Kinetics of the Rapid Reaction 
\( \text{Cl}_2 + 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{Cl}^- \) in Aqueous Solution 

T. S. Rao, S. I. Mali, and V. T. Dangat

Department of Chemistry, University of Poona, Pune - 411 007 (India)

Z. Naturforsch. 33 a, 391-392 (1978) ; received January 8, 1978

A competition technique has been employed to study the kinetics of the rapid reaction \( \text{Cl}_2 + 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{Cl}^- \) in aqueous solution. The specific rate at 25 °C and the energy of activation for the reaction are found to be 88.8 M\(^{-1}\) s\(^{-1}\) and 71.1 kJ mole\(^{-1}\), respectively.

The displacement of bromine from aqueous solutions of bromide ions by chlorine is a well-known reaction, but its kinetics has not yet been studied, presumably due to its rapidity. We have studied this kinetics on the basis of a comparison of the rate of this reaction with that of the chlorination of salicylic acid (SA) in aqueous solution. A small, measured amount of \( \text{Cl}_2 \) is added to a mixture of SA and \( \text{Br}^- \) of large, known concentrations. Both of these compete for the \( \text{Cl}_2 \) according to the reactions

\[
\begin{align*}
\text{OH} & \quad \text{COOH} \\
+ \text{Cl}_2 & \quad \rightarrow \quad \text{OH} & \quad \text{COOH} & \quad + H^+ + \text{Cl}^- \\
& \quad (1) \\
\text{Cl}_2 & \quad + 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{Cl}^- & \quad (2)
\end{align*}
\]

The \( \text{Br}_2 \) liberated in reaction (2) reacts with SA, but this does not affect our study. For every mole of \( \text{Cl}_2 \) reacted, one mole of \( \text{Cl}^- \) is produced in reaction (1), and two moles in reaction (2). The actual value will lie between one and two, depending upon the rates of the two competing reactions. The kinetics of reaction (1) has been studied [1] in a manner similar to that of the bromination of some substituted anilines [2]. Since the specific rate of reaction (1) is thus known, that of reaction (2) can be evaluated on the basis of the determination of the amount of \( \text{Cl}^- \) produced in the competition. This involves the prior determination of the order of the reaction.

**Experimental**

Analytical grade chemicals are used to prepare 0.01 M SA, 0.01 M KBr, 0.50 M KNO\(_3\), 0.004 M AgNO\(_3\) and 0.02 M Cl\(_2\) solutions in distilled water. AgNO\(_3\) solution is standardized with KCl by potentiometric titration and the Cl\(_2\) solution is standardized iodometrically.

Starting with these solutions 10.0 cm\(^3\) of SA and 1.0 cm\(^3\) of KNO\(_3\) are mixed with 5.0 cm\(^3\) of KBr. The mixture is diluted to 24.7 cm\(^3\). The ionic strength of the mixture is the same as in the study of reaction (1). The mixture is kept vigorously stirred, and 0.30 cm\(^3\) of 0.0167 M Cl\(_2\) is added from a micropipette. The total amount of KCl produced in the experiment is then determined by potentiometric titration with AgNO\(_3\). This determination is performed several times and with utmost care since it largely determines the accuracy of the results. The temperature is varied in the range 10 to 30 °C.

For determining the order of the reaction, the above experiment is repeated at 25 °C with the same SA concentration and various KBr concentrations.

The results are presented in Tables 1 and 2.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>= 25.0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific rate of the chlorination of salicylic acid in aqueous solution at 25.0 °C</td>
<td>= 25.0 M(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Concentration of salicylic acid</td>
<td>= 4.0 ×10(^{-3}) M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of bromide ions/10(^{-3}) M</th>
<th>1.2</th>
<th>2.0</th>
<th>2.8</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^{-}) produced per mole of ( \text{Cl}_2 ) reacted</td>
<td>1.52</td>
<td>1.64</td>
<td>1.71</td>
<td>1.78</td>
<td>1.82</td>
</tr>
<tr>
<td>Competition ratio ( X )</td>
<td>1.08</td>
<td>1.78</td>
<td>2.39</td>
<td>3.50</td>
<td>4.46</td>
</tr>
<tr>
<td>Third order rate constant ( k/10^4 \text{M}^{-2} \text{s}^{-1} )</td>
<td>7.50</td>
<td>4.44</td>
<td>3.05</td>
<td>2.19</td>
<td>1.78</td>
</tr>
<tr>
<td>Second order rate constant ( k/\text{M}^{-1} \text{s}^{-1} )</td>
<td>90.0</td>
<td>88.8</td>
<td>85.4</td>
<td>87.5</td>
<td>89.2</td>
</tr>
</tbody>
</table>

**Results and Discussion**

The rates \( R_1 \) and \( R_2 \) of the reactions (1) and (2) are, respectively,

\[
-\frac{d[\text{SA}]}{dt} = R_1 = k_2[\text{Cl}_2][\text{SA}],
\]

\[
-\frac{d[\text{Br}^-]}{dt} = R_2 = k[\text{Cl}_2]^y[\text{Br}^-]^y,
\]

where \( k_2 \) and \( k \) are the specific rates.

In the reaction mixture, the concentrations of the competitors are much larger than that of the chlorine reacting with it and hence may be con-
Table 2. Determination of the energy of activation for the reaction Cl<sub>2</sub>+2 Br<sup>-</sup> → Br<sub>2</sub>+2 Cl<sup>-</sup>.

<table>
<thead>
<tr>
<th>Temperature t/°C</th>
<th>10.0</th>
<th>15.0</th>
<th>20.0</th>
<th>25.0</th>
<th>30.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt; produced per mole of Cl&lt;sub&gt;2&lt;/sub&gt; reacted</td>
<td>1.52</td>
<td>1.56</td>
<td>1.60</td>
<td>1.64</td>
<td>1.68</td>
</tr>
<tr>
<td>Competition ratio X</td>
<td>1.08</td>
<td>1.29</td>
<td>1.51</td>
<td>1.78</td>
<td>2.13</td>
</tr>
<tr>
<td>k&lt;sub&gt;2&lt;/sub&gt;/M&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>8.6</td>
<td>12.3</td>
<td>17.6</td>
<td>23.7</td>
<td>33.2</td>
</tr>
<tr>
<td>k/M&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>18.8</td>
<td>31.6</td>
<td>53.2</td>
<td>88.8</td>
<td>140.0</td>
</tr>
</tbody>
</table>

Slope of the curve log k versus T<sup>-1</sup> = -3.8×10<sup>3</sup> K
Energy of activation for the reaction = 71.1 kJ mole<sup>-1</sup>
Entropy of activation for the reaction = 21.1 J K<sup>-1</sup> mole<sup>-1</sup>

Mechanism of the reaction: Chlorine hydrolyzes in aqueous solution according to the equilibrium

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- 
\]

in which both the forward and reverse reactions are rapid [3]. While the predominant chlorinating species in reaction (1) is known to be Cl<sub>2</sub> [4], that in reaction (2) could be either Cl<sub>2</sub> or HOCl.

The following two mechanisms are therefore likely, although a proof is not feasible considering the special technique used in this study.

**Mechanism I**

\[
\text{Cl}_2 + \text{Br}^- \rightarrow \text{BrCl} + \text{H}_2\text{O} \\
\text{BrCl} + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{H}^+ + \text{Cl}^- \\
\text{HOBr} + \text{Br}^- \rightarrow \text{Br}_2 + \text{OH}^- \\
\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} 
\]

**Mechanism II**

\[
\text{Cl}_2 + \text{H}_2\text{O} \nleftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \\
\text{HOCl} + \text{Br}^- \rightarrow \text{HOBr} + \text{Cl}^- \\
\text{HOBr} + \text{H}^+ + \text{Br}^- \nleftrightarrow \text{Br}_2 + \text{H}_2\text{O} 
\]

Mechanism I seems less likely as it involves the formation and the subsequent hydrolysis of the interhalogen compound which is known to be very unstable [5]. In mechanism II, which is more likely, the first step is a first order reaction while the third is a very rapid third order reaction [3].

In view of the observed second order kinetics of the reaction under study, the second step could be the rate determining one.

**References**


