Chemistry in Action: Space Shuttle Fuel Chemistry

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Outline

- **Student’s Perception of Chemistry**

- **Role In Science and Technology**
  - Traditional Areas
  - Recent and Emerging Technologies

- **Space Shuttle-Atmospheric Interactions**

- **New Hypergolic Fuels**

- **Closing Remarks**
  - Acknowledgements
  - Career in the Government
  - Web Resources
Student’s Perception of Chemistry

- It is too Hard! Too Much Math! I do not Like Cooking!
- It is Only for Academicians!
- What use is it for Getting Good Jobs?
- I Also Thought This! Until I met my Mentor, Ian Worthington

- **Definition:**
  - Study of MATTER and the Changes That Take Place With That MATTER

- **Importance:**
  - MATTER is Everywhere! Therefore it Matters a lot!
    - To Understand the Energetics of Breaking and Making Chemical Bonds
    - We Seek Microscopic Explanation of Macroscopic Changes we Experience
Role in Science and Technology

TRADITIONAL CHEMISTRY

- Organic
- Physical
- Analytical
- Inorganic
- Quantum
- Petrochemicals
- Pharmaceuticals
- Chemical Physics
- Chemical Engineering
- Electro Chemistry
- Math Nerd
- ?...

RECENT CHEMISTRY

- Atmospheric Chemistry
- Combustion Chemistry
- Biochemistry
- Geochemistry
- Astrochemistry
- Nuclear Chemistry
- Air Pollution
- Ozone Hole
- Fuels, Energy Production
- DNA Gene Mapping
- Volcanoes
- Earthquakes
- Space Matter
- Energy/Weapons
- ?...

EMERGING CHEMISTRY

- NanoChemistry
- InfoChemistry
- Chemometrics
- Femtosecond Chemistry
- Attosecond Chemistry
- Super Materials for Propulsion,
- Electronics
- Chemical Data Processing
- Real-time Bond Breaking/Forming
- Lasers/Computers
- Real-time Electron Movement
- Lasers/Computers
- ?...

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Space Shuttle Propulsion System

- **Space Propulsion (PRC, OMS, Veneers):**
  - **Hypergolic Liquids**
    - \( \text{CH}_3\text{NHNH}_2 + \text{N}_2\text{O}_4 \rightarrow \text{products} + \Delta H \)
    - **NO External Ignition Required!**

- **Boost Phase (2 x 3.1 Mlb):**
  - **Solids**
    - \( \text{HTPB} + \text{NH}_4\text{ClO}_4 \rightarrow \text{products} + \Delta H \)
    - **One-time Squib**

- **Launch (3 x 0.4 Mlb):**
  - **Cryogenic Liquids**
    - \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \Delta H \)
    - **One-time Torch**

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Strong Emissions From CO(a):

Cause of Chemiluminescence:

Rocket Plume-Atmospheric Interactions

UV-Chemistry Questions:

Precursors?
Its Formation?
Its Reactions?

Space Experiment

Observation Platforms

Space Shuttle
Mir Space Station
MSX

Thrusters

Space Shuttle
Progress-M
Soyuz-TM
Proposed CO(a) Source Chemistry

Unreacted CH₃NHNH₂ → Precursor(s)

Precursor(s) + O → Products

→ CO(aᵥ'), R
→ CH₂ + OR'
→ CH + OR''

CH₂ + O → Products

k = 1.3 x 10⁻¹⁰
→ CO(aᵥ≤8), aᵥ(≤5), dᵥ(≤1) + H₂

CH + O → Products

k = 9.5 x 10⁻¹¹
→ CO(aᵥ≤8), aᵥ(≤5), dᵥ(=0) + H

- CO + H₂ (Main)
- 2H + CO (~ 20%)
- CH + OH (~ 6%)

- CO + H (Main)
- HCO (HCO*)
- HCO⁺ + e⁻ (~ 0.03%)
- C + OH (? +ve Eₐ)

200 km-Thermosphere
[O] >> [O₂]
Apparatus

He/CHBr$_3$

He/O$_2$(O-atoms)

248-nm Laser

Pump

Calorimeter

vuv-Spectrometer

uv/vis-Spectrometer

Distribution A: Approved for public release, distribution is unlimited
CHBr₃ Photolysis To Produce CH Radicals

\[
\begin{align*}
\text{CHBr} + \text{Br}_2 & \rightarrow \text{Br} + \text{CHBr}_2 (\Delta H = -49.6) \\
\text{(H + Br)} & \rightarrow \text{CBr}_2 + \text{HBr} \\
\text{CBr}_2 + \text{HBr} & \rightarrow \text{Br} + \text{CHBr} \\
\text{CH} & \rightarrow \text{CH(A)} + \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH} + \text{Br} & \rightarrow \text{CHBr} \\
\text{CHBr} + \text{Br} & \rightarrow \text{CH}(^4\Sigma^-) + \text{Br} \\
\text{CH}(^2\Pi) + \text{Br} & \rightarrow \text{HBr} + \text{C} \\
\end{align*}
\]
CO(A) Source Reactions

Chemiluminescence Intensity Varied as (Laser Fluence)$^2$

\[
\begin{align*}
C(^3P) + O(^3P) & \rightarrow CO(A^1\Pi) \\
CHBr + O(^3P) & \rightarrow HBr(X^1\Sigma^+) + CO(A^1\Pi) \\
CH + O(^3P) & \rightarrow H(^2S) + CO(A^1\Pi) \\
CBr + O(^3P) & \rightarrow Br(^2P_{3/2}) + CO(A^1\Pi) \\
CBr_2 + O(^3P) & \rightarrow Br_2(^1\Sigma^+) + CO(A^1\Pi)
\end{align*}
\]

$\Delta H_{298K}^{\circ}$ (kcal mol$^{-1}$)

\(-71.8\) \hspace{1cm} (+1.3) \hspace{1cm} (+9.2) \hspace{1cm} (+3.8) \hspace{1cm} (+29.1)

Diatomics or Triatomics Need to be Internally Excited
Comparison of CO & OH-Chemiluminescence

Strong CO(A) Signal in O/O₂

Very Weak CO(A) Signal in O₂ only

Weakened OH(A) Signal in O/O₂

Strong OH(A) Signal in O₂ only

\[ k = (2.3-5.9) \times 10^{-11} \]

\[ \text{CH} + \text{O}_2 \rightarrow \text{Products} \]
\[ \rightarrow \text{CO}(a'_{v\leq4}, a'_{v'=0}) + \text{OH} \]

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Bimolecular Reaction Rate Coefficients of Added Substrate When CH₄ Present

\[ k_{O_2} = (2.2 \pm 0.3) \times 10^{-11} \]
\[ k_{N_2O} < 7 \times 10^{-14} \]
\[ k_{NO} = (3.4 \pm 0.5) \times 10^{-11} \]
\[ k_{H_2} < 2 \times 10^{-13} \]
\[ k_{CH_4} < 6 \times 10^{-14} \]

(C + O) not the Source

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CHBr$_3$ Versus CBr$_4$ Photolysis

- Stronger VUV Signal in CHBr$_3$ Photolysis
  \[ \text{(CH}^\# \text{ (or CHBr}^\#\text{) + O) Important} \]

- Signal in CBr$_4$ Photolysis Varies as (Fluence)$^2$
  \[ \text{(CBr}_2^\# + O) \text{ not Important, Since Br}_2^* \text{ Signal Varies as (Fluence)}^1 \]

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CBr$_4$ Photolysis

- CBr$_2$ + O → CO + Br$_2^*$
- CBr$_2$ Formed in Absence of Photolysis
- CBr$_2$ Formed in Photolysis
- CBr + O → CO* + Br

CBr$_2$ + O → CO* + Br$_2$ not Important

Distribution A: Approved for public release, distribution is unlimited
CHBr$_3$ Versus CBr$_4$ Photolysis

- **CHBr$_3$**
  
  \[
  k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}
  \]

- **CBr$_4$**
  
  \[
  k_{O_2} = (2.4 \pm 0.4) \times 10^{-12}
  \]

\[\downarrow\]

(CBr\# + O) Source is not as Important as (CH\# + O) in CHBr$_3$ Photolysis

- **CHBr\#** has Very Short Lifetime (~ 5 \(\mu\)s) and \(k_{(CHBr + O_2)} < 2 \times 10^{-14}\)

\[\downarrow\]

(CHBr\# + O) Source not Important in CHBr$_3$ Photolysis

*Distribution A: Approved for public release, distribution is unlimited*
**CH(a^4\Sigma^-) + O**

**Reaction Rate Coefficient**

\[
(\kappa' - \kappa_{eff}) \text{ (s}^{-1})
\]

**Excess CH\textsubscript{4}, 2 Torr He**

\[
[O] \text{ (1 x 10^{14} molec cm}^{-3})
\]

- \[k_{(CH(a) + O)} = (1.35 \pm 0.47) \times 10^{-10}\]

Previously:
- \[k_{(CH(X) + O)} = (9.5 \pm 1.4) \times 10^{-11}\]
Space Shuttle-Atmospheric Interaction: Conclusions

- 248-nm Photolysis of CHBr₃/O-atom Mixtures

  Strong Emissions From:
  - CO(A), CO(a)
  - OH(A) when O₂ Present
  - Br₂(D)

  Kinetic & Laser Fluence Trend Analyses of the Chemiluminescence:
  - CH(X²Π, a⁴Σ⁻) + O
  - CBr₂ + O

- Plume Fragments (CH) + Thermosphere (O-atoms) → UV Emissions
New Hypergolic Fuels

AFRL’s Motivation:
- Replace Highly Toxic CH₃NHNH₂ (MMH)
- Design Better Performing Fuels

AFRL’s Approach:
- Tune Fuel Structure for;
  - Energy Content: High Heat of Combustion
  - Oxygen Balance: Lower Spacecraft Mass
  - Physical Properties: Higher \( \rho \), Lower \( mp \), Reduced Sensitivities
  - Ignition/Combustion Behavior: Short ID Time

Propellant Performance \((I_{sp})\)

Fuel + Oxidizer \(\rightarrow\) Products + \(\Delta H\)

\[
\Delta H = K.E = \frac{1}{2}mv^2
\]

\[
I_{sp} = \frac{1}{g} \int F(t) dt / \int \dot{M}(t) dt = \frac{1}{g} (2H/m)^{1/2}
\]

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Search For Hypergolic Fuels

- **Definition:** A Pair of Compounds, Upon Contact, Chemically React and Release Sufficient Heat to Spontaneously Ignite

- **Discovery/Research of Hypergolic Propellants:** 1930’s, Germany (e.g. BMW)

- **No a Priori Method to Predict Hypergolicity:** NEW Fuel & Oxidizer Hypergol Pair Must be Experimentally Verified!

<table>
<thead>
<tr>
<th></th>
<th>N₂O₄/MMH</th>
<th>N₂O₄/HEHN</th>
<th>N₂O₄/HEATN</th>
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<tr>
<td>KE(MJ kg⁻¹)</td>
<td>4.7</td>
<td>3.9</td>
<td>4.0</td>
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<tr>
<td>ρ(kg m⁻³)</td>
<td>1189</td>
<td>1424</td>
<td>1454</td>
</tr>
<tr>
<td>FOM</td>
<td>1.0</td>
<td>1.03</td>
<td>1.05</td>
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Distribution A: Approved for public release, distribution is unlimited
## Screening Fuels For Hypergolicity

### Drop-test Apparatus Employed: O/F = ~ 20

<table>
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<tr>
<th>Fuel</th>
<th>IRFNA</th>
<th>N₂O₄</th>
<th>WFNA</th>
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<tr>
<td>CH₃NHNH₂ (L) (MMH)</td>
<td>HGI</td>
<td>HGI</td>
<td>HGI</td>
</tr>
<tr>
<td>HOCH₂CH₂N⁺H₂NH₂ NO₃⁻ (L) (HEHN)</td>
<td>HGI*</td>
<td>VR</td>
<td>HGI*</td>
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<tr>
<td>(1-ethan-2-ol)-4-amino-1,2,4-triazolium nitrate (L) (HEATN)</td>
<td>SR</td>
<td>VR</td>
<td></td>
</tr>
<tr>
<td>1H-1,2,3-triazole (L)</td>
<td>SR</td>
<td>SR</td>
<td></td>
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<tr>
<td>1-amino-1,2,3-triazole (M)</td>
<td>HGI*</td>
<td></td>
<td></td>
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<tr>
<td>3-methyl-1-amino-1,2,3-triazolium nitrate (S)</td>
<td>VR</td>
<td>VR</td>
<td></td>
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<tr>
<td>ν−≡−H (L)</td>
<td>VR</td>
<td>VR</td>
<td>VR</td>
</tr>
<tr>
<td>ν−≡−ν (L)</td>
<td>HGI*</td>
<td>HGI*</td>
<td>HGI*</td>
</tr>
<tr>
<td>ν−≡−≡−ν (L)</td>
<td>HGI*</td>
<td>HGI*</td>
<td>HGI*</td>
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HGI=hypergolic ignition, VR=vigorous reaction, SR=slow reaction. At room temperature, fuel is solid (S), liquid (L), or heated to its melting point (M).

*New hypergols

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Fuel Functionality Affects Ignition

WFNA / $\checkmark \equiv \checkmark$ is Hypergolic

$\checkmark \equiv \checkmark$ H

Not Hypergolic

$\checkmark \equiv \equiv \equiv \checkmark$

Is Hypergolic;
ID = 5.0 ms
Complexity of the Pre-ignition Chemistry

\[ \nabla \equiv \nabla / N_2O_4 \]

ID = 40.6 ms
Characterization of Pre-ignition Chemistry is the Key for Designing new Hypergols

- Apply Spectroscopic Probing Tools
  - Rapid-Scan FTIR
  - Time-Resolved Raman
  - Time-Resolved Emission
  - High Speed Video
- Develop Global Initiatory Mechanism
- Construct Pre-Ignition Models
- Kinetic Modeling of Ignition
- Tune Fuel Chemical Functionalities

- Apply Quantum Chemistry Tools
  - ΔH of Intermediates
  - PES (Reaction Coordinates)
  - Reaction Rates
- Provide Initial Rationale to Experimental Observations

Focused/Intelligent Approach to new Synthesis of Hypergolic Fuels

New Hypergolic Fuels: Conclusions

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Closing Remarks

Acknowledgements:

- AFOSR
  - Drs. M. Berkin & M. Berman ($$$$
- AFRL/PRSP
  - Drs. Alfano (Experimental), Mills & Boats (Theory), Suri & Hawkins (Synthesis)

Career in the Government:

- DoD
  - AFRL, ONR, ARL, etc
- DoE
  - LLNL, ANL, ONL, LANL, etc
- DoC
  - NOAA, NIST, etc
- NASA
  - Dryden, Ames, JPL, etc
- And Many More ……

Web Resources:

- American Chemical Society  www.chemistry.org
- Edwards AFB  www.edwards.af.mil
- NASA  www.nasa.gov
- New Scientist  www.sciencesjob.com

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Backup Slides
UV/Vis Plumes

Radiance Data

⇔ Plume Data ⇔

↓

Modeling Studies

↓

Laboratory Studies

↓

Chemiluminescent Processes

↓

Identify Spacecraft Atmospheric Interactions

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Absence of O-atoms

X-trace: \((O_2, 8.8 \times 10^{14})\)

\(\Delta\)-trace: \((O_2) + (CH_4, 5.0 \times 10^{15})\)

\[
CH(X^2\Pi) + O_2 \rightarrow CO + OH(A)
\]

\[
CH(a^4\Sigma^-) + O_2 \rightarrow CO + OH(A)
\]

5.0 x 10^{13} of O-atoms

- trace: \((O_2, 8.8 \times 10^{14})\)

- trace: \((O_2) + (CH_4, 5.0 \times 10^{15})\)

\[
CBr_2 + O \rightarrow CO + Br_2(D)
\]

(CBr_2 + CH_4) Slow Reaction
Br$_2^*$-Chemiluminescence

<table>
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<tr>
<td>CHBr$_3$ + O → CBr$_3$ + OH</td>
</tr>
<tr>
<td>CBr$_3$ + O → CBr$_2$ + BrO</td>
</tr>
<tr>
<td>⊳</td>
</tr>
<tr>
<td>CBr$_2$ + O → Br$_2^*$ + CO</td>
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<table>
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<tr>
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<tbody>
<tr>
<td>Br$_2^*$ ∝ (Fluence)$^1$</td>
</tr>
<tr>
<td>⊳</td>
</tr>
<tr>
<td>CHBr$_3$ + hν → CHBr$_2^*$ + Br</td>
</tr>
<tr>
<td>CHBr$_3$ + hν → CBr$_2$ + HBr</td>
</tr>
<tr>
<td>CHBr$_2^*$ + hν → CBr$_2$ + H</td>
</tr>
<tr>
<td>CHBr$_2^<em>$ + O ↝ Br$_2^</em>$ + HCO</td>
</tr>
<tr>
<td>CHBr$_2$ + O → CBr$_2$ + OH</td>
</tr>
<tr>
<td>CHBr$_2^*$ + O ↝ CBr$_2$ + OH(A)</td>
</tr>
<tr>
<td>CHBr* + O ↝ CBr + OH(A)</td>
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Time Resolved Br$_2^*$-Signal

- Fast Br$_2^*$ Rise
- Also:
  - $k_{O_2} < 9 \times 10^{-14}$
  - $k_{CH_4} < 7 \times 10^{-14}$
  - $k_O = (5.4 \pm 1.0) \times 10^{-11}$

\[ CHBr_3 + h\nu \rightarrow CBr_2 + HBr \]

Less Important
\[ CBr_3 + h\nu \rightarrow CBr_2 + Br \]

- Since:
  - $CBr_4 + h\nu \rightarrow CBr_3^* + Br$
  - $CBr_2 + Br$

\[ CBr_4 + h\nu \rightarrow CBr_2 + Br_2 \{ ? \} \]
$\text{CH}^\# + \text{O} \rightarrow \{\text{HCO}\}^* \rightarrow \text{CO}^* + \text{H}$

$\text{M} \rightarrow \text{CO}(X,a,a',d,A)$

**CO* Production Mechanism**
Hypergolic Action

- **No a Priori Method:** Hypergolicity Between any Pair of Fuel & Oxidant System Must be Experimentally Verified

- **Know Your Calories:** < 0.05 cc of a Fuel can Lead to a Spectacular Interaction With an Oxidizer

\[
2N_2H_4 + N_2O_4 \rightarrow 3N_2 + 4H_2O \quad \Delta H = -279 \text{ kcal/mol} \quad (51 \text{ mg} = 220 \text{ calories})
\]

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