Mechanisms: Haloform Reaction

**Chlorine + acetone**

- Morris & Baum, 1978
- Brezonik, 1994

Figure 6.35: Reaction scheme for production of haloform from acetone by the classic haloform reaction.
Haloform reaction: initial step

- Three potential pathways to enolate
  - Reaction with water ($K_O$), hydroxide ($K_{OH}$), and proton ($K_H$)
    - $k_f = K_O + K_{OH} [OH^-] + K_H [H^+]$
  - For acetone, the OH pathway dominates above pH 5.5

<table>
<thead>
<tr>
<th>Substance</th>
<th>$pK_a$</th>
<th>$K_{OH}$ l/mole-sec</th>
<th>$K_H$ l/mole-sec</th>
<th>$t_{10}$ pH 7, hr</th>
<th>$t_{10}$ pH 8.5, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>20</td>
<td>$4.7 \times 10^{10}$</td>
<td>0.25</td>
<td>2.9 $\times 10^9$</td>
<td>7500 385</td>
</tr>
<tr>
<td>Chloroacetone</td>
<td>16.5</td>
<td>5.3 $\times 10^8$</td>
<td>93</td>
<td>6.3 $\times 10^8$</td>
<td>21 1.0</td>
</tr>
<tr>
<td>Acetylacetone</td>
<td>15</td>
<td>7.3 $\times 10^8$</td>
<td>450</td>
<td>1.3 $\times 10^8$</td>
<td>3.7 0.21</td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.5 $\times 10^7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ethyl pyruvate</td>
<td>16</td>
<td>4.7 $\times 10^8$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formylacetone</td>
<td>9.0</td>
<td>1.1 $\times 10^9$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetacetate</td>
<td>10.7</td>
<td>1.2 $\times 10^9$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malonic acid</td>
<td>1.7 $\times 10^8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What is $k_r$?

Reactions in Series

$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$

$k_1 = k_2 = k_3 = 0.1 \text{ day}^{-1}$

Stumm & Morgan
Fig. 2.9
Pg. 68
Consecutive Reactions I

- Overall rate determined by slowest step
  - If $k_i >> k_{ii}$
    - A rapidly forms B which then reacts slowly
    - $\frac{d[C]}{dt} = k_{ii}[B]$  
  - If $k_i << k_{ii}$
    - B never builds up; it reacts as soon as it is formed
    - $\frac{d[C]}{dt} = k_i[A]$  
  - If $k_i ~ k_{ii}$
    - B slowly builds up then disappears
    - Rate must consider both reactions

Consecutive Reactions II

- Writing a separate equation for each species

\[
\begin{align*}
\frac{d[A]}{dt} &= -k_i[A] \\
\frac{d[B]}{dt} &= k_i[A] - k_{ii}[B] = k_i \left[A \right] - k_{ii}[B] \\
\frac{d[C]}{dt} &= k_{ii}[B] \\
\end{align*}
\]

\[
\begin{align*}
[A] &= [A]_0 e^{-k_i t} \\
[B] &= \frac{k_i [A]_0}{k_{ii} - k_i} (1 - e^{-k_{ii} t} - e^{-k_i t}) \\
[C] &= \frac{k_i [A]_0}{k_{ii} - k_i} (1 - e^{-k_{ii} t}) \\
\end{align*}
\]

Note that this $k_i$ was inadvertently left out of equ. 2-47 in Brezonik

$$k_i = 1 \text{ hr}^{-1} \quad k_{ii} = 4 \text{ hr}^{-1}$$

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Limiting Cases

- If $k_i >> k_{ii}$
  \[ [B] = \frac{k_i [A]_0}{k_i - k_{ii}} \left( e^{-k_{ii} t} - e^{-k_i t} \right) \]
- If $k_{ii} >> k_i$
  \[ [B] = \frac{k_i [A]_0}{k_{ii}} e^{-k_i t} \]

Focusing on $[B]$

- Often we are concerned with the maximum concentration of “B”
  - This occurs when $d[B]/dt = 0$
    \[ \frac{d[B]}{dt} = k_i [A] - k_{ii} [B] \]
    \[ k_i [A] = k_{ii} [B]_{\text{max}} \]
    \[ [B]_{\text{max}} = \frac{k_i}{k_{ii}} [A] \]
    \[ \frac{k_i}{k_{ii}} [A]_0 e^{-k_{ii} t_{\text{max-B}}} \]
  - And combining this with the general solution for $[B]$: \[ t_{\text{max-B}} = \frac{1}{k_i - k_{ii}} \ln \left( \frac{k_i}{k_{ii}} \right) \]
Chlorination of Phenol

<table>
<thead>
<tr>
<th>pH</th>
<th>Phenol</th>
<th>2-Chlorophenol</th>
<th>4-Chlorophenol</th>
<th>2,4-Dichlorophenol</th>
<th>2,4,6-Trichlorophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.08E2</td>
<td>4.03E3</td>
<td>9.40E1</td>
<td>2.08E2</td>
<td>6.29E2</td>
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<tr>
<td>6</td>
<td>4.03E2</td>
<td>5.84E3</td>
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<td>4.03E2</td>
<td>8.84E2</td>
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<tr>
<td>7</td>
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<td>2.25E3</td>
<td>6.03E3</td>
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<tr>
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<tr>
<td>9</td>
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<td>4.60E3</td>
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<td>5.44E2</td>
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<tr>
<td>12</td>
<td>4.50E1</td>
<td>4.65E1</td>
<td>8.39E1</td>
<td>3.15E1</td>
<td>1.81E1</td>
</tr>
</tbody>
</table>


pH effects

- Role of pH in reactant speciation
  - HOCl vs OCl⁻
  - Phenolic vs phenate
- Maximum at mid-pH
- Between $K_a$’s for HOCl and phenolic
Models I

From: Lee, 1967

Modeling phenol chlorination II

[Diagrams showing reactions and concentrations over time]
Scientist & Acuchem

Time (min)

Concentration (M)

Phenol
2-Chlorophenol
4-Chlorophenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4,6-Trichlorophenol
Ring Cleavage Products

0.10 mM Chlorine Dose

To next lecture