The Kinetic Study for the Fast Bromination Reaction of the Regioisomers of Cresol in Aqueous Medium by Competition Techniques

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Abstracts: The kinetic study for the bromination of the regioisomers of cresol in aqueous medium by molecular bromine has been carried out using the competition technique. These reactions are rapid and are found to be of the second order. The specific reaction rates determined at 27.0°C are 0.8 x 10⁴, 1.78 x 10⁴ and 4.4 x 10⁴ M⁻¹ s⁻¹ for the ortho, para and meta isomers respectively. These values quantitatively justify the relative reactivity of these regioisomers in aqueous medium which has been qualitatively speculated hitherto for these rapid bromination reactions.

I. Introduction

The competition technique is used to study the fast bromination of the regioisomers of Cresol. A chemical reaction has kinetic and thermodynamic aspects. Chemical kinetics furnishes information regarding reactivity of the reactants from the determination of the rate constant which is in turn associated with the height of the energy barrier between the reactants and products. The mechanism of a reaction in one sense is the sequence of several elementary steps involved in the conversion of the reactants into products. Reaction mechanism gives the analytical information about the make and break of the chemical bonds involved in the reaction and identification of products. These are electrophilic substitution reactions generally and are rapid in aqueous solutions. Of these, Brominations are the fastest and Iodinations the slowest. Various brominating reagents are used such as molecular bromine.

The significant equilibrium in aqueous solutions is

\[ \text{X}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOX} + \text{HX} \]

Table 1: The formation of \( \text{H}_2\text{OX}^+ \) as the probable electrophile in these aqueous solutions is easily ruled out as the following table

<table>
<thead>
<tr>
<th>Halogen</th>
<th>( [X] )</th>
<th>( [X]/[X] )</th>
<th>( [\text{H}_2\text{OX}^+] / [X]/[X] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}_2 )</td>
<td>10⁻⁵⁰</td>
<td></td>
<td>10⁻⁵⁰</td>
</tr>
<tr>
<td>( \text{Br}_2 )</td>
<td>10⁻⁴⁰</td>
<td></td>
<td>10⁻³⁰</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>10⁻⁴⁰</td>
<td></td>
<td>10⁻¹⁰</td>
</tr>
</tbody>
</table>

Table 2: The relative reactivities of some brominating reagents was estimated by Shilov and Kaniaev as

<table>
<thead>
<tr>
<th>( \text{Br}^+ )</th>
<th>( \text{BrCl} )</th>
<th>( \text{Br}_2 )</th>
<th>( \text{HOBr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>110000</td>
<td>43000</td>
<td>80</td>
<td>0.12</td>
</tr>
</tbody>
</table>

However, Rao et al. have convincingly ruled out the formation of positive protonated cations in aqueous brominations and has proposed a catalytic route to explain the increased rates of these reactions in acidified solutions. The bromination of aromatic compound by \( \text{N-bromoSuccinimide} \) and bromine molecule as a brominating reagent

A rapid reaction may proceed slowly enough for conventional measurements provided the low concentrations of the reactants reached are measurable.

B] The Competition Technique

When A and B do not react with each other but C reacts with both A and B then a competition can be arranged between A and B to react with C wherein C is in insufficient quantity and A and B are in large excess. If the rate constant for one of the competing reactions is known, the other can be found out. Taft and Cook have determined the rate constant by the competition technique.\(^7\)
C] The Capacity flow Technique
The reactant solution is mixed at a constant rate and the outflow too of the reaction mixture is maintained at a constant rate along the route of which a property of the reactant or product is monitored.

D] Temperature Maximum Technique
If a reaction is first carried out under adiabatic and then isothermal conditions, then the quantity of heat evolved or consumed may be monitored. The rise or fall in temperature is a measure of the rate constant of the reaction.

E] Flow Techniques
The reaction carried out by mixing the reactants in a specially constructed mixing chamber and allowing the reaction solution to flow at a fast rate through a capillary. Some property along a reactant or product is measured along the flow tube.

F] Relaxation Techniques
Investigation of the kinetics of rapid reactions in aqueous solution scientist Eigen and co-workers used relaxation methods in reaction in equilibrium is subjected to perturbation in terms of physical parameter. The rate of change of the system towards the new equilibrium is relaxation. Relaxation studies are carried out in terms of a parameter such as temperatures, pressure or electric field.

G] Temperature Maximum Technique
If a reaction is first carried out under adiabatic and then isothermal conditions, then the quantity of heat evolved or consumed may be monitored. The rise or fall in temperature is a measure of the rate constant of the reaction.

H] Electro-analytical Techniques
If one of the reactants or products is electro-active, the reaction can be followed using electrochemical techniques e.g. If a voltage is applied to aPolarographic cell in which species is in equilibrium at the cathode with two reactants A and B, then,

\[ A + B \rightarrow R \]

\[ R + Ze \rightarrow P \]

If the second reaction is rapid, the cell current depends on the concentration of R. Evidently the rate of first reaction producing R is measurable from the observed current, The current is direct measurement of reaction rate, change in reaction rate due to variation of concentration and temperature. The goal of electron transfer relates to measured electrode current.

I] Pulse Radiolysis
If a reactionBis disturbed, the departure from equilibrium alters concentration value of the reactants and products and the disturbed reaction follows the exponential law,

\[ d = d_0 e^{-\frac{t}{\tau}} \]

\( d_0 \) = difference in the concentration before and after perturbation.
\( d \) = concentration at equilibrium before perturbation at the time \( \tau \).
\( \tau \) = relaxation time i.e. time taken for d to fall to 1/e of its initial value and depends on the reaction.

In pulse radiolysis a pulse of high energy electrons is passed through the reaction solution and changes produced are monitored spectrophotometrically. Kinetics of the hydrolysis of iodine mono-chloride has been measured by the pulsed accelerated flow technique by Wang.

J] Femtochemistry Techniques
Femtochemistry means study of chemical reaction occur in short timescale which is approximately 10^{-15} sec i.e femto-second. A femto-second pulse is used to excite a molecule. Femtochemistry has proved to be an exciting tool to study electron transfer reactions in photo-stimulated processes. These have applications in biological reactions to determine the conformation of RNA. A.H.Zewail has won the Nobel Prize in 1999 for his work in this field. In 1942 Ziegler investigate that N-bromosuccinimide was effective reagent for bromination of aromatic compound.
K) Atto-second Techniques

Zewail and Baum have generated atto-second electron pulses for 4D diffraction to study ultra fast electron dynamics. Chemical reactions occur in attosecond timescale\(^9\) (attosecond=\(10^{-18}\) sec.) Study of atomic clusters, phase transitions and transition states has been possible by using optical pulses in the wavelength region 15-40 nm.

Fig. 1 Electrophilic aromatic substitutions

1. Formation of carbonium

\[
\begin{align*}
\text{I} + E^+ & \xrightarrow{\text{addition of electrophile}} \text{I}^+ \text{E} \\
\text{C} + E^+ & \xrightarrow{\text{addition of electrophile}} \text{C}^+ \text{E}
\end{align*}
\]

2. Aromaticity

\[
\begin{align*}
\text{C}^+ \text{E} & \xrightarrow{\text{loss of proton}} \text{C} \text{E}
\end{align*}
\]

First, the electrophile \(E^+\) attacks the aromatic ring to form a pia complex in the second step pia complex or pia electron system donates the electron density to the electrophile to form a sigma bond. This is called as sigma complex or carbocation or aronium ion or Wheland intermediate. In the last step, loss of a proton which is fast step and the aromaticity of the ring is formed. The sigma complex is highly reactive but is stabilized by delocalisation of the charge to the two ortho positions and the paraposition\(^10\).

Bromination in aromatic compounds

In benzene, electrons have to be arranged in octets around the six carbon atoms. This arrangement introduces a symmetrical placement of the electrons. Kekule's concept of the molecule consists of three sets of pairs of carbon atoms. The plane of the benzene ring is the node for all \(\pi\) orbitals. Six \(\pi\) electrons fit in three stable \(\pi\) orbitals and are delocalized over the entire benzene ring. The applied field during nmr produces an induced field that opposes the ring current inside the ring but reinforces the induced current outside the ring. Scientist Dewar proposed that pia complex play an important role in electrophilic aromatic substitution reaction.\(^11\) Electronegative atoms attached to a ring carbon atom withdraw electrons by conjugation, de-shielding the latter resulting in larger chemical shifts at ortho and para positions.

The bromination of aromatic compounds in aqueous solutions is very rapid and studies on their kinetics are rare because of the extreme rapidity of the reactions. Conventional methods of determination of specific reaction rates are of no avail in these cases under such circumstances in the present work, we have studied the kinetics of bromination of aromatic compound by bromine in aqueous solution.

Reports on halogenations of aromatic substrates in aqueous medium are not rare but only qualitative. A quantitative assessment through kinetic studies for most of these reactions is lacking presumably due to their rapidity which necessitates special techniques for such studies.

Brominations using brominating agent are the fastest among these halogenations. Since all these substitution reactions are electrophilic in nature, special techniques like the stopped flow technique, relaxation technique and rotating platinum electrode technique (RPE) have to be employed for these reactions. Half-lives for these reactions are less than a second but time period can be extended to about fifty seconds by diluting the reactants by water since these are second order reactions. Convenient Competition Techniques applied can sense very low concentrations of Bromine up to \(10^{-5}\) M since these are electro reducible species.

When a small amount of reagent A is treated to a large excess of two substances B and C which do not react with each other but compete to react with A, then the rate of the reaction between A and B can be evaluated provided that for the reaction between A and C is known. This is the principle of the competition technique used to study the rapid bromination kinetics of the regioisomers of cresol in aqueous solution. This is the principle of the competition technique used to study the rapid bromination kinetics of the regioisomers of cresol in aqueous solution. The known reaction is the displacement of iodine from aqueous KI solution. The velocity constant for the three reactions studied by this technique in this chapter elucidate the consequences of the substrate regiospecificity and reveal steric compulsions in these reactions. Electrophile bromine ion as the chain carrying species in Comitative method.\(^12\)
Regioisomers of cresol Cresols are known as hydroxytoluneor Methylphenol. They are a occur as a naturally obtained from coal tar or petroleum. All three region-isomers of Cresols are toxic and acts as germicides-antiseptic. These are three forms Orto-Cresol, Para-Cresol, Meta-Cresol.

II. Experimental Method

Francis reported that values for relative rates of bromination of various aromatic compound based on competition method\textsuperscript{13} The kinetic study for the bromination of the regioisomers of cresol in aqueous medium by molecular bromine has been carried out using the competition technique. These reactions are rapid and are found to be of the second order. The specific reaction rates determined at 27.0°C are $0.8 \times 10^4$, $1.78 \times 10^4$ and $4.40 \times 10^3\text{M}^{-1}\text{s}^{-1}$ for the ortho, para and meta isomers respectively. These values quantitatively justify the relative reactivity of these regioisomers in aqueous medium which has been qualitatively speculated hitherto for these rapid bromination reactions. Bromination by molecular bromine is the fastest among halogenations.\textsuperscript{14}

The reactions investigated herein are electrophilic substitutions and are very rapid in aqueous medium necessitating a special technique for this study. This technique is based on a competition for bromine by cresol and iodide ions. The reaction between potassium iodide and bromine is very rapid. When an aqueous solution of a large excess of both, potassium iodide and cresol in known concentrations is treated with a small concentration of bromine, there is a competition for bromine between potassium iodide and cresol according to the following equations.

Displacement of iodine from potassium iodide by bromine

\[
2\text{KI} + \text{Br}_2 \rightarrow \text{KBr} + \text{I}_2
\]

Cresol does not react with potassium iodide or iodine at any significant rate under these conditions. The amount of iodine liberated in the competition is determined iodometrically and compared with that, $V$ liberated in the absence of the competition by an equal amount of bromine. Rates of the two competing reactions are thus compared and after establishing the order of the reaction under study (I), its specific reaction rate is evaluated having known that for (II).\textsuperscript{15}

In order to ascertain the order of the reaction under study, the competition for bromine is carried out with different ratios of cresol and potassium iodide concentrations. Order determines the dependence of the reaction rate on reactant concentrations hence variation in the competitor concentration ratio elucidates the reaction order.\textsuperscript{16}

Preparation Chemicals:

AR grade samples of the cresol isomers, potassium iodide and bromine are used to prepare the required stock solutions in conductivity water. The bromine solution is standardized using iodometry.

Determination of the specific reaction rate:

$v$ cm$^3$ of sodium thiosulphate in the iodometric titration corresponds to the bromine reacted with potassium iodide and $(V-v)$ cm$^3$ corresponds to that reacted with cresol in the competition. The ratio $v/(V-v)$ is the competition ratio.\textsuperscript{17}

Set I:

\[10 \text{cm}^3 \times 0.0025 \text{M} \text{Br}_2 + 40 \text{cm}^3 \times 0.04 \text{M} \text{KI} + 50 \text{cm}^3 \text{H}_{2}\text{O} \text{Vs} 0.005 \text{M} \text{Na}_2\text{S}_2\text{O}_3 = V \text{ cm}^3\]

Set II:

\[10 \text{cm}^3 \times 0.0025 \text{M} \text{Br}_2+ 40 \text{cm}^3 \times 0.04 \text{M} \text{KI} + 50 \text{cm}^3 \text{0.2 M o-cresol Vs} 0.005 \text{M} \text{Na}_2\text{S}_2\text{O}_3 = v \text{ cm}^3\]

Set III:

\[10 \text{cm}^3 \times 0.0025 \text{M} \text{Br}_2+ 40 \text{cm}^3 \times 0.04 \text{M} \text{KI} + 50 \text{cm}^3 \text{0.1 M p-cresol Vs} 0.005 \text{M} \text{Na}_2\text{S}_2\text{O}_3\]

Set IV:

\[10 \text{cm}^3 \times 0.0025 \text{M} \text{Br}_2+ 40 \text{cm}^3 \times 0.04 \text{M} \text{KI} + 50 \text{cm}^3 \text{0.04 M m-cresol Vs} 0.005 \text{M} \text{Na}_2\text{S}_2\text{O}_3\]
Mechanism of bromination reaction of cresol

Fig. Mechanism of bromination reaction of cresol

I. Bromination of o-cresol by molecular bromine

II. Bromination of p-cresol by molecular bromine

III. Bromination of m-cresol by molecular bromine

<table>
<thead>
<tr>
<th>Table: 3</th>
<th>Bromination of o-cresol: Initial concentrations of the reactants in 100 cm³ reaction mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr. No.</td>
<td>Reactant</td>
</tr>
<tr>
<td>1</td>
<td>Bromine</td>
</tr>
<tr>
<td>2</td>
<td>o-cresol</td>
</tr>
<tr>
<td>3</td>
<td>potassium iodide</td>
</tr>
</tbody>
</table>

| Titrate values | V = 5.5 cm³  | v = 2.7 cm³ |

<table>
<thead>
<tr>
<th>Table: 4</th>
<th>Bromination of p-cresol: Initial concentrations of the reactants in 100 cm³ reaction mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr. No.</td>
<td>Reactant</td>
</tr>
<tr>
<td>1</td>
<td>Bromine</td>
</tr>
<tr>
<td>2</td>
<td>p-cresol</td>
</tr>
<tr>
<td>3</td>
<td>potassium iodide</td>
</tr>
</tbody>
</table>

| Titrate values | V = 5.5 cm³  | v = 2.7 cm³ |

<table>
<thead>
<tr>
<th>Table: 5</th>
<th>Bromination of m-cresol: Initial concentrations of the reactants in 100 cm³ reaction mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr. No.</td>
<td>Reactant</td>
</tr>
<tr>
<td>1</td>
<td>Bromine</td>
</tr>
<tr>
<td>2</td>
<td>m-cresol</td>
</tr>
<tr>
<td>3</td>
<td>potassium iodide</td>
</tr>
</tbody>
</table>

| Titrate values | V = 5.5 cm³  | v = 2.7 cm³ |

III. Results and Discussion

The competition ratio [V-v]/v is arranged to be near to unity as the error in it is then minimum. This is achieved by the prudent choice of the concentrations of the competitors in the reaction mixture ensuring precise determination of the velocity constant. In this study, we have used the appropriate concentration of each of the three regio-isomers of cresol in the three competition reactions studied with the aim of maintaining the
The competition ratio nearly 1 and in view of the observed rapidity of the reactions. The concentrations of both the competitors are large and almost constant compared to that of bromine in the competition.

\[
\begin{align*}
K_1 & [\text{Cresol}]^x [\text{Br}_2]^y \\
K_2 & [\text{KI}] [\text{Br}_2]
\end{align*}
\]

When \(x\) and \(y\) are both taken as 1, over a variation of the concentration range of cresol, the velocity constant values \(k_1\) obtained for the bromination of cresol are found to be constant suggesting an overall order of 2 for the reaction in all the three reactions studied.

The velocity constant values obtained are presented in Table 6.

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Regioisomer</th>
<th>Velocity constant for bromination/10^4 M^{-1}s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o-cresol</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>p-cresol</td>
<td>1.78</td>
</tr>
<tr>
<td>3</td>
<td>m-cresol</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Green chemistry principles are inherent in this study since microgram chemicals are used in these rapid reactions besides all solutions being aqueous and very dilute.

**Application of Competition technique**

1) Micro grams reagent used for the technique hence pollution hazards become less.
2) Reactions are carried out in aqueous solution therefore easy to handle and safe.

**References**

[16] Dangat V.Tand Borkar V.T.; Research Link, Vol. – X (5) p 8-10 (July 2011)