CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #10

Special Topics: DCP in Water
Primary Literature (e.g., Guthrie & Cossar, 1986)
Guthrie

- J. Peter Guthrie
  - Department of Chemistry
  - Western University, London, Ontario, Canada, N6A 5B7

- B.Sc.
  - Univ. Western Ontario

- PhD Chemistry, 1968
  - Harvard University
  - DECARBOXYLATION AND ENAMINE FORMATION: MODEL SYSTEMS FOR ACETOACETATE DECARBOXYLASE
    - By James Peter Guthrie

- Princeton Univ.

- 1970, Faculty, Western University

Mechanisms: Haloform Reaction

- Chlorine + acetone
  - Morris & Baum, 1978
  - Brezonik, 1994

![Diagram of haloform reaction]

Figure 1. The reaction pathway of the 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 I. Rates of Ionization of Ketones

<table>
<thead>
<tr>
<th>Substance</th>
<th>pK_a</th>
<th>K_O sec^{-1}</th>
<th>K_{OH} 1/mol, sec</th>
<th>K_H 1/mol, sec</th>
<th>t_{50} pH 7, hr</th>
<th>t_{50} pH 8.3, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>20</td>
<td>4.7 x 10^{-10}</td>
<td>0.25</td>
<td>2.9 x 10^{-5}</td>
<td>7500</td>
<td>385</td>
</tr>
<tr>
<td>Chloroacetone</td>
<td>16.5</td>
<td>5.3 x 10^{-8}</td>
<td>93</td>
<td>6.3 x 10^{-5}</td>
<td>21</td>
<td>1.0</td>
</tr>
<tr>
<td>as-Dichloroacetone</td>
<td>15</td>
<td>7.3 x 10^{-6}</td>
<td>450</td>
<td>1.1 x 10^{-5}</td>
<td>3.7</td>
<td>0.21</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td>4.5 x 10^{-7}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl pyruvate</td>
<td>16</td>
<td>4.7 x 10^{-7}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetylacetone</td>
<td>9.0</td>
<td>1.1 x 10^{-2}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetoacetate</td>
<td>10.7</td>
<td>1.2 x 10^{-3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malonic acid</td>
<td>10.7</td>
<td>1.7 x 10^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What is k_r?
Guthrie & Cossar Pathway

Scheme 1

\[ \begin{align*}
    
    &\text{Scheme 1.} \\
    &\text{\small (Guthrie & Cossar Pathway)} \\
    &\text{\small David A. Reckhow CEE697K Lecture #10} \\
    &\text{\small Scheme 1} \\
    &\text{\small Scheme 1.} \\
\end{align*} \]
Hydrolysis of 1,1-DCP

The many forms of 1,1-DCP

The product

\[ \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \]

\[ \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \]

\[ \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \]

\[ \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \xrightarrow{K_{LE}} \text{CH}_3\text{CCHCl}_2 \]
DCP equilibria I

- Bell K’s

![Graph showing pH against Alpha with various alpha values for different reactions: alpha E, alpha Q, alpha L, and alpha 5. The graph illustrates how the values change with pH.]
Bell K's

- $\alpha_E$
- $\alpha_Q$
- $\alpha_L$
- $\alpha_5$

The graph shows the variation of $\alpha$ with pH. The pH is plotted on the x-axis, ranging from 0 to 14, and $\alpha$ is plotted on the y-axis, ranging from $10^{-8}$ to $10^1$. The graph includes lines for $H^+$, $\alpha_E$, $\alpha_Q$, $\alpha_L$, and $\alpha_5$, each represented by a different style and color.
Guthrie K’s
**DCP equilibria IV**

- **Guthrie K’s**

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Graph showing the relationship between pH and various alpha values (alpha E, alpha Q, alpha L, alpha 5) with specific pH ranges from 0 to 14 and alpha values ranging from 1e-8 to 1e+1.
Loss of intermediates in lab water

- 21°C, ultrapure water
  - (Nikolaou et al., 2001)
chlorine

\[ \text{Scheme 1.} \]
\[ \begin{align*}
    \text{CH}_3\text{C} & \text{CHCl}_2 \xrightarrow{K_{5L}} \text{OH} \\
    \text{CH}_3\text{C} & \text{-CHCl}_2 \xrightarrow{K_{1E}^*} \text{CH}_3\text{C} & \text{CHCl}_2 \\
    \text{CH}_3\text{C} & \xrightarrow{k_{56}^*} \text{CH}_3\text{C} & \text{CCl}_2 \\
    \text{CH}_3\text{C} & \xrightarrow{k_{67}} \text{CH}_3\text{C} & \text{CCl}_3 \xrightarrow{K_{5E}^*} \text{OH} \\
    \text{CH}_3\text{C} & \text{CHCl}_2 \xrightarrow{k_{5L}} \text{OH} \\
    \text{CH}_3\text{C} & \xrightarrow{k_{65}} \text{CH}_3\text{C} & \text{CCl}_2 \\
    5 & \xrightarrow{k_{57}} 7 \\
\end{align*} \]
Guthrie model for 1,1-DCP degradation
Baiyang Chen analysis
- pH 7-7.5
- 20-25°C

Predicted hydrolysis rate constant for 1,1-DCP is $10^{-1.66}$ hr$^{-1}$
- Half-life of 31.7 hr
- $6.1 \times 10^{-6}$ sec$^{-1}$
- (Chen, 2011).

Data point estimated from Nikolaou et al., 2001

Comparison with Chen 2001

Guthrie model for 1,1-DCP degradation

Chen, 2011

- pH
- Half-Life (hrs)
- Chlorine
- Hydrolysis

Chen, 2011
Liu et al., 2013

In review
1,1-Dichloropropanone concentrations compared to the corresponding TTHM concentration for all samples.
1,1-Dichloropropanone concentrations compared to the corresponding TTHM concentration for all samples: focus on free chlorine plants
1,1,1-Trichloropropanone concentrations compared to the corresponding TTHM concentration for all samples

- San Francisco Jan (Cl₂/NH₄Cl)
- Charleston (ClO₂/ NH₄Cl)
- San Francisco Apr (Cl₂/NH₄Cl)
- Ann Arbor (O₃/NH₄Cl)
- East Bay (Cl₂/NH₄Cl)
- Cincinnati (Cl₂)
- Minneapolis (NH₄Cl/NH₄Cl)
- Monroe (O₃/Cl₂)
- Knoxville (ClO₂/Cl₂)
- Pinellas County (Cl₂/Cl₂)
- Pinellas County (Cl₂/NH₄Cl)
- Knoxville (ClO₂/Cl₂)
15 Oct 2013 experiment

\[
\text{abs}_{\text{inf}} = 0.012
\]
1st order plot

![Graph showing a first-order plot with reaction time (sec) on the x-axis and \( \ln(\text{Abs-Abs}_{\infty}) \) on the y-axis. The graph shows a straight line with data points and the following information:

- \( \text{abs}_{\infty} = 0.012 \)
- \( b[1] = -0.0128851211 \)
- \( K = 46 \text{ hr}^{-1} \)
2nd order plot

![Graph showing a 2nd order plot with reaction time on the x-axis and 1/(abs-absinf) on the y-axis. The graph shows a nonlinear trend with data points and a line of best fit.](image-url)
Guthrie model

![Graph showing pH and Half-Life (hrs)]

- Chlorine
- Hydrolysis
To next lecture