From SURE to GREF through Bourbon St.: Great Years!!
Halogenated Hydrocarbons and Halomethanediols: A Study of the Atmospheric Implications of Proposed Replacements for Chlorofluorocarbons (CFCs)

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Department of Chemistry
Purdue University
Outline

✓ Atmospheric Chemistry
✓ Research Interests and Approach
✓ Taste of My Research
   ✓ Atmospheric Oxidation Mechanisms of Bromoethane and Bromopropane
   ✓ Structure and Vibrational Spectra of Bromine Reservoir Species from the Atmospheric Oxidations of Bromoethane and Bromopropane
   ✓ Atmospheric Modeling of Bromopropane
   ✓ Methylhydroperoxide (CH₃OOH)
   ✓ Conformational Topography of Halomethanediols XCH(OH)₂ (X = H,F,Cl)

✓ Conclusions
Atmospheric Layers

- Variations are due to alterations in the chemical and physical nature of the atmosphere with altitude.
- Troposphere contains about 75% of the total mass of the atmosphere.
- Stratosphere is also called the ozone layer.
Atmospheric Chemistry

• Study of the atmosphere and its chemistry
  – Experimental studies of atmospheric processes
  – *Ab initio* calculations
  – Climate modeling
Halogenated Compounds

• CFCs, chlorinated and brominated compounds
• Potential environmental effects
  – Tropospheric and Stratospheric chemistry
• Replacement
Research Interest & Approach

• Gas phase reactions involving halogens that can be responsible for the catalysis of ozone depletion.
  – Chemical removal mechanisms and energetics of gas phase reactions involving halogens.
  – Characterization of the potential energy surface (PES) of the proposed mechanisms for the degradation of the halogenated hydrocarbons and their by-products.
• High level molecular orbital *ab initio* calculations
<table>
<thead>
<tr>
<th>Method</th>
<th>Method Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Best for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab Initio</td>
<td>• uses quantum physics • mathematically rigorous, no empirical parameters • uses approximation extensively</td>
<td>• useful for a broad range of systems • does not depend on experimental data • capable of calculating transition states and excited states</td>
<td>• computationally expensive</td>
<td>• small systems (tens of atoms) • systems involving electronic transitions • molecules or systems without available experimental data (&quot;new&quot; chemistry) • systems requiring rigorous accuracy</td>
</tr>
<tr>
<td>Semi-Empirical</td>
<td>• uses quantum physics • uses experimentally derived empirical parameters • uses approximation extensively</td>
<td>• less demanding computationally than <em>ab initio</em> methods • capable of calculating transition states and excited states</td>
<td>• requires experimental data (or data from <em>ab initio</em>) for parameters • less rigorous than <em>ab initio</em> methods</td>
<td>• medium-sized systems (hundreds of atoms) • systems involving electronic transitions</td>
</tr>
<tr>
<td>Molecular Mechanics</td>
<td>• uses classical physics • relies on force-field with embedded empirical parameters</td>
<td>• Computationally least intensive - fast and useful with limited computer resources • can be used for molecules as large as enzymes</td>
<td>• particular force field applicable only for a limited class of molecules • does not calculate electronic properties • requires experimental data (or data from <em>ab initio</em>) for parameters</td>
<td>• large systems (thousands of atoms) • systems or processes with no breaking or forming of bonds</td>
</tr>
</tbody>
</table>
Ab initio Calculations

• Software
  – Gaussian 03

• Geometry optimizations and frequency calculations
  – Levels of theory and basis sets

• Single point energy calculations
Levels of Theory

• Hartree-Fock (HF)
  – Simplest and least expensive ab initio wavefunction

• Møller-Plesset (MP) Perturbation Theory
  – Second-order Møller-Plesset (MP2) perturbation theory
  – Least-expensive traditional method including electron correlation

• CCSD(T)
  – Coupled-cluster, singles and doubles with approximate triples
  – Most popular high-level (i.e., lots of electron correlation) method
  – Very expensive (e.g. bromopropane’s TS)
  – Describes a calculation that gives the same energy for two atoms (or molecular fragments) separated by a large distance as is obtained from summing the energies for the atoms (or molecular fragments) computed separately
Atmospheric Degradation of Bromoethane
PES for the reaction of Bromoethane + OH / Cl using CCSD(T)/6-311++G(2df,2p)

\[
\begin{align*}
[\text{BrCH}_2\text{CH}_3 + \text{OH} & \rightarrow \text{BrCH}_2\text{CH}_2 + \text{H}_2\text{O}]^+ \quad 20.70 \\
\text{H}_2\text{O} & \quad 20.40 \\
[\text{BrCH}_2\text{CH}_3 + \text{Cl} & \rightarrow \text{BrCH}_2\text{CH}_2 + \text{HCl}]^+ \quad 2.37 \\
\text{HCl} & \quad 2.49 \\
[\text{BrCH}_2\text{CH}_3 + \text{Cl} & \rightarrow \text{BrCH}_3 + \text{HCl}]^+ \quad 4.86 \\
\text{Cl} & \quad 1.76 \\
[\text{BrCH}_2\text{CH}_3 + \text{Cl} & \rightarrow \text{BrCH}_3 + \text{HCl}]^+ \quad 3.07 \\
\text{Cl} & \quad 1.31
\end{align*}
\]
Atmospheric Degradation of Bromoethane
What is Bromopropane?

- Short-lived halocarbon
- Possible replacement for CFCs
- Toxic effects
  - Male and female reproductive and hematopoietic organs
  - Neurotoxicity
Why Bromopropane?

• Catalytic ozone destruction
• Release of Br atoms
• Atmospheric lifetime
• Ozone Depletion Potentials (ODP)
Atmospheric Degradation of Bromopropane
PES for the reaction of Bromopropane + radical OH using CCSD(T)/6-311++G(2df,2p)
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PES for the reaction of Bromopropane + radical OH using CCSD(T)/6-311++G(2df,2p)
Atmospheric Degradation of Bromopropane
Structure and Vibrational Spectra of Bromine Reservoir Species from the Atmospheric Oxidations of Bromoethane and Bromopropane

Table 1. Rotational Constants (MHz) of the Reservoir Species

<table>
<thead>
<tr>
<th>Species</th>
<th>MP2/6-31G(d)</th>
<th>QCISD/6-31G(d)</th>
<th>B3LYP/6-31++G(3df,3pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Aldehydes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC(O)H</td>
<td>287167</td>
<td>37972</td>
<td>33538</td>
</tr>
<tr>
<td>BrC(O)H</td>
<td>73742</td>
<td>3982</td>
<td>3778</td>
</tr>
<tr>
<td>HC(O)CH₃</td>
<td>56528</td>
<td>10092</td>
<td>9043</td>
</tr>
<tr>
<td>BrCH₂C(O)H</td>
<td>24018</td>
<td>1925</td>
<td>1859</td>
</tr>
<tr>
<td>BrCH₂CH₂C(O)H</td>
<td>20333</td>
<td>974</td>
<td>966</td>
</tr>
<tr>
<td>Ketones</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BrC(O)CH₃</td>
<td>9985</td>
<td>2980</td>
<td>2328</td>
</tr>
<tr>
<td>BrC(O)CH₂CH₃</td>
<td>8274</td>
<td>1545</td>
<td>1323</td>
</tr>
<tr>
<td>BrCH₂C(O)CH₃</td>
<td>7421</td>
<td>1603</td>
<td>1422</td>
</tr>
</tbody>
</table>

Among molecules with the same amount of heavy atoms, aldehydes will have higher values for A than ketones; whereas the inverse is true for B and C.
Theoretical IR Spectra for Aldehydes

Symmetric CO stretch ~1800 cm\(^{-1}\)
CBr stretch ~ 600 cm\(^{-1}\)
Theoretical IR Spectra for Ketones

Symmetric CO stretch $\sim 1800$ cm$^{-1}$
CBr stretch $\sim 600$ cm$^{-1}$
To submit...

- Theoretical calculations are completed!
- Obtain FTIR of at least 2 of the brominated species (i.e., bromoacetone and propionyl bromide)
- Literature values of HC(O)H and HC(O)CH₃
Hmm.
Wonder what became of yesterday's smoke.
Atmospheric Degradation of Bromopropane
2D Atmospheric Modeling

• MOZART2-2D
  – 2D: less computationally expensive
  – All thermal and photochemical reactions
    • Rate constants: JPL and Multiwell
    • Thermal: Arrhenius values
    • Photochemical: Absorption cross sections
    • Analogous treatment
Table 1. Estimates of Reaction Rate Constants and Mass Accommodation Coefficients for the Degradation Chemistry of n-Propyl Bromide

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant in Appropriate Units or Analogous Compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂CH₂Br + OH → CH₂CH₂CH₂BrO₂ + H₂O</td>
<td>4.0 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1995] distribution; Nelson et al. [1997] total</td>
</tr>
<tr>
<td>CH₂CH₂CH₂Br + OH → CH₂CH₂CH₂Br + H₂O</td>
<td>1.8 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1995] for T dependence; Adam et al. [1997] for preexponential factors</td>
</tr>
<tr>
<td>CH₂CH₂CH₂Br + OH → 2CH₂CH₂CH₂Br + H₂O</td>
<td>7.2 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>RCHO₂ + NO → RCHO + NO₂</td>
<td>3.9 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)O₂ + NO → XCO + CO₂ + NO₂</td>
<td>3.6 × 10⁻¹⁲ cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XO₂ + NO₂ + M → XCO(O)OOH + M</td>
<td>1.2 × 10⁻¹⁰ cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)O₂ + NO + M → XCO(O)OOH + M</td>
<td>1.2 × 10⁻¹⁰ cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
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<tr>
<td>XCO(O)O₂ → XCO + NO₂</td>
<td>3.6 × 10⁻¹³ cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)OOH + OH → RCHO + OH + H₂O</td>
<td>2.66 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)OH + OH → XCO + CO₂ + H₂O</td>
<td>2.66 × 10⁻¹² cm³ (300°C)</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>OH + XCHO, RCHO, CH₂OCHO, CH₂OCHO, XCO(O)O₂, CH₂OCHO,</td>
<td>as well as OH + XCO(O) + XOH as XCO(O)OH at ( \beta = 0.75 ) along X</td>
<td>Adam et al. [1997]</td>
</tr>
</tbody>
</table>

Photolysis reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant in Appropriate Units or Analogous Compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂CO + hv</td>
<td>CH₂CH₂CHO + hv</td>
<td>Gerczyk et al. [1998]</td>
</tr>
<tr>
<td>CH₂CH₂CO + hv, CHOCH₂CH₂Br + hv, CHOCH₂CH₂Br + hv</td>
<td>CH₂CH₂CHO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>CH₂CH₂Br + hv, CH₂CH₂CHO + hv</td>
<td>CH₂CH₂CHO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>CH₂CH₂Br + hv, CH₂CH₂CHO + hv</td>
<td>CH₂CH₂CHO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)O₂ + hv, CH₂CO + hv, ZCO(O)CO + CH₂Br + hv</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)O₂ + hv, CH₂CO + hv</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>CH₂CO + hv, XCO(O)O₂ + hv except when X</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
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<td>CH₂CO + hv, XCO(O)O₂ + hv except when X</td>
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Mass accommodation coefficients for “n-based” reactant

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<td>CH₂CO + hv, CH₂CO + hv</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>or CH₂CO + hv</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
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<td>CH₂CO + hv</td>
<td>CH₂CO + hv</td>
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<tr>
<td>or CH₂CO + hv</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
<tr>
<td>XCO(O)OH</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
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<tr>
<td>XCO(O)OH</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
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<tr>
<td>XCO(O)OH</td>
<td>CH₂CO + hv</td>
<td>Adam et al. [1997]</td>
</tr>
</tbody>
</table>

Additional notes:
- \( k_{ij} \) and \( k_{ji} \) are rate constants for second-order reactions or third-order reactions (including the \( k_{ij}M \) low-pressure term). \( T \) is the temperature in K, \( M \) is in molecules cm⁻³.
- An additional O₂ not shown on the left side reacts instantly with the initially formed radical to produce HO₂ (see section 3.7).
- “Three-body” rate constant given by the Treanor expression, \( f = \frac{k_{ij}M}{k_{ij}(k_{ij} + k_{ji})} \) with \( f = \log_{10}(f) + 1 + \log_{10}(k_{ij}M(k_{ij} + k_{ji})) \).
3D Atmospheric Modeling

- MOZART2-3D
  - 3D: much more computationally expensive
  - Minimum amounts of thermal and photochemical reactions
Conformational Topography of Halomethanediols $XCH(OH)_{2}$ ($X = H,F,Cl$)

• Long story short…
  – $CF_3CHXY$ (where $X, Y = H, F$ or $Cl$)
    • Proposed CFC alternative
  – Degrades to carbonyl compounds: $HXCO$
  – $HXCO + H_2O \rightarrow XCH(OH)_{2}$

• Methodology: *Ab initio* calculations!!
  – 2 optimizations (HF & MP2) + 3 SP calculations
  – $CCSD(T)/cc$-$PVTZ//MP2/6-311+G(d,p)$
CH$_2$(OH)$_2$

ap (antiperiplanar), sp (synperiplanar), ac (anticlinal), sc (synclinal)
ClCH(OH)$_2$
It is nice to work while you TRAVEL!!!
The purpose of the studies was to generate the spectra of the vibration overtone states of the methyl hydroperoxide, examine the dissociation spectral profile and characterization of the product state distribution.

- Synthesize CH₃OOH
- Lasers alignment
- SPECTRA!!

Vibrational mediated photodissociation was used to study this organic peroxide’s photochemistry. The studies were performed by exciting the ν = 2 and 3 OH vibration modes. Dissociation light in the visible region was used to initiate dissociation, which was followed by probing the dissociation OH fragment using laser induced fluorescence (LIF).

- Data Analysis
- Simulations
$2\nu_{\text{OH}}$
$3v_{\text{OH}}$
Conclusions

• I love to work while I am traveling!!
• Graduate school + GREF = Great experience!!
• When it does not work…
  – Don’t get discouraged, but also be realistic…
• Experience
  – Computational chemistry
  – Laser Induced Fluorescence (LIF)
  – Atmospheric modeling
• Missing = Post Doc
  – In situ studies of halogenated compounds in the marine environment…marine biological activity is the major source of brominated compounds…
Acknowledgments

• Dr. Joseph S. Francisco and Francisco Research Group (Purdue University)
• Graduate Research Environmental Fellowship
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• Dr. Ian Williams and Williams Research Group (Bath University)
• Dr. Donald Wuebbles and Wuebbles Research Group (UIUC)
• Rose and Alex for…
FOOD

ANYONE??!!

QUESTIONS?? =)