for obtaining a desired product on a large scale. However, of the greatest interest to chemists is the fact that kinetics helps in studying the mechanism of reaction. The reaction may really occur in several consecutive stages which are not represented by the stoichiometric equation. The presence of such series of stages may often be searched by the study of chemical kinetics. Thus, the study of chemical kinetics may provide a complete picture of reaction involving the equilibrium state. This involves the complexities where often postulations have to be made, and consequently the application becomes very difficult. The primary reactants and products of the slow step in a reaction sequence can not be detected from the kinetic results. However, they can be detected by the knowledge of empirical formula of the activated complex. The nature of reactions and identification of the products will provide as evidence for mechanism when the reactions will attain the equilibrium state rapidly before the slow step. However, the reaction may involve complexities due to the formation
of intermediate products which are short lived or have some life to be identified.

The rate of a reaction is determined principally by intrinsic properties of the participating molecules. The main factors influencing the instantaneous rate of any reaction in solution are found to be the molecular concentration, 'c' at the instant of measurement, the pressure 'p', temperature, T of solution and the nature of the solvent, assuming that the solution is free from impurities, of which the most insidious is dissolved air.

A complete kinetic study, for elucidation of reaction mechanism, will involve the following determinations.

1) Order with respect to each of the reactants and overall order of a reaction.

2) Solvent effect

3) Effect of neutral electrolyte
   (Ionic strength effect)

4) Entropy of activation (Activation - parameters)

In addition to the above mentioned determinations, the determination of chemical stoichiometry and the identification of transient intermediates will also help to establish the mechanism of reaction.

1. Order of the reaction:

The order of the reaction indicates the number of reactants involved in the rate determining step with
respect to the different reactants. If only one molecule of a reactant is involved in the rate determining step, the rate of reaction depends on the concentration of just one reactant. In the bromination of aromatic compound by molecular bromine in acetic acid medium, it has been reported that the rate of reaction depends upon both the reactants i.e. bromine and substrate.

2. **Solvent effect:**

Solvent plays an important role in understanding the mechanism and nature of the reaction. In the case of bromination of aromatic compounds by bromine, more often, water, acetic acid, carbontetrachloride etc. are used as solvents. The reaction rate is found to depend on dielectric constant of a solvent. Acetic acid has an intermediate dielectric constant value. Hence most of the bromination reactions involving aromatic compounds and bromine have been studied in acetic acid medium.

3. **Effect of neutral electrolytes:**

For a bimolecular reaction, the relationship between the rate constant and ionic strength \( u \) is:

\[
\log k = \log K_o + 2 Z_A Z_B \kappa \sqrt{u} \quad \ldots \quad (1)
\]
where \( Z_A \) and \( Z_B \) = the charges on reacting ions A & B

\( u \) = ionic strength,

\( \alpha \) = constant,

\( K_0 \) = the velocity constant at zero ionic strength.

Equation (1) is an approximation and is valid only for dilute solutions, which have small ionic strength. The above equation shows a linear relationship, if LogK is plotted against the square-root of ionic strength, with a slope proportional to the product, \( Z_A Z_B \), which may be either positive or negative depending on the nature of the ionic charges. If \( Z_A \) and \( Z_B \) are of the same charges, the rate of reaction increases, while an increase in ionic strength will decrease the reaction rate in case of oppositely charged ions.

If one of the reactants is a neutral species so that \( Z_B \) is zero, equation (1) predicts no effect of ionic strength, which is the case of very dilute solutions. At higher ionic strength, the rate constant may change due to the differences in the activity co-efficients of the ions. The activity coefficient of a neutral molecule is also influenced at higher ionic strength. The relationship between the activity coefficient \( (V_o) \) of a neutral molecule and ionic strength can be expressed as:

\[
\log V_o = b_o u
\]  

(2)
where $b_0$ is a constant. This equation will lead to another expression\(^2\), given by,

$$
\log K = \log K_0 + (b_0 + b_A - b_x) u \quad .. \quad (3)
$$

where $b_A$ and $b_x$ are constants.

Thus it is observed that the logarithms of the rate constants are a linear function of the first power of the ionic strength. According to Bronsted, the linear salt effect can be either positive or negative. In case of a negative salt effect, the rate determining step must be between two oppositely charged ions and a neutral molecule. In the former case, it will be exponential and, in the latter it would be linear.

In a termolecular reaction, three species are involved, as in the following reactions:

$$
A + B + C \quad \rightarrow \quad \text{Products}
$$

$$
2A + B \quad \rightarrow \quad \text{Products}
$$

The effect of ionic strength on a termolecular reaction involving the species $A, B, C$ can be expressed by the equation

$$
\log K = \log K_0 + \log f_A f_B f_C / f^*
$$

where $f_A, f_B, f_C$ are the activity coefficients of the ionic species $A, B, C$, respectively, $f^*$ is the activity coefficient of the activated complex. The above equation may even be written as:
$$\log K = \log K_0 + 2Q \sqrt{u} \left( z_A z_B + z_A z_C + z_B z_C \right)$$

where \( z \) = the charge
\( Q \) = constant \( \approx 0.51 \)
\( u \) = ionic strength

As a result of the limitations of equation (1), in the investigation of salt effect quantitatively, some qualitative results also help us to draw conclusions about the species involved in the rate determining step.

4. **Entropy changes:**

From the thermodynamic treatment, the mathematical equation relating entropy change and energy of activation for a unimolecular reaction can be given:

$$K_T = \frac{K_I}{h} e^{\frac{\Delta S}{R}} e^{-\frac{E_a}{RT}} \quad \ldots (4)$$

where
\( K_T \) = velocity constant
\( K \) = Boltzmann constant,
\( h \) = Plank's constant
\( E_a \) = Energy of activation,
\( \Delta S \) = Change in the entropy

Also
$$K_T = A e^{-\frac{E_a}{RT}} \quad \ldots (5)$$
Where, $A = \text{frequency factor}$

Hence, $A = \frac{KT}{h} \cdot \Delta S/R$ \hspace{1cm} \ldots (6)

But, $\frac{KT}{h} \approx 10^{13}$ \hspace{1cm} \ldots (7)

Hence $A = 10^{13} \cdot \frac{\Delta S}{R}$ \hspace{1cm} \ldots (8)

It is evident that if $A$ is greater than $10^{13}$, $S$ is positive and vice-versa. The frequency factor $A$ can be calculated from equation (5) by the determination of energy of activation, $E_a$ from the well-known Arrhenius equation. If $\Delta S$ is negative, the rate is slower and the formation of activated complex is less probable. For the reactions between ions of unlike charges, there is probably an increase in entropy, while going from the reactants to activated complex. For the ions of like charges, there is a decrease in entropy. In terms of frequency factor, $A$, it is found that for the reactions between ions of unlike charge, frequency factor is greater than $10^{13}$, for the ions of like charge, frequency factor much less than $10^{13}$. For a reaction between an ion and a neutral molecule, frequency factor is less than $10^{13}$. The reactions having much larger or much smaller frequency factor values than $10^{13}$ can be described as "abnormal" reactions for which an explanation must be
sought in terms the complex mechanisms, the effect of charges etc. This justification lies in a consideration of the experimental facts for the bimolecular reactions known in solution. In the most cases where an ion and a neutral molecule are involved, the frequency factor has been found to be of the order of $10^{11}$. The utility of the calculations for the increase or the decrease of entropy has been well explained by Moelwyn-Hughes\textsuperscript{1} and Frost and Pearson\textsuperscript{2}.

**Reagents used for bromination:**

- Bromination of organic compounds can be effected by using a number of reagents like molecular bromine ($\text{Br}_2$), hypobromous acid ($\text{HOBr}$), bromonium ion ($\text{Br}^+$), hypobromous acidium ion ($\text{H}_2\text{OBr}^+$), bromine acetate ($\text{BrOAc}$), iodine bromide ($\text{IBr}$), N-bromo-succinimide (NBS) and dioxime dibromide.

**Molecular bromine:**

Molecular bromine can be used for the bromination of aromatic nuclei activated by electron releasing substituents. The ortho isomer is produced to a greater extent in chlorination, while in brominations and iodinations, the para-isomer is formed to a greater extent\textsuperscript{3} which may be attributed to steric effect associated with the later atoms. Even though the substrates like
phenol, aniline etc. react quite rapidly with molecular bromine in the case of aromatic compounds of reactivity similar to or less than that of benzene, it is usually necessary to add the so called "halogen carrier" or "polar catalysts" like anhydrous aluminium chloride, anhydrous ferric chloride, iodine, iron powder etc.

In the bromination by molecular bromine and in the absence of catalyst, using organic solvents such as acetic acid, carbontetrachloride and in water, the molecular bromine itself is responsible for bromination and not the positive bromine ion (Br$^+$). If Br$^+$ formed through the dissociation is the brominating species, the rate of reaction should be inversely proportional to the bromide ion concentration,

$$\text{Br}_2 \rightarrow \text{Br}^+ + \text{Br}^- \quad \ldots (9)$$

This is not usually observed. However, it is found that the transition state for bromination is more polar than the starting materials. Further the reaction is facilitated by the addition of electrolyte, water etc. which increase the ionising power of the environment.

Brominations by the solutions of molecular bromine with aromatic substrates in organic solvents, like acetic acid, carbontetrachloride are often kinetically complex.
From the investigations on the bromination of a number of aromatic substrates in acetic acid medium, DelaMare has summarized the following general features.

(I) The reaction is generally of third order, second order in bromine and first order in substrate, especially in the concentration range 0.25 M to M/100. At low concentration (less than M/100), the order decreases to one. The order in bromine is also decreased by increasing the temperature, by adding water to the organic solvent or by adding salts to acids. Still higher orders in bromine are possible with less reactive substrates like toluene, naphthalene etc.

(II) The overall rate expression for bromination by molecular bromine could be represented as:

\[
\]

(III) The proposed mechanisms are:

\[
\begin{align*}
ArH + Br_2 & \rightleftharpoons ArHBr_2 \\
ArHBr_2 & \rightleftharpoons \text{Products} \quad \text{(II - order)} \\
ArH + Br_2 & \rightarrow ArHBr_2 \\
ArHBr_2 + Br_2 & \rightarrow \text{Products} \quad \text{(III - order)}
\end{align*}
\]
\[ \text{Br}_2 + \text{Br}_2 \rightleftharpoons \text{Br}_4 \]
\[ \text{ArH} + \text{Br}_4 \rightarrow \text{Products (III - order)} \]
\[ \text{ArH} + \text{Br}_4 \rightarrow \text{ArHBr}_4 \]
\[ \text{ArHBr}_4 + \text{Br}_2 \rightarrow \text{Products (IV - order)} \]

The mechanism in detail of second order\textsuperscript{10} reaction can be expressed as follows:

\[ \text{ArH} + \text{Br}_2 \rightleftharpoons \text{ArHBr}_2 \quad (11) \]
\[ \text{ArHBr}_2 \overset{\text{slow}}{\rightarrow} \text{ArHBr}^+ + \text{Br}^- \quad (12) \]
\[ \text{ArHBr}^+ \overset{\text{fast}}{\rightarrow} \text{ArBr} + \text{H}^+ \quad (13) \]
\[ \text{H}^+ + \text{Br}^- \overset{\text{fast}}{\rightarrow} \text{HBr} \quad (14) \]

This leads to the rate expression

\[ -\frac{d[\text{ArH, Br}]}{dt} = K \frac{[\text{ArH}] [\text{Br}_2]}{[\text{ArHBr}_2]} \quad (15) \]

Second order

The details of mechanism in the case of third order\textsuperscript{9} reaction are as follows:

\[ \text{ArH} + \text{Br}_2 \rightleftharpoons \text{ArH.Br}_2 \quad (16) \]
\[ \text{ArH.Br}_2 + \text{E} \rightleftharpoons \text{ArHBr}^+ + \text{E Br}^- \text{(slow)} \quad (17) \]
\[ \text{ArHBr} \xrightarrow{+} \text{ArBr} + \text{H}^+ \ldots \text{(fast)} \] (18)

\[ \text{H}^+ + \text{EBr}^- \xrightarrow{} \text{HBr} + \text{E} \ldots \text{(fast)} \] (19)

This leads to the rate expression,

\[ -\frac{d[\text{ArBr}]}{dt} = k \frac{[\text{ArH}][\text{Br}_2]}{[\text{E}]} \] (20)

Where 'E' is an electrophile. The formation of the species \( \text{ArH}.\text{Br}_2 \) seems to have been firmly established in the case of benzene and its alkyl derivatives in carbontetrachloride medium\(^{11}\), in case of mesitylene\(^{12}\) and diphenyl ether\(^{13}\) in acetic acid medium. It is assumed that the electrophile is used to polarise the Br-Br bond in the substrate-bromine complex and to remove the bromide ion as EBr\(^-\). The higher order observed in bromine in many cases may be due to another molecule of bromine acting itself as the electrophile. The factors which promote this heterolysis, such as adding water, salts etc. to the medium tend to reduce the overall order of reaction. Even a higher order in chlorine is not observed in the chlorination since it can not readily form an ion like Cl\(^-\). Medander\(^{14}\) has shown that if hydrogen to be substituted is replaced by deuterium or tritium in the reacting substrate, a primary kinetic effect, with the lighter compound reacting faster should occur in those
reactions where a carbon–hydrogen bond loosening occurs in or prior to the rate determining step, in such a case, the proton removal (equation 13 and 18) is not the rate determining step in brominations. Exactly similar observations have been made in the bromination of phenol\textsuperscript{15} anisole\textsuperscript{16} and p-bromophenol\textsuperscript{17} by molecular bromine.

**Iodine Bromide:**

It can be prepared in situ by mixing equal volumes of equimolar solutions of iodine and bromine. In carbon-tetrachloride, the degree of dissociation of iodine bromide is about 9\%\textsuperscript{18} and by comparison with low value for the degree of dissociation in HBr\textsuperscript{19}, it has been assumed that iodine bromide does not dissociate appreciably in acetic acid. Iodine bromide, therefore, has been reported as a mild brominating agent\textsuperscript{20-22}.

Militzer\textsuperscript{20} represented the bromination of phenol by iodine bromide as:

\[
\text{C}_6\text{H}_5\text{OH} + \text{IBr} \rightarrow \text{p-Br-C}_6\text{H}_4\text{-OH} + \text{HI} \quad (21)
\]

\[
\text{HI} + \text{IBr} \rightarrow \text{I}_2 + \text{HBr} \quad (22)
\]

Sharpe\textsuperscript{23} ruled out the above proposed mechanism as it involves the polarisation of IBr into I\textsuperscript{-} and Br\textsuperscript{+}. According to him, the bromine formed by thermal dissociation of IBr acted as the brominating agent, while iodine probably acted as a catalyst. It has been suggested that
in the "iodine catalysed brominations" iodine bromide is the effective catalyst\textsuperscript{24,25}.

Iodine bromide acts as an electrophile, and it removes the bromine ion as $\text{IBr}_2^-$ from the complex between the aromatic substrate and bromine.

**Iodine catalysed bromination:**

A kinetic investigation of iodine catalysed bromination of benzene was attempted by Bruner\textsuperscript{26} and reported the reaction to be second order in bromine in excess of carbontetrachloride. On the basis of Bruner's results of bromination of phenanthrene in carbontetrachloride, Price\textsuperscript{27} proposed the following rate expression

$$\frac{-d[\text{Br}_2]}{dt} = K [\text{ArH}] [\text{Br}]^{3/2} [\text{I}_2]^{5/2} \quad (23)$$

This rate expression was not obeyed by Bruner's results, the rate showed a maximum with the increase in concentration of iodine. Robertson et al\textsuperscript{28} interpreted the bromination of mesitylene in carbontetrachloride and of benzene on the basis of the assumed existence of such species is lacking. The "Iodine catalysed" bromination of p-bromophenol has been investigated by J. Rajaram and J.C. Kuriacose\textsuperscript{29} in acetic acid and carbontetrachloride. They reported that iodine bromide (IBr) does not function
as a brominating agent but it probably acts as an electrophile.

Some common features of the iodine catalysed bromination reactions are, the first order dependence of the rate on the substrate concentration and variability of the orders in bromine and iodine bromide. It has been reported that at constant initial concentration of the reactants, the rate passed through a maximum with added iodine and the position of the maximum depends upon the ratio of total iodine to total bromine as well as on the substrate concentration. Tsuruta\(^{30}\) deduced a relation between the ratio of total iodine (\(y\) moles/litre) and total bromine (\(x\) moles/litre) and the order in IBr as

\[
\frac{y}{x} = \frac{M}{M+1} \tag{24}
\]

In case of benzene, at the maximum rate, \(M=3\) and so \(y/x = 0.75\). Whereas Robertson reported the value of 0.61. For iodine bromide-catalysed bromination of toluene (\(m=2\)), Tsuruta\(^{31}\) reported a value of 0.75 in accordance with equation (24).

The modified expression by Gnanapragasam and Yeddnapalli\(^{33}\), for the catalytic maximum is

\[
\frac{y}{x} = \frac{M}{M+2} \tag{25}
\]
Based on their kinetic investigations in the bromination of phenol and anisole, the following equation has been suggested.

\[
\frac{\overline{I\text{Br}}}{\overline{\text{Free bromine}}} = M \tag{26}
\]

At the maximum rate, \(x\) and \(y\) represent the initial concentrations of iodine and bromine respectively. The equation (25) seems to agree with the reported values for the iodine bromide catalysed reactions such as, the bromination of phenol in carbontetrachloride and in acetic acid media\(^{25}\), \((m=1)\), bromination of mesitylene\(^{32}\), p-bromophenol\(^{29}\) and of anisole\(^{34}\) in carbontetrachloride \((m=2)\) and bromination of benzene\(^{26}\) \((m=3)\).

**N-Bromocompounds:**

N-bromo-succinimide, a well-known brominating agent among the N-bromo compounds used for bromination\(^{35}\), is prepared by the bromination of an ice-cold alkaline solution of succinimide. Brominations by NBS are usually carried in dry chloroform or carbontetrachloride. Depending upon the conditions allylic, nuclear or side chain brominations can be effected. In the presence of catalysts such as aluminium chloride, ferric chloride or zinc chloride or sulphuric acid, nuclear brominations can
be effected, especially in the case of hydrocarbons. However, the reactive compounds such as polynuclear hydrocarbons, aromatic ethers, aromatic amines etc. undergo nuclear bromination even in the absence of a catalyst. In the presence of per oxides, side chain bromination occurs\textsuperscript{36}.

**Dioxane dibromide:**

This is also a mild brominating reagent which is prepared by adding bromine rapidly to a cold solution of distilled dioxane and pouring the reaction mixture into ice-cold water\textsuperscript{37}. It functions as an electrophilic catalyst via oxonium ion formation viz\textsuperscript{38}

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{Br}^+ \rightarrow \text{Br}^- \\
\text{ArH}^+
\end{array}
\end{array}
\]

This is found to be a better brominating reagent than molecular bromine.

**Bromination of phenols:**

Oda and Tamura\textsuperscript{39}, from a systematic study of the halogenation of various substrates in acetic acid medium reported that the brominations of phenol, dihydric phenols and trihydric phenols were too fast to be studied. The greater reactivity of phenol compared to anisole is not due to the participation of the phenoxide ion but due to O-H hyperconjugation\textsuperscript{40-43}. 
Yeddnapalli and Gnanapragasam have investigated the bromination of phenol$^{25}$ and anisole$^{44}$ in acetic acid and carbontetrachloride media. The bromination in acetic acid is of second order, first order in each reactant, while that in carbontetrachloride is of third order, first order in phenol and second order in bromine. The temperature coefficient of the reaction between bromine and phenol in acetic acid medium is positive but in carbontetrachloride medium, it is negative in the temperature range 20–40$^\circ$C. This has been attributed to the thermal dissociation of the 1:1 complex between the substrate and bromine. In the bromination of anisole in acetic acid medium, the order decreases from 3 to 2.3 at the concentrations 0.1 M to 0.001 M of anisole and the energy of activation increases from 4.04 Kcal/mole at 0.04 M to 9.92 Kcal/mole at 0.001 M, but in carbontetrachloride medium, the reaction is autocatalytic and of third order. The catalysis is due to the formation of HBr in the reaction, as shown by the experiments with initially added HBr. The mechanism proposed is the general one$^9$. On the basis of spectroscopic measurements on the mixtures of iodine and anisole, iodine and benzene, 1:1 complexes have been reported to be formed in carbontetrachloride but not in acetic acid$^{44}$. 
The bromination of phenol and anisole has been studied using IBr as the source of bromine in acetic acid and in carbontetrachloride media. The reaction in the case of phenol and anisole in acetic acid medium is of third order, first order in the substrate and second order in the iodine bromide. The following mechanism has been suggested:

\[
\begin{align*}
2 \text{IBr} & \rightleftharpoons I_2 + \text{Br}_2 \\
\text{Br}_2 + C_6H_5O \cdot R & \rightleftharpoons \overset{K}{\text{C}_6\text{H}_5\text{ORBr}^+ \text{Br}^-} \quad \overset{K'}{\rightleftharpoons} \\
\overset{\text{C}_6\text{H}_5\text{ORBr}}\text{+} + \text{IBr}_2^- & \quad \text{(slow)} \quad \text{(28)} \\
\overset{\text{C}_6\text{H}_5\text{ORBr}}\text{+} & \rightarrow \text{Br}^- \cdot C_6H_4 \cdot \text{OR} + H^+ \quad \text{(fast)} \quad \text{(29)} \\
H^+ + \text{IBr}_2^- & \rightarrow \text{HBr} + \text{IBr} \quad \text{(fast)} \quad \text{(30)}
\end{align*}
\]

(\(R = H \text{ or } \text{Me}\))

This leads to the rate expression:

\[
\frac{-d}{dt} \overset{\text{Br}^- \cdot C_6H_4 \cdot \text{OR}}\text{+} = \overset{K}{\leftarrow} \overset{K'}{\text{C}_6\text{H}_5\text{OR}} \overset{\text{Br}_2}\text{+} \overset{\text{IBr}}\text{+} \quad \text{(31)}
\]
substituting for \( \int \text{Br}_2 \) from equation (25),

\[
-d \frac{\int \text{Br} \cdot \text{C}_6\text{H}_4\text{OH}}{\text{dt}} = k' \cdot K^{1/2} \frac{\int \text{C}_6\text{H}_5\text{OR}}{\int \text{IBr}} \int \text{Br}_2^2 \cdot (32)
\]

In carbon tetrachloride medium, the reaction between phenol and iodine bromide is of third order, first order in the substrate, and second order in iodine bromide. The mechanism suggested in this case is very similar to the one suggested for the reaction in acetic acid, except that a molecular complex is supposed to be formed between phenol and bromine in carbon tetrachloride medium. Taking into consideration the additional equilibrium, the rate expression can be stated as:

\[
-d \frac{\int \text{Br} \cdot \text{C}_6\text{H}_4\text{OH}}{\text{dt}} = k \cdot K \frac{\int \text{C}_6\text{H}_5\text{OH}}{\int \text{Br}_2} \frac{\int \text{IBr}}{\int \text{Br}_2} \cdot (33)
\]

Or

Substituting for \( \int \text{Br}_2 \) from equation (27)

\[
-d \frac{\int \text{Br} \cdot \text{C}_6\text{H}_4\text{OH}}{\text{dt}} = k \cdot k' \cdot K^{1/2} \frac{\int \text{C}_6\text{H}_5\text{OH}}{\int \text{IBr}} \int \text{Br}_2 \int \text{IBr}^2 \cdot (34)
\]

Where \( k' \) = equilibrium constant for phenol–bromine complex.

For the reaction between anisole and iodine bromide in
carbontetrachloride medium, the orders are one with respect to anisole and three with respect to IBr.

On the basis of the proposed mechanism, it is suggested that the rate determining step involves the attack of two molecules of IBr on the 1:1 complex between the substrate and bromine, formed by the dissociation of IBr. This leads to the rate expression:

$$\frac{-d\sum_{\text{MeO-C}_6\text{H}_4\text{-Br}}}{dt} = K.K'' \sum_{\text{C}_6\text{H}_5\text{OMe}} \sum_{\text{Br}_2} \sum_{\text{IBr}}^2$$

...(35)

where $K''$ is the equilibrium constant for the anisole-bromine molecular complex. Substituting for $\sum_{\text{Br}_2}$ from equation (27), the expression becomes:

$$\frac{-d\sum_{\text{MeO-C}_6\text{H}_4\text{-Br}}}{dt} = K.K.K^{1/2} \sum_{\text{C}_6\text{H}_5\text{OMe}} \sum_{\text{IBr}}^3$$

...(36)

The higher order with respect to iodine bromide observed in this reaction has been explained as follows. The weaker bond between anisole and bromine in the molecular complex leaves the Br-Br bond fairly strong and so apparently two molecules of iodine bromide are required to rupture the bond. The activation energies even show the same trend as in the case of phenol-bromine reaction.
The bromination of a number of phenolic ethers in acetic acid solvent has been studied by Sheshadri\textsuperscript{13}. The compounds investigated by him were found to obey the rate law:

\[
\frac{-d \sum \text{Br}_2 \cdot J}{dt} = K_3 \sum \text{ArH} \cdot J \sum \text{Br}_2 \cdot J^2
\]  

(37)

The mechanism proposed involves in the rate determining step, the attack of bromine on a 1:1 molecular complex of the substrate and bromine, the presence of which has been established spectroscopically with diethyl ether as a representative substrate.

The bromination of a number of \( p \)-substituted phenols in water has been investigated by Kulic and Vecera\textsuperscript{45} and concluded that phenol and phenolate ion both react with two reagents molecular bromine and tribromide ion and derived the rate expression:

\[
\frac{-d \sum \text{Br}_2 \cdot J}{dt} = K_{2 \cdot OH} \sum \text{Br}_2 \cdot J \sum \text{Ar.OH} \cdot J + K_{2O} \cdot \sum \text{Br}_2 \cdot J \sum \text{ArO}^- \cdot J
\]  

(38)

Bromination of \( p \)-bromophenol in detail, using the solvent acetic acid has been studied by Rajaram and Kuriacose\textsuperscript{17} and concluded that the substrate agrees the general mechanism involving the attack of one molecule
of an electrophile E on one of the complex ArH•Br\textsubscript{2} in
the rate determining step.

In the third order process, E is another molecule
of bromine whereas in the pseudo second order process,
it is one molecule of the solvent. Further the same
authors\textsuperscript{29} studied the bromination of p-bromophenol by
iodine bromide and reported that IBr does not function
as a brominating agent and it probably acts as the
electrophile for bromination by molecular bromine.

The bromination of p-bromophenol has even been
studied by Rajaram and Kuriacose\textsuperscript{46} using molecular
bromine in carbon tetrachloride, acetic acid medium.
Bromination of p-nitrophenol in solvent acetic acid has
been studied by Kuriacose et al\textsuperscript{47} and they reported
variable orders in bromine and p-nitrophenol at varying
concentrations of the reactants. A rate expression of
the type,

\[
\text{Rate} = K \left[ \text{ArH} \right] \left[ \text{Br}_2 \right] + K' \left[ \text{ArH} \right]^2 \left[ \text{Br}_2 \right] + \]

\[
K'' \left[ \text{ArH} \right] \left[ \text{Br}_2 \right] (39)
\]

has been proposed.

Vibhute and Jagdale\textsuperscript{48-50} studied the brominations
of o-chlorophenol, vaniline, o-bromophenol, salicylic acid,
p-chlorophenol and m-chlorophenol using molecular bromine
as a brominating agent in acetic acid medium. The over
all order determined was found to be three in the higher concentration region, but at the lower concentration, region, the order decreased, except for o-nitro phenol. The over all order was found to be dependent on the concentrations of the reactants. In case of o-nitrophenol, the order at higher concentration i.e. 0.2 to 0.1 M was three and at 0.04 M to 0.02 M was nearly three. The observed results in the order were explained by assuming simultaneous occurrence of second and third order processes so that the rate expression,

\[
\text{Rate} = K_3 \sum A \int \sum B \int^2 + K_2 \sum A \int \sum B \int
\]  

(40)

was suggested.

**Bromination of phenols by NBS:**

Liquid bromine is difficult and it is hazardous to handle. N-bromosuccinimide is a more convenient brominating agent\(^\text{61-63}\) for the bromination of aromatic compounds.

N-Bromosuccinimide (NBS) is a very versatile brominating agent. The bromination of aromatic compounds by NBS, mostly depends on the nature of solvent\(^\text{51}\). In nonpolar solvents, NBS is almost insoluble. NBS substitutes bromine in the allyl position in olefins\(^\text{52}\) and side chain bromination occurs in aromatic compounds\(^\text{53-54}\). In polar solvents, NBS is soluble and it reacts similar to bromine. Addition of bromine occurs across double bond in olefins\(^\text{55-56}\).
and nuclear substitution takes place in the case of aromatic compounds\textsuperscript{57}.

Nuclear bromination\textsuperscript{58}, in polar solvent was found to be favoured in the presence of catalysts like sulphuric acid\textsuperscript{59} and Lewis acids (AlCl\textsubscript{3}, FeCl\textsubscript{3} and ZnCl\textsubscript{2}). Lambert and Coworkers\textsuperscript{54} studied the halogenation of benzene and substituted benzenes by NBS in sulphuric acid-water solvent and reported only nuclear bromination. Further, they stated that the attacking species are protonated NBS and not free bromine. V.Calo and et al\textsuperscript{60} studied the bromination of phenol by NBS in several solvents and suggested the intermediate to be free bromine formed by reaction between HBr and NBS.

Sivakamasundari and R.Ganesan\textsuperscript{64} have studied the bromination of some aromatic compounds such as anisoles, anilides and phenols by NBS and reported order one with respect to substrate and zero with respect to NBS and proposed a probable mechanism:

1. \[
\text{NBS} \xrightleftharpoons[k_1]{k_{-1}} \text{Br}^+ + \text{A}^- \]
2. \[
\text{Ar.H} + \text{Br}^+ \xrightarrow[k_2]{\text{fast}} \text{ArBr} + \text{H}^+ \]
3. \[
\text{H}^+ + \text{A}^- \xrightarrow[\text{fast}]{\text{HA}} \text{(Succinimide)} \]
Radhakrishnamurti and Damodarrao\textsuperscript{65} have investigated the kinetics of bromination of phenol and substituted phenol by NBS in pure acetic acid - sodium acetate system. The order in NBS is unity and in substrate it is dependent on the nature of the substrate.

A composite rate law of the type,

\[
-d \frac{[\text{ArBr}]}{dt} = k [\text{NBS}] [\text{CH}_3\text{COONa}] + k'[\text{NBS}] [\text{ArH}]
\]

\[
+ k'' [\text{NBS}] [\text{CH}_3\text{COONa}] [\text{ArH}]
\]

has been derived. The reaction involves the formation of the initial complex between substrate and NBS which breaks down to the products.

Substrate + NBS \xrightarrow{K_1} Complex \xrightarrow{K_2} products

Radhakrishnamurti and Damodarrao\textsuperscript{66} have studied the kinetics of NBS bromination of anisole and p-methyl-anisole in pure and aqueous acetic acid in the presence of perchloric acid and mercuric acetate. The order of reaction depends on the solvent composition of the medium. In pure acetic acid, the reaction shows a zero order dependence with respect to NBS and first order with respect to anisoles as well as perchloric acid HClO$_4$. At and below 90% acetic acid, the reaction shows first
order with respect to NBS, Zero, first and second order with respect to HClO₄, depending on its concentration and zero, fractional and first order dependence with respect to substrate.

Srinivasan and Gnanapragasam⁶⁷ showed that in the NBS-bromination of anisole in 50% aqueous acetic acid, the reaction is Ag⁺ catalysed bromination. Further they reported that as the water content in aqueous acetic acid solution is increased, the rate constant is found to increase.

**Scope and object of the present work:**

Recently, kinetics of bromination of number of phenols have been studied in water⁴⁵, acetic acid¹⁷,²⁵,⁴⁷-⁵⁰ and carbontetrachloride²⁹,⁴⁶ media. Many workers have studied bromination, mostly on p-substituted phenols. Further, only a few attempts have been made to elucidate the structure and reactivity in the bromination of p-phenylphenols and substituted phenols. Hence ortho and para-hydroxybiphenyls and other substituted phenol substrates are considered for the bromination for the detail study. Further to elucidate the structure and reactivity relationship in the bromination reaction, the following para substituted compounds were selected viz: p-hydroxybenzophenone, p-cresol, p-chloro-m-cresol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-methoxyphenol.
In the case of bromination in acetic acid medium, the simultaneous second and third order processes have been reported\textsuperscript{13,17,44,48} and in many cases the contribution of the second order process to the overall rate has been reported to be rather small\textsuperscript{12} in comparison with that of third order process so that all the brominations in acetic acid medium are of third order. At the low concentrations (less than $5 \times 10^{-3}$ M) of bromine and phenol, second order process predominates. The acetic acid solvent molecules have been assumed to solvate the bromide ion into aromatic substrate-halogen complex. This facilitates the rupture of the Br-Br bond in the complex. Attempts have been made to establish an order in acetic acid and the occurrence of simultaneous orders in o-hydroxybiphenyl and p-substituted phenyl phenols. It was also thought interesting to elucidate the structure and reactivity from the study of bromination of phenyl phenols in acetic acid using molecular bromine, iodine bromide and N-bromosuccinimide as the brominating agents.

In the catalytic bromination of aromatic substrates, iodine bromide is found to be the effective catalyst\textsuperscript{24,25}. In all these investigations, iodine bromide has been used both as the catalyst and as the source of bromine.
Attempts have been previously made to correlate the ratio of the reactants at the catalytic maximum observed in iodine bromide catalysed reactions, with the order with respect to iodine bromide. Tsuruta et al.\textsuperscript{30} have proposed the equation,

\[
\frac{y}{x} = \frac{m}{m+1} \tag{24}
\]

where \(y\) and \(x\) refer to the molecular concentrations of iodine and bromine respectively. This equation has been further modified by Gnanapragasam and Yeddanapalli\textsuperscript{33} as

\[
\frac{y}{x} = \frac{m}{m+2} \tag{25}
\]

on the basis of their kinetic investigations on the bromination of phenol and anisole by iodine bromide, it was considered useful to find out the proper working conditions under which it should be possible to arrive at a relationship between the ratio of the reactants at the catalytic maximum and the order with respect to the catalyst. In the present study, the iodine bromide catalysed bromination of \(p\)-hydroxy and \(o\)-hydroxybiphenyls is investigated in acetic acid in order to seek unifying threads in the mechanism.
A very few attempts have been made to study the brominations of the various aromatic compounds (phenylphenols) by N-bromosuccinimide, as a brominating agent in acetic acid medium. Literature reveals that kinetics of bromination of only few phenols by NBS have been studied. It is observed in NBS-bromination of phenols, that it has been carried out in the presence of perchloric acid\textsuperscript{66}, mercuric acetate or sodium acetate\textsuperscript{65} or aqueous acetic acid (50\%)\textsuperscript{67}, the reaction is highly fast and consequently, the kinetic study of bromination becomes difficult. Therefore, present work is carried out in acetic acid and in the absence of mercuric acetate etc.

The aim of the present investigation is to study the kinetics of bromination of ortho and para hydroxybiphenyl and some other phenols by NBS in acetic acid (pure) and aqueous acetic acid medium in the absence of catalyst to elucidate the structure and reactivity, in order to find out the mechanism of bromination of hydroxybiphenyl by NBS.

The brominations of various para substituted phenols and ortho and para-hydroxybiphenyls by the different reagents such as molecular bromine, IBr and NBS, have been carried in the light of the following points:
1. To find out the over all order of bromination of substrate by a reagent in given medium of solvent.
2. To find out the order with respect to bromine or NBS
3. To find out the order with respect to the substrate (or phenol)
4. To study the effect of solvent on the rate of bromination of phenols.
5. To establish an order in acetic acid and elucidate the occurrence of simultaneous orders in the bromination.
6. To study the effect of temperature on the rate of reaction and to calculate the thermodynamic parameters.
7. To elucidate the structure and reactivity in order to find out mechanisms of bromination of the phenols.