CHAPTER II

RAPID CHLORINATION KINETICS OF THE REGIOISOMERS 2, 3-XYLIDINE, 2, 5-XYLIDINE, 3,4-XYLIDINE AND 3,5-XYLIDINE BY MOLECULAR CHLORINE IN AQUEOUS MEDIUM USING THE COMPETITION TECHNIQUE: A QUANTITATIVE ASSESSMENT OF SUBSTITUENT REGIOSPECIFICITY
2.1 INTRODUCTION

Numerous organic substrates can undergo reactions with chlorine. For better understanding of these reactions kinetic and mechanistic information on chlorine reactivity is desired. For most of the reactions, HOCl is the major chlorinating reagent in acidic medium. Molecular chlorine is more often used in aqueous medium.\(^1\) The second order rate constants for chlorination vary over several orders of magnitude depending on the reaction conditions.\(^2\)

In the chlorination of aromatic substrates, the substituent on the aromatic ring influences the substitution reaction rate. The nucleophilicity of the ring and steric compulsions in the reaction mechanics also are significant in the reaction rates. Electron donor properties of the substituent increase the charge density of the aromatic ring and leads to faster substitution reaction. In the present study four reactions are investigated.

The kinetic study for the chlorination of the regioisomers of xylidine by molecular chlorine in aqueous medium has been carried out using the competition technique. The reactions studied here are very rapid requiring a special technique for this study. The competition technique is one of the simpler techniques to study very fast reactions in spite of its limitations.\(^3\) A competition is arranged between two reactants that do not react with one another but compete with each other to react with a reagent that is present in an insufficient quantity.

The aromatic substrates used in the present investigation are four regioisomers of xylidine. They are 2,3-xylidine, 2,5-xylidine, 3,4-xylidine and 3,5-xylidine. The chemical formula of xylidines is \((\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2\). They are all stable isomers and combustible and react with strong oxidizing agents. All isomers are toxic and care has to be taken while handling them.\(^4\) The properties of the various isomers are as follows:

1. **2,3-xylidine** - It is a liquid with melting point 2.5 °C and boiling point 222 °C. Its flash point is 96°C. It is mainly used as a raw material to produce imaging chemicals like pigments and dyestuffs. It is used in the production of mefenamic acid.
2. **2,5-xylidine** - It is a liquid with melting point 11.5 °C and boiling point is 215 °C. It is used in the production of antioxidants, agricultural products and pharmaceuticals.
3. **3,4-xylidine** - It is a crystalline solid with melting point 51 °C and boiling point 226°C. It is used as a raw material for production of vitamin B2, dyes, chemicals and pesticides.

4. **3,5-xylidine** - It is a liquid with melting point 9.8 °C and boiling point is 220-221°C. It is used for production of dyes, rubber chemicals, pesticides and pharmaceuticals.

In the present study, xylidine and potassium iodide are the two competitors. They do not react with each other but compete with each other to react with molecular chlorine. This fulfils the main requirement of the competition technique. The second mandatory condition for the competition technique to be adopted is that the specific reaction rate of one of the two competing reactions should be known. This is then treated as the reference reaction. In this study, the displacement of iodine from KI solution is the known reference reaction. The specific reaction rate for this reaction $k_1$ is reported in literature as $88.88 \text{ M}^{-1}\text{s}^{-1}$ at 26.0 °C. The competition between KI and xylidine is complete once the chlorine is fully used up. The amount of chlorine liberated in the competition when compared to that formed in the displacement reaction alone in the absence of competition, provides the basis of evaluating the kinetics of the reaction under study.

From the known specific rate constant $k_1$ for the displacement reaction, that for the reaction between $\text{Cl}_2$ and xylidine $k_2$ has been evaluated.

The reactions of the regioisomers of xylidine with $\text{Cl}_2$ are as follows:

$$\begin{align*}
\text{H}_2\text{N}\quad & + \text{Cl}_2(aq.) \quad \rightarrow \quad \text{H}_2\text{N} - \quad + \quad \text{H}^+_{(aq.)} + \text{Cl}^-_{(aq.)} \\
\text{2,3-XYLIDINE} & \\
\text{H}_2\text{N}\quad & + \text{Cl}_2(aq.) \quad \rightarrow \quad \text{H}_2\text{N} - \quad + \quad \text{H}^+_{(aq.)} + \text{Cl}^-_{(aq.)} \\
\text{2,5-XYLIDINE} &
\end{align*}$$
$\text{H}_2\text{N} + \text{Cl}_2(\text{aq.}) \rightarrow \text{H}_2\text{N} + \text{H}^{+} + \text{Cl}^{-}$

3,4-XYLIDINE

$\text{H}_2\text{N} + \text{Cl}_2(\text{aq.}) \rightarrow \text{H}_2\text{N}-\text{Cl} + \text{H}^{+} + \text{Cl}^{-}$

3,5-XYLIDINE
2.2 EXPERIMENTAL

i) Preparation of solutions:

a. A.R. grade samples of the regioisomers of xylidine and potassium iodide are used to prepare stock solutions. Large volumes of all the solutions are prepared in double distilled water to ensure minimum error while weighing.

b. Chlorine water is prepared from bleaching powder and concentrated hydrochloric acid. It is bubbled through conductivity water to free it from HCl. It is then standardized iodometrically.

The following sets of solutions are prepared for the kinetic investigations. The total volume of all the reactants is 100 cm$^3$ in each set.

Set-I  The Displacement | Reference] Reaction in the absence of competition

\[
10 \text{ cm}^3 0.0025 \text{ M } \text{Cl}_2 + 50 \text{ cm}^3 0.400 \text{ M } \text{KI} + 40 \text{ cm}^3 \text{H}_2\text{O} \\
Vs 0.0100 \text{ M } \text{Na}_2\text{S}_2\text{O}_3 = V \text{ cm}^3
\]

Set-II The iodination of 2,5-xylidine [During the competition]

\[
10 \text{ cm}^3 0.0025 \text{ M } \text{Cl}_2 + 50 \text{ cm}^3 0.400 \text{ M } \text{KI} + 40 \text{ cm}^3 0.0250 \text{ M } 2,5\text{-xylidine} \\
Vs 0.0100 \text{ M } \text{Na}_2\text{S}_2\text{O}_3 = v \text{ cm}^3
\]

Set-III  The iodination of 2,3-xylidine [During the competition]

\[
10 \text{ cm}^3 0.0025 \text{ M } \text{Cl}_2 + 50 \text{ cm}^3 0.200 \text{ M } \text{KI} + 40 \text{ cm}^3 0.0250 \text{ M } 2,3\text{-xylidine} \\
Vs 0.0100 \text{ M } \text{Na}_2\text{S}_2\text{O}_3 = v \text{ cm}^3
\]

Set-IV  The iodination of 3,4-xylidine [During the of competition]

\[
10 \text{ cm}^3 0.0025 \text{ M } \text{Cl}_2 + 50 \text{ cm}^3 0.200 \text{ M } \text{KI} + 40 \text{ cm}^3 0.0250 \text{ M } 3,4\text{-xylidine} \\
Vs 0.0100 \text{ M } \text{Na}_2\text{S}_2\text{O}_3 = v \text{ cm}^3
\]
Set-V  The iodination of 3,5-xylidine [ During the competition]

\[ 10 \text{ cm}^3 0.0025 \text{ M Cl}_2 + 50 \text{ cm}^3 0.200 \text{ M KI} + 40 \text{ cm}^3 0.0250 \text{ M 3.5-xylidine} \]
\[ \text{Vs} 0.0100 \text{ M Na}_2\text{S}_2\text{O}_3 = v \text{ cm}^3 \]

KI and xylidine solutions are first thoroughly mixed and while stirred in a reaction vessel, to which Cl\textsubscript{2} solution is slowly added. The iodine liberated is iodometrically analysed by titrimetry using a micropipette. Repeated titre values agree within 0.01 cm\textsuperscript{3}.

ii) Determination of the specific rate of the reactions:

In the competition, \( v \text{ cm}^3 \) represents the amount of Cl\textsubscript{2} reacted with KI and \( V - v \text{ cm}^3 \) represent that reacted with xylidine. \([V - v] / v\) is the competition ratio.

Analysis was done iodometrically. The exact quantity of iodine liberated in the absence of competition is \( 'V' \text{ cm}^3 \) and that liberated in the competition is \( 'v' \text{ cm}^3 \). \( v \text{ cm}^3 \) of sodium thiosulphate in the iodometric titration corresponds to the Cl\textsubscript{2} reacted with potassium iodide and \( (V - v) \text{ cm}^3 \) corresponds to that reacted with xylidine in the competition. The ratio \([ (V - v) / v]\) is the competition ratio.\(^5\) The experimental error in \( V \) is smaller than that in \( v \) and hence the latter is of significance in the accuracy of determining the competition ratio. For any error in \( v \), the error in the competition ratio is the minimum when the ratio is unity. This is possible when \( v = V / 2 \). The experiment is hence repeated several times to explore conditions leading to the case in which the \([\text{KI}] / [\text{xylidine}]\) ratio is such that the competition ratio is nearly 1.

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2.3 OBSERVATION TABLES

Table –I: Set I

Initial Reactant concentrations in the 100 cm$^3$ Reaction Mixture after all the additions: The Displacement | Reference Reaction in the absence of competition

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Component</th>
<th>Concentration / M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl$_2$</td>
<td>0.00025</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.20000</td>
</tr>
</tbody>
</table>

Titre value using 0.01 M Sodium thiosulphate. $V = 5.00$ cm$^3$

Table –II: Set II

Initial Reactant concentrations in the 100 cm$^3$ Reaction Mixture after all the additions:
The iodination of 2,5-xylidine | During the competition|

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Component</th>
<th>Concentration / M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl$_2$</td>
<td>0.00025</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.20000</td>
</tr>
<tr>
<td>3</td>
<td>2,5-xylidine</td>
<td>0.01000</td>
</tr>
</tbody>
</table>

Titre value using 0.010 M Sodium thiosulphate, $v = 2.50$ cm$^3$
Table – III: Set III
Initial Reactant concentrations in the 100 cm³ Reaction Mixture after all the additions:
The iodination of 2,3-xylidine | During the competition|

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Component</th>
<th>Concentration/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CI₂</td>
<td>0.00025</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.10000</td>
</tr>
<tr>
<td>3</td>
<td>2.3-xylidine</td>
<td>0.01000</td>
</tr>
</tbody>
</table>

Titre value using 0.010 M Sodium thiosulphate, \( v = 2.60 \) cm³

Table – IV: Set IV
Initial Reactant concentrations in the 100 cm³ Reaction Mixture after all the additions:
The iodination of 3,4-xylidine | During the competition|

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Component</th>
<th>Concentration/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CI₂</td>
<td>0.00025</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.10000</td>
</tr>
<tr>
<td>3</td>
<td>3.4-xylidine</td>
<td>0.01000</td>
</tr>
</tbody>
</table>

Titre value using 0.010 M Sodium thiosulphate, \( v = 3.03 \) cm³

Table – V: Set V
Initial Reactant concentrations in the 100 cm³ Reaction Mixture after all the additions:
The iodination of 3,5-xylidine | During the competition|

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Component</th>
<th>Concentration/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CI₂</td>
<td>0.00025</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.10000</td>
</tr>
<tr>
<td>3</td>
<td>3.5-xylidine</td>
<td>0.01000</td>
</tr>
</tbody>
</table>

Titre value using 0.010 M Sodium thiosulphate, \( v = 2.77 \) cm³
2.4 RESULTS AND DISCUSSION

The concentration of each of the two competitors is much larger than that of Cl₂. Further, each competitor reacts with about half the Cl₂ concentration as the competition ratio is kept near to unity. Under these conditions, the concentrations of the competitors may be considered as almost unchanged as compared to Cl₂, during the competition.

The ratio \( \frac{(V-v)}{v} \) is arranged close to 1.0 by choosing the appropriate concentrations of the two competitors in the reaction mixture since at this value of the competition ratio, the error in the calculations of the specific reaction rate is the minimum. The following equation is used to calculate the specific reaction rates for the chlorination of the four regioisomers of xylidine.

\[
\frac{[k_2[Xylidine] \cdot [Cl_2]^2]}{[k_1[KI] \cdot [ICl]]} = \frac{(V-v)}{v}
\]

x and y are both are taken as one over a variation of the concentration range of xylidine. The velocity constant \( k_2 \) obtained for the chlorination of xylidine remains constant with respect to different initial concentrations of the reactants. Therefore, the order of the reactions studied is inferred to be two.

The specific reaction rate for the reference reaction in the competition is reported in literature as 88.88 M⁻¹s⁻¹ at 26.0°C. The present kinetic investigations are carried out under identical conditions as in the reference reaction.

The velocity constant values determined in this study are presented in the following table.

Table VI: The reactivity of regioisomers of xylidine at 26.0°C as evidenced from kinetic data for chlorination by molecular chlorine.

<table>
<thead>
<tr>
<th>Regioisomers of xylidine</th>
<th>Second order velocity constant at 26.0°C / M⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2,3-xylidine</td>
<td>819</td>
</tr>
<tr>
<td>2 2,5-xylidine</td>
<td>1776</td>
</tr>
<tr>
<td>3 3,4-xylidine</td>
<td>577</td>
</tr>
<tr>
<td>4 3,5-xylidine</td>
<td>710</td>
</tr>
</tbody>
</table>
Conclusions:

The amino group is para and ortho directing and the methyl group is ortho directing in electrophilic substitution reactions. The combined effect of the two methyl groups and the amino group has been speculated on stereochemistry principles but has rarely been quantitatively ascertained. This has been the objective of the present study through kinetic investigations. All the reactions in this study are very rapid. Hence the special fast reaction technique—the competition technique has been employed. Each specific reaction rate obtained may be explained as follows.

In 2,3-xylidine, the combined influence of amino group and methyl groups is weakened due to proximity of the two –CH₃ groups that cause lack of co-planarity of the amino group. This directs the incoming chloro group at the position para to the amino group at a rate constant of 819 M⁻¹s⁻¹.

In 2,5-xylidine, the effect of the amino group and methyl groups operate in unison to direct the incoming chloro group at the position para to the amino group. This results in higher specific reaction rate for chlorination of 2,5-xylidine viz. 1776 M⁻¹s⁻¹.

In 3,4-xylidine the position para to the amino group is blocked by a –CH₃ group. Hence the incoming chloro group enters the position ortho to the amino group. Therefore, the observed rate constant is low at 577 M⁻¹s⁻¹.

In 3,5-xylidine a specific reaction rate of 710 M⁻¹s⁻¹ is observed. In this case the para chloro product is formed but at a reduced rate because of the steric congestion experienced among the two methyl groups and incoming chloro group.

Thus a quantitative justification of the qualitatively speculated aspects of the steric compulsions involved in these reaction dynamics has been achieved.
The plausible mechanisms might be proposed as follows.

1. \[
\begin{align*}
H_2N\begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons & \quad H_2C \begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons \quad H_2N\begin{array}{c}
\text{Cl}\end{array} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

2. \[
\begin{align*}
H_2C \begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons & \quad H_2C \begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons \\
\text{H}_2N & \quad \text{H}_2N
\end{align*}
\]

3. \[
\begin{align*}
H_2N\begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons & \quad H_2N\begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

4. \[
\begin{align*}
H_2N\begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons & \quad H_2N\begin{array}{c}
\text{Cl}\end{array} \rightleftharpoons \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]
2.5 REFERENCES


