Lecture #2

**Rate Expressions:** Bromide + Chlorine

case study & lab project

Kumar & Margerum paper
Reactions with Chlorine

HOCl + natural organics (NOM)

The Precursors!

Oxidized NOM and inorganic chloride
- Aldehydes

Chlorinated Organics
- TOX
- THMs
- HAAs

The THMs

Chloroform
Bromodichloromethane
Chlorodibromomethane
Bromoform

CEE 697K Lecture #2
David A. Reckhow
The Haloacetic Acids

Trichloroacetic Acid (TCAA)

Bromodichloroacetic Acid

Chlorodibromoacetic Acid

Tribromoacetic Acid

Dichloroacetic Acid (DCAA)

Bromochloroacetic Acid

Dibromoacetic Acid
Distribution: Variability within a single system

- Example: New Haven Service Area
  - DS model
Sept 11, 1997

22:00

chlorine

3,400 pipes
2,500 junctions

3 MG

Millrock Basins

2.0 mg/L DOC (Treated)

pH 7

1.8 mg/L chlorine dose
Sept 11, 1997
22:00
TTHM
Sept 11, 1997
22:00
HAA6
Single Cell Gel Electrophoresis Genotoxicity Potency
Log Molar Concentration (4 h Exposure)

Not Genotoxic: DCAA, TCAA, BDCAA, Dichloroacetamide,
3,3-Dibromopropenoic Acid,
3-Iodo-3-bromopropenoic Acid, 2,3,3-Tribromopropenoic Acid

DBP Chemical Class

Other DBPs

Haloacetamides

Haloacetonitriles

Halonitromethanes

Halo Acids

Haloacetic Acids

IAA BAA CAA DIAA TBAA DBAA CDBAA

3,3-Dibromo-4-oxopentanoic Acid
2-Bromobutenedioic Acid
2-Iodo-3-bromopropenoic Acid
2,3-Dibromopropenoic Acid

DBNM BDCNM TBNM TCNM BNM BCNM DBCNM DCNM CNM

Bromoacetamide Dibromoacetamide Tribromopyrrole

Bromate EMS + Control

Bromoacetonitrile Dibromoacetonitrile Bromochloroacetonitrile Chloroacetonitrile

3,3-Bromochloro-4-oxopentanoic Acid
Iodoacetonitrile Trichloroacetonitrile Dichloroacetonitrile

BIAA CDBAA

Not Genotoxic: DCAA, TCAA, BDCAA, Dichloroacetamide,
3,3-Dibromopropenoic Acid,
3-Iodo-3-bromopropenoic Acid, 2,3,3-Tribromopropenoic Acid

X Work of Michael Plewa
Univ. of Illinois

CEE 697K Lecture #2

David A. Reckhow
Bromide: THM Formation

Data from: Minear & Bird, 1980
96 hours, pH 7.0
5 mg/L Chlorine Dose
1 mg/L Humic Acid

Bromide Concentration (mg/L)

Percent of TTHM

CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃

96 hours, pH 7.0
5 mg/L Chlorine Dose
1 mg/L Humic Acid
Impact of Bromide on DHAA Formation

CHCl₂COOH

CHClBrCOOH

CHBr₂COOH

pH 7, 25°C, 7 days
25 mg/L chlorine dose
2.9 mg/L TOC

From Pourmoghaddas, 1990
Formation of Brominated THMs

\[ \text{HOCl} + \text{Br}^- \xrightarrow{k} \text{HOBr} + \text{Cl}^- \]
Bromo speciation

Full-scale data (small symbols)
from Weinberg et al., 2002
(All 12 plants)

Lab data (large symbols)
from Hua & Reckhow, 2004

Lines are geometric model

THM Mole Fraction (THM4 only)

CHCl3
CHBrCl2
CHBr2Cl
CHBr3
CHCl3 Lab tests
CHBrCl2 Lab tests
CHBr2CI Lab tests
CHBr3 Lab tests
Case study: chlorine + bromide

- **Observed reaction**: 
  
  \[ \text{HOCl} + \text{Br}^- \xrightarrow{k_2} \text{HOBr} + \text{Cl}^- \]

  - Nucleophilic attack of bromide on oxygen in hypochlorous acid
    - \( k_2 = 2.95 \times 10^3 \text{ M}^{-1}\text{s}^{-1} \) at 25°C
      - Note that HOCl deprotonates at elevated pHs
      - From Farkas et al., 1949

- **Transfer of Cl\(^+\) to form intermediate (BrCl)**
  
  \[ \text{HA} + \text{HOCl} + \text{Br}^- \xrightarrow{k_3} \text{A}^- + \text{H}_2\text{O} + \text{BrCl} \]

  \[ \text{BrCl} + \text{Br}^- \xrightarrow{\text{fast}} \text{Br}_2 + \text{Cl}^- \]

  - From: [Kumar & Margerum, 1987](#)
Background

- Absorbance for monitoring reaction
- Known equilibria

Table I. Absorption Spectral Characteristics of Halogen Species

<table>
<thead>
<tr>
<th>species</th>
<th>$\lambda_{\text{max}}, \text{nm}$</th>
<th>$\epsilon, \text{M}^{-1} \text{cm}^{-1}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OCl}^-$</td>
<td>292</td>
<td>350</td>
<td>a</td>
</tr>
<tr>
<td>$\text{OBr}^-$</td>
<td>329</td>
<td>345</td>
<td>b</td>
</tr>
<tr>
<td>$\text{HOCl}$</td>
<td>230</td>
<td>100</td>
<td>c</td>
</tr>
<tr>
<td>$\text{HBr}$</td>
<td>260</td>
<td>160</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Br}_2$</td>
<td>390</td>
<td>175</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Br}_3^-$</td>
<td>266</td>
<td>35000</td>
<td>b</td>
</tr>
<tr>
<td>$\text{BrCl}_2^-$</td>
<td>380</td>
<td>560</td>
<td>d</td>
</tr>
</tbody>
</table>


Table II. Protonation, Hydrolysis, and Formation Constants

<table>
<thead>
<tr>
<th>equilibrium</th>
<th>$K$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OCl}^- + H^+ \rightleftharpoons \text{HOCl}$</td>
<td>$2.75 \times 10^7$</td>
<td>13</td>
</tr>
<tr>
<td>$\text{OBr}^- + H^+ \rightleftharpoons \text{HBr}$</td>
<td>$5 \times 10^8$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$</td>
<td>$5.2 \times 10^{-7}$</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^-$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>13</td>
</tr>
<tr>
<td>$\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HBr} + \text{H}^+ + \text{Br}^-$</td>
<td>$4.4 \times 10^{-9}$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{Br}_3^- \rightleftharpoons \text{Br}_2 + \text{Br}^-$</td>
<td>$17$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{BrCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HBr} + \text{H}^+ + \text{Cl}^-$</td>
<td>$2.95 \times 10^{-3}$</td>
<td>b</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HO}^-$</td>
<td>$1.82 \times 10^{-14}$</td>
<td>13</td>
</tr>
</tbody>
</table>

Alkaline Experiments

- Pseudo-1\textsuperscript{st} order
- Bromide in great excess
- Slow reactions
- Could be monitored directly by conventional UV spectrophotometer
  - 292 nm peak for hypochlorite (OCl\textsuperscript{-})
- Followed for 4 half-lives
  - Complete from: 1.1 sec – 4 hr
- Plot ln(A\textsubscript{t} - A\textsubscript{∞}) vs time
  - Slope is $k_{\text{obs}}$

### Table III. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorite in Base\textsuperscript{a}

<table>
<thead>
<tr>
<th>[Br\textsuperscript{-}], M</th>
<th>[OH\textsuperscript{-}], M</th>
<th>$k_{\text{obs}}$, s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.450</td>
<td>$(1.90 \pm 0.01) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.350</td>
<td>$(2.09 \pm 0.01) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.300</td>
<td>$(2.41 \pm 0.01) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.250</td>
<td>$(2.65 \pm 0.01) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0972</td>
<td>$(2.12 \pm 0.08) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.030</td>
<td>0.0972</td>
<td>$(2.57 \pm 0.01) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.200</td>
<td>0.0972</td>
<td>$(1.87 \pm 0.01) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.010</td>
<td>0.0493</td>
<td>$(1.731 \pm 0.003) \times 10^{-4}$</td>
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<tr>
<td>0.020</td>
<td>0.0493</td>
<td>$(2.705 \pm 0.004) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.080</td>
<td>0.0493</td>
<td>$(1.28 \pm 0.01) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.0493</td>
<td>$(1.42 \pm 0.01) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.150</td>
<td>0.0493</td>
<td>$(2.037 \pm 0.001) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.200</td>
<td>0.0493</td>
<td>$(2.738 \pm 0.002) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.250</td>
<td>0.0493</td>
<td>$(3.14 \pm 0.01) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0756</td>
<td>$(1.942 \pm 0.002) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0256</td>
<td>$(5.783 \pm 0.003) \times 10^{-4}$</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0106</td>
<td>$(1.278 \pm 0.003) \times 10^{-3}$</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0056</td>
<td>$(2.410 \pm 0.002) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

### Table III. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorite in Buffer\textsuperscript{b}

<table>
<thead>
<tr>
<th>[Br\textsuperscript{-}], M</th>
<th>-log ([H\textsuperscript{+}])</th>
<th>[buffer], M</th>
<th>$k_{\text{obs}}$, s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td>0.050</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.035 ± 0.005</td>
</tr>
<tr>
<td>0.080</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.055 ± 0.002</td>
</tr>
<tr>
<td>0.100</td>
<td>11.01</td>
<td>0.025 (P)</td>
<td>0.066 ± 0.001</td>
</tr>
<tr>
<td>0.120</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.091 ± 0.005</td>
</tr>
<tr>
<td>0.150</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.107 ± 0.005</td>
</tr>
<tr>
<td>0.050</td>
<td>10.97</td>
<td>0.0125 (P)</td>
<td>0.0305 ± 0.0006</td>
</tr>
<tr>
<td>0.050</td>
<td>11.01</td>
<td>0.050 (P)</td>
<td>0.043 ± 0.001</td>
</tr>
<tr>
<td>0.050</td>
<td>11.01</td>
<td>0.0625 (P)</td>
<td>0.045 ± 0.002</td>
</tr>
<tr>
<td>0.100</td>
<td>9.48</td>
<td>0.005 (C)</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>0.100</td>
<td>9.45</td>
<td>0.0125 (C)</td>
<td>1.88 ± 0.03</td>
</tr>
<tr>
<td>0.100</td>
<td>9.46</td>
<td>0.025 (C)</td>
<td>2.05 ± 0.03</td>
</tr>
<tr>
<td>0.100</td>
<td>9.46</td>
<td>0.0375 (C)</td>
<td>2.02 ± 0.08</td>
</tr>
<tr>
<td>0.100</td>
<td>9.48</td>
<td>0.0625 (C)</td>
<td>2.03 ± 0.07</td>
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<tr>
<td>0.100</td>
<td>9.48</td>
<td>0.075 (C)</td>
<td>2.25 ± 0.07</td>
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<td>0.100</td>
<td>9.48</td>
<td>0.100 (C)</td>
<td>2.54 ± 0.07</td>
</tr>
</tbody>
</table>

\textsuperscript{a} [OCl\textsuperscript{-}] = 6.00 × 10\textsuperscript{-4} M, $\mu$ = 0.5 M (NaClO\textsubscript{4}), 25.0 °C, $\lambda$ = 292 nm. \textsuperscript{b} Buffers used are P = phosphate and C = carbonate.
$K_{obs}$ is a linear function of Bromide

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**pH dependency**

Table III. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorite in Base

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<th>[OH⁻], M</th>
<th>k_{obsd} s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.450</td>
<td>(1.90 ± 0.01) × 10⁻⁴</td>
</tr>
<tr>
<td>0.100</td>
<td>0.350</td>
<td>(2.09 ± 0.01) × 10⁻⁴</td>
</tr>
<tr>
<td>0.100</td>
<td>0.300</td>
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<td>0.100</td>
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<tr>
<td>0.030</td>
<td>0.0972</td>
<td>(2.57 ± 0.01) × 10⁻⁴</td>
</tr>
<tr>
<td>0.200</td>
<td>0.0972</td>
<td>(1.87 ± 0.01) × 10⁻³</td>
</tr>
<tr>
<td>0.010</td>
<td>0.0493</td>
<td>(1.731 ± 0.003) × 10⁻⁴</td>
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<td>(2.378 ± 0.002) × 10⁻³</td>
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</tr>
</tbody>
</table>
Overall pH dependence

- How to explain pH effect on 2nd order rate constant?
  - See also, Brezonik, pg 230; figure 4-20

Figure 7. Dependence of the second-order rate constant (in terms of \([OCl^-]_T\) and \([Br^-]\)) on the acidity (without buffer catalysis effects).
Buffer Tests

- Low pH
- High pH

### Table IV. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorous Acid

<table>
<thead>
<tr>
<th>Buffer Solutions</th>
<th>[Br(^-)] M</th>
<th>(-\log [H^+])</th>
<th>[buffer] (_T), M</th>
<th>(k_{\text{obd}}, s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.016 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.035 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>0.080</td>
<td>10.99</td>
<td>0.025 (P)</td>
<td>0.055 ± 0.002</td>
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<td>0.050</td>
<td>10.97</td>
<td>0.0125 (P)</td>
<td>0.0305 ± 0.0006</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>11.01</td>
<td>0.050 (P)</td>
<td>0.043 ± 0.001</td>
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</tr>
<tr>
<td>0.050</td>
<td>11.01</td>
<td>0.0625 (P)</td>
<td>0.045 ± 0.002</td>
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</tr>
<tr>
<td>0.100</td>
<td>9.48</td>
<td>0.005 (C)</td>
<td>1.6 ± 0.1</td>
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<tr>
<td>0.100</td>
<td>9.45</td>
<td>0.0125 (C)</td>
<td>1.88 ± 0.03</td>
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<td>9.46</td>
<td>0.025 (C)</td>
<td>2.05 ± 0.03</td>
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<td>0.100</td>
<td>9.46</td>
<td>0.0375 (C)</td>
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<td>0.100</td>
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<td>0.0625 (C)</td>
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<td>0.075 (C)</td>
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<tr>
<td>0.100</td>
<td>9.48</td>
<td>0.100 (C)</td>
<td>2.54 ± 0.07</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Perchloric Acid Solutions</th>
<th>[Br(^-)] M</th>
<th>(10^4[H^+]) M</th>
<th>(k_{\text{obd}}, s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0020</td>
<td>1.063</td>
<td>6.33 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.003</td>
<td>1.063</td>
<td>9.75 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>0.004</td>
<td>1.063</td>
<td>12.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>1.063</td>
<td>16.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>1.063</td>
<td>31.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.020</td>
<td>1.063</td>
<td>63.2 ± 0.7</td>
<td></td>
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<td>0.005</td>
<td>1.59</td>
<td>19.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>2.66</td>
<td>26.4 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>5.84</td>
<td>45.1 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>11.16</td>
<td>81 ± 2(^c)</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>21.79</td>
<td>154 ± 2(^c)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) [OCl\(^-\)] = 6.00 × 10\(^{-4}\) M, \(\mu = 0.5\) M (NaClO\(_4\)), 25.0 °C, \(\lambda = 292\) nm. \(^b\) Buffers used are P = phosphate and C = carbonate.

\(^c\) Rate constants are corrected for mixing.\(^{12}\)
Buffer Effect

- Proposed dependence on HA

\[ k_{obs} = (k_0 + k_H[H^+] + k_{HA}[HA])[Br^-] \]

\[ [HA] = \alpha_0 C_T = \frac{1}{K_a[H^+]} + 1 \]

\[ C_T = \frac{[H^+] C_T}{K_a + [H^+]} \]

\[ \left( \frac{k_{obs}}{[Br^-]} \right) - k_0 = k_H + k_{HA} \left( \frac{[buffer]_T}{K_a + [H^+]} \right) \]
High pH only

\[ k_{obs} = \left(k_0 + k_H[H^+] + k_{HA}[HA]\right)[Br^-] \]

\[ -\frac{d[OCl^-]}{dt} = \left(k_0 + k_H[H^+] + k_{HA}[HA]\right)[OCl^-][Br^-] \]

More generally

\[ -\frac{d[Cl(+I)]}{dt} = \left(k_0[OCl^-] + k_{HOC}[HOCl] + k_{HA}[HA][OCl^-]\right)[Br^-] \]
Acidic Experiments

- Pseudo-1\textsuperscript{st} order
  - Bromide in great excess
- Fast reactions
  - Required high-speed setup
    - Stopped-flow spectrophotometer
  - Could monitor 2º product
    - 266 nm peak for tribromide (Br\textsubscript{3}\textsuperscript{-})
  - Followed for 4 half-lives
    - Complete from 0.40-0.01 sec
  - Plot \( \ln(A_t - A_\infty) \) vs time
    - Slope is \( k_{\text{obs}} \)

<table>
<thead>
<tr>
<th>Buffer Solutions\textsuperscript{b}</th>
<th>( [\text{Br}^{-}] ), M</th>
<th>-log [H\textsuperscript{+}]</th>
<th>[buffer], M</th>
<th>( k_{\text{obs}}, \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>5.23</td>
<td>0.05 (A)</td>
<td>24.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.020</td>
<td>5.22</td>
<td>0.05 (A)</td>
<td>46.1 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>5.22</td>
<td>0.05 (A)</td>
<td>115 ± 4\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>5.30</td>
<td>0.05 (A)</td>
<td>245 ± 4\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>4.78</td>
<td>0.01 (A)</td>
<td>10.83 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>4.78</td>
<td>0.02 (A)</td>
<td>11.27 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>4.78</td>
<td>0.05 (A)</td>
<td>12.58 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>4.78</td>
<td>0.10 (A)</td>
<td>14.65 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>4.78</td>
<td>0.20 (A)</td>
<td>18.8 ± 0.8</td>
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</tr>
<tr>
<td>0.0050</td>
<td>2.90</td>
<td>0.01 (C)</td>
<td>16.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>2.87</td>
<td>0.025 (C)</td>
<td>19.44 ± 0.08</td>
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</tr>
<tr>
<td>0.0050</td>
<td>2.85</td>
<td>0.050 (C)</td>
<td>22.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>2.84</td>
<td>0.100 (C)</td>
<td>27.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>2.83</td>
<td>0.125 (C)</td>
<td>30.0 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Perchloric Acid Solutions</th>
<th>( [\text{Br}^{-}] ), M</th>
<th>( 10^3[H\textsuperscript{+}], \text{M} )</th>
<th>( k_{\text{obs}}, \text{s}^{-1} )</th>
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<tr>
<td>0.005</td>
<td>21.79</td>
<td>154 ± 2\textsuperscript{c}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} [HOCI] = (0.5-6.00) \times 10^{-4} \text{M}, \mu = 0.5 \text{ M (NaClO\textsubscript{2})}, 25.0 \degree \text{C}, \lambda = 266 \text{ or } 392 \text{ nm.} \textsuperscript{b} Buffers used are A = acetic acid and C = chloroacetic acid. \textsuperscript{c} Rate constants are corrected for mixing.\textsuperscript{12}
Stopped-flow

- **Principle**

- **Commercial instruments**

- **Limitations**
  - Correct for slow mixing speed ($k_m$)
  - For Durrum instrument: $k_m = 1700$ s$^{-1}$

\[
k_{obs} = \frac{k'_{obs}}{1 - (k'_{obs}/k_m)}
\]
$K_{obs}$ is still linear with Br-

- No difference in mechanism?

Figure 4. Pseudo-first-order rate constants (25.0 °C, $\mu = 0.50$) for the reaction of HOCl and Br$: (A) [H^+] = 1.063 \times 10^{-3}$ M; (B) $-\log [H^+] = 5.22$ (0.05 M acetate buffer).
Acidic data: impact of acids

☐ General and specific acid

Figure 5. Dependence of the second-order rate constant (HOCl + Br⁻) on HClO₄ concentration.

Figure 6. Dependence of the second-order rate constant (HOCl + Br⁻) on the concentration of general acids.
Overall pH dependence

- Three effective zones

- See also, Brezonik, pg 230; figure 4-20

\[
\text{H}^+ + \text{HOCl} \rightarrow \text{HOCI}
\]

**Figure 7.** Dependence of the second-order rate constant (in terms of \([\text{OCI}^-]_T\) and \([\text{Br}^-]\)) on the acidity (without buffer catalysis effects).
**Catalysis: comparison with pKa**

- **Bronsted catalysis**

\[ k_{HA} = G_A(K_a)^\alpha \]

- Indicates that HA engages in greater donation of proton to OCl\(^-\) than to HOCl

<table>
<thead>
<tr>
<th>HA</th>
<th>( pK_a )</th>
<th>( k_{OC\ell} )</th>
<th>( k_{HOCl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{O}^+ )</td>
<td>1.72 ( ^b )</td>
<td>( 3.65 \pm 0.05 \times 10^{10} )</td>
<td>( 1.32 \pm 0.03 \times 10^6 )</td>
</tr>
<tr>
<td>( \text{ClCH}_2\text{COOH} )</td>
<td>2.6 ( ^c )</td>
<td>( 6.11 \pm 0.34 \times 10^{4} )</td>
<td>( 2.09 \pm 0.01 \times 10^4 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COOH} )</td>
<td>4.6 ( ^d )</td>
<td>( 1.25 \pm 0.15 \times 10^{2} )</td>
<td>( 8.9 \pm 1.3 )</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>9.8 ( ^e )</td>
<td>( 8.9 \pm 1.3 )</td>
<td>( 27.9 \pm 5.5 )</td>
</tr>
<tr>
<td>( \text{HPO}_4^{2-} )</td>
<td>11.3 ( ^f )</td>
<td>( 1.6 \pm 0.3 \times 10^{-5} )</td>
<td>( 27.9 \pm 5.5 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>15.52 ( ^g )</td>
<td>( 1.6 \pm 0.3 \times 10^{-5} )</td>
<td>( 27.9 \pm 5.5 )</td>
</tr>
</tbody>
</table>

\[ \alpha = 0.75 \] \quad \[ \alpha = 0.27 \]

**Figure 8.** Bronsted plots for the general-acid-assisted reactions of OCl\(^-\) and Br\(^-\) and of HOCl and Br\(^-\).
Mechanisms

- Proposed mechanism

- Alternative
  - Less likely
Temperature: Arrhenius Equation

- Arrhenius Equation
  \[ k = A e^{-\frac{E_a}{RT}} \]
  - Where \( R \) is the universal gas constant
  \[ R = 8.3145 \frac{J}{mol \cdot K} \]

- Transforms to:
  \[ \ln(k_T) = \ln(A) - \left( \frac{E_a}{R} \right) \frac{1}{T} \]
  \[ k_{T_b} = k_{T_a} e^{-\frac{E_a}{R} \left( \frac{1}{T_b} - \frac{1}{T_a} \right)} \]
Pizza Kinetics

- Leeson, 1999
  - What are the kinetics of pizza spoilage?
  - Do they conform to Arrhenius?

J. Chem Ed., 76:4:504-505
Pizza II

- Arrhenius plot
  - $t \sim k$

Figure 1. Arrhenius plot of the storage time data provided on the frozen pizza package.
Lab Project Example Data #1

0.1 M NaOH

What is the Abs_{inf}?
Lab Project Example Data #II

0.1 M NaOH

Set \( A_{\text{inf}} = 0.085 \)
Lab Project Example Data #III

- **0.05 M NaOH**

![Absorbance at 292 nm (cm⁻¹) vs Time (min) graph]

Set $\text{Abs}_{\text{inf}} = ?$
0.05 M NaOH

Set $Abs_{inf} = 0.094$

Maybe too high?
Downward curvature
0.05 M NaOH

Set $A_{\text{inf}} = 0.092$

Looks better, except for final data where relative error is high. Use only earlier data?
Lab Project Example Data #VI

☐ 0.05 M NaOH

Set $A_{\text{inf}} = 0.092$

Using only earlier data where relative error is low, Better linearity and estimate of $k_{\text{obs}}$?
Related systems

<table>
<thead>
<tr>
<th>reactants</th>
<th>$k$, M$^{-2}$ s$^{-1}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ + \text{OCl}^- + \text{Br}^-$</td>
<td>$3.65 \times 10^{10}$</td>
<td>a</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{OCl}^- + \text{I}^-$</td>
<td>$4.4 \times 10^{15}$</td>
<td>b</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HOCl} + \text{Cl}^-$</td>
<td>$2.8 \times 10^{4}$</td>
<td>c</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HOCl} + \text{Br}^-$</td>
<td>$1.3 \times 10^{6}$</td>
<td>a</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HOBr} + \text{Br}^-$</td>
<td>$1.6 \times 10^{10}$</td>
<td>d</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HOI} + \text{I}^-$</td>
<td>$4.4 \times 10^{12}$</td>
<td>d</td>
</tr>
</tbody>
</table>

*This work.  b Reference 2.  c Reference 13.  d Reference 5.*

\[ \text{H}_2\text{O}_2 + \text{Br}^- \xrightarrow{2.3 \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}} \text{OH}^- + \text{HOBr} \quad (22) \]

\[ \text{H}^+ + \text{H}_2\text{O}_2 + \text{Br}^- \xrightarrow{1.4 \times 10^{-2} \text{ M}^{-2} \text{s}^{-1}} \text{H}_2\text{O} + \text{HOBr} \quad (23) \]
Introduction: Simple Rate Laws

Brezonik, pp.31-39
Variable Kinetic Order

- Any reaction order, except $n=1$

\[
\frac{dc}{dt} = -k_n c^n
\]

\[
\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)k_n t
\]

\[
c = c_o \frac{1}{\left[1 + (n-1)k_n c_o^{n-1} t\right]^{1/(n-1)}}
\]
Half-lives

- Time required for initial concentration to drop to half, i.e., \( c = 0.5c_0 \)
  - For a zero order reaction:
    \[
    c = c_0 - kt
    \]
    \[
    0.5c_0 = c_0 - kt_{1/2}
    \]
  - For a first order reaction:
    \[
    c = c_0 e^{-kt}
    \]
    \[
    0.5c_0 = c_0 e^{-kt_{1/2}}
    \]
    \[
    t_{1/2} = \frac{\ln(2)}{k}
    \]
    \[
    \approx \frac{0.693}{k}
    \]
Example: Benzyl Chloride

- **Use:**
  - Manufacture of benzyl compounds, perfumes, pharmaceuticals, dyes, resins, floor tiles

- **Toxicity**
  - Intensely irritating to skin, eyes, large doses can cause CNS depression

- **Emission**
  - 45,000 lb/yr

- **Fate**
  - Benzyl chloride undergoes slow degradation in water to benzyl alcohol
Benzyl chloride II

- Benzyl chloride to benzyl alcohol

\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{H}_2\text{O} \\
\text{HCl} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

- Nucleophilic substitution
  - \( S_{N\,1} \) or \( S_{N\,2} \)?
  - How to distinguish?
  - Salt effects

Sources:
- Schwarzenbach et al., 1993, Env. Organic Chemistry

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( 0.1^\circ\text{C} )</th>
<th>( 25^\circ\text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>( 0.042 \times 10^{-5} , \text{s}^{-1} )</td>
<td>( 1.38 \times 10^{-5} , \text{s}^{-1} )</td>
</tr>
<tr>
<td>( T_{1/2} )</td>
<td>19.1 d</td>
<td>0.58 d</td>
</tr>
</tbody>
</table>

\[
\frac{d[A]}{dt} = -k[A]
\]
Mixed Second Order

- Two different reactants
  \[ \text{rate} = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{v_A} \frac{d[A]}{dt} = \]
  \[
  \frac{dx}{dt} = k_2 [A][B] = k_2 ([A]_0 - x) ([B]_0 - x)
  \]

- Initial Concentrations are different; \([A]_0 \neq [B]_0\)
  - The integrated form is:
    \[
    \frac{1}{[A]_0 - [B]_0} \ln \left( \frac{[B]_0 [A]}{[A]_0 [B]} \right) = k_2 t
    \]
  - Which can be expressed as:
    \[
    \log \left( \frac{[A]}{[B]} \right) = 0.43k_2 ([A]_0 - [B]_0)t - \log \left( \frac{[B]_0}{[A]_0} \right)
    \]
Mixed Second Order

Initial Concentrations are the same; \([A]_0 = [B]_0\)

\[
\frac{dx}{dt} = k_2[A][A]
\]

\[
= k_2 ([A]_0 - x)([A]_0 - x)
\]

The integrated form is:

\[
\int \frac{d[A]}{[A]^2} = \int v_A k_2 dt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = 2k_2 t
\]

Which can be integrated:
Pseudo first order

For most reactions, \( n = 1 \) for each of two different reactants, thus a second-order overall reaction

\[
A + B \xrightarrow{k_2} \text{products}
\]

Many of these will have one reactant in great excess (e.g., B)

These become “pseudo-1st order in the limiting reactant, as the reactant in excess really doesn’t change in concentration

\[
k = 3.9 \times 10^{-5} \text{ L mg}^{-1} \text{ min}^{-1}
\]

\[
\frac{dc}{dt} = -k_2 c_A^1 c_B^1
\]
Since $C_2$ changes little from its initial 820 mg/L, it is more interesting to focus on $C_A$.

- $C_A$ exhibits simple 1st order decay, called pseudo-1st order.

The pseudo-1st order rate constant is just the “observed rate” or $k_{obs}$.
How long will it take for ozone (4.8 mg/L dose) to reduce the concentration of naphthalene by 99%?

- Used in moth balls and as a chemical intermediate
- 2nd order reaction; \( k_2 = 3000 \, M^{-1}s^{-1} \)
  - Table 1 in Hoigne & Bader, 1983 [Wat. Res. 17:2:173]

Industrial WW with 0.1 mM naphthalene

- Both reactants are at same (0.1 mM) concentration
  - Therefore, this reduces to a simple 2nd order reaction

\[
\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t
\]

\[
\frac{1}{10^{-6}} = \frac{1}{10^{-4}} + 3000 t
\]

\[
3000 t = 990,000
\]

\[
t = 330 \, \text{sec}
\]

\[
= 5.5 \, \text{min}
\]
Contaminated river water (0.001 mM)

Now ozone is in great molar excess, so this is a pseudo-1\textsuperscript{st} order reaction

\[
[A] = [A]_0 e^{-k_2[B]_0 t}
\]

\[
\ln\left(\frac{[A]}{[A]_0}\right) = -k_2[B]_0 t
\]

\[
\ln\left(\frac{10^{-8}}{10^{-6}}\right) = -3000(10^{-4})t
\]

\[-4.605 = -0.3t\]

\[t = 15.4\ \text{sec}\]
Molecularity of three: 3rd order kinetics

- Quite improbably, but sometimes happens
  - Three different reactants
    \[ A + B + C \xrightarrow{k_3} \text{products} \]
    \[ \frac{dx}{dt} = k_3[A][B][C] = k_3([A]_0 - x)([B]_0 - x)([C]_0 - x) \]
    - Complicated integrated form exists
  - Two different reactants
    \[ 2A + B \xrightarrow{k_3} \text{products} \]
    \[ \frac{dx}{dt} = k_3[A]^2[B] = k_3([A]_0 - 2x)^2([B]_0 - x) \]
    - Integrated form:
    \[ \frac{([A]_0 - [A])(2[B]_0 - [A]_0)}{[A]_0[A]} + \ln \frac{[B]_0[A]}{[A]_0[B]} = (2[B]_0 - [A]_0)^2 k_3 t \]
Only one reactant or Initial Concentrations are the same

\[ \frac{dx}{dt} = k_3[A][A][A] \]
\[ = k_3([A]_0 - x)([A]_0 - x)([A]_0 - x) \]

- The integrated form is:
  \[ \int \frac{d[A]}{[A]^3} = \int v_A k_3 \, dt \]
  \[ \frac{1}{[A]^2} - \frac{1}{[A]_0^2} = -2v_A k_3 t = 6k_3 t \]

- Which can be integrated:
  \[ \frac{1}{[A]^2} = 6k_3 t + \frac{1}{[A]_0^2} \]
Pseudo-2nd order reactions

- When one of the reactants has a fixed concentration
  - E.g., present in excess or buffered, or acts catalytically
- Like a regular 2nd order reaction with two reactants but observed constant is fundamental rate constant times concentration of the 3rd reactant.

The integrated form:

\[
\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]} = k_3[C]t - k_{obs}
\]
Example: chlorate formation

- Formation of chlorate in concentrated hypochlorite solutions
  - Concern: chlorate is toxic
    - MCLG=0.2 mg/L
  - Stoichiometry
    $$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$
    - Is this 3rd order? Be skeptical!
  - Observed kinetics
    $$\frac{d[ClO_3^-]}{dt} = k_{obs} [OCl^-]^2$$
    - So, why is it 2nd order?
Answer: this is a reaction pathway composed of two elementary reactions

- **Step #1** $2\text{OCI}^- \xrightarrow{\text{slow}} \text{ClO}_2^- + \text{Cl}^-$
- **Step #2** $\text{OCI}^- + \text{ClO}_2^- \xrightarrow{\text{fast}} \text{ClO}_3^- + \text{Cl}^-$

- In multi-step reactions such as these, we say that
  - the overall rate is determined by the slowest step
    - Called the “rate-limiting step” or RLS
  - **Rate law is written based on the RLS**
    - Subsequent steps are ignored
    - Prior steps are incorporated as they determine the concentrations of the RLS reactants

Homework #2 is based on this reaction
Reversible reaction kinetics

For a general reversible reaction:

\[ aA + bB \leftrightarrow pP + qQ \]

And the rate law must consider both forward and reverse reactions:

\[ \text{rate} = k_f C_A^a C_B^b - k_r C_P^p C_Q^q \]

where,

- \( k_f \) = forward rate constant, [units depend on \( a \) and \( b \)]
- \( k_b \) or \( k_r \) = backward rate constant, [units depend on \( a \) and \( b \)]
- \( C_P \) = concentration of product species \( P \), [moles/liter]
- \( C_Q \) = concentration of product species \( Q \), [moles/liter]
- \( p \) = stoichiometric coefficient of species \( P \)
- \( q \) = stoichiometric coefficient of species \( Q \)
Reversible 1st order reactions

- **Kinetic law**
  \[
  \frac{d[B]}{dt} = k_1[A] - k_2[B]
  \]

- **Eventually the reaction slows and,**
  - Reactant concentrations approach the equilibrium values
    \[
    \frac{d[B]}{dt} = 0 = k_1[A] - k_2[B]
    \]
    \[
    \frac{[B]}{[A]} = \frac{k_1}{k_2} \equiv K_{eq}
    \]

- **Stumm & Morgan**
  - Fig. 2.10
  - Pg. 69
  - Reversible Reaction
    - \[ A \xrightleftharpoons[k_2]{k_1} B \]
    - \[ [A]_0 = 4.0 \times 10^{-3} \text{ M} \]
    - \[ [B]_0 = 0.0 \text{ M} \]

---

**Figure 2.10.** Single reversible reaction.

**Note:**
- Case 1
  - \( k_1 = 0.15 \text{ day}^{-1} \)
  - \( k_2 = 0.05 \text{ day}^{-1} \)
  - \( K = \frac{k_1}{k_2} = 3.0 \)
Solution to non-equilibrium reaction period

See Brezonik, pg 37-38 for details

\[
[A] = \frac{1}{k^*} [A]_0 \left\{ k_r + k_f e^{-k^*_t} \right\}
\]

Where \( k^* = k_f + k_r \)

And:

\[
\frac{[A] - [A]_{equ}}{[A] - [A]_{equ}} = e^{-k^*_t}
\]

Linearized version

Where:

\[
\frac{k_f}{k_r} (= K_{equ}) = \frac{[P]_{equ}}{[A]_{equ}}
\]