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Ab initio Quantum Chemical and Experimental Reaction Kinetics Studies in the Combustion of Bipropellants

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Ab initio Quantum Chemical and Experimental Reaction Kinetics Studies in the Combustion of Bipropellants

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March 24, 2017

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Where and how big is AFRL at Edwards AFB?
Premier Rocket Test Facilities (+$3B) In Beautiful Mojave Desert, CA

A Cool Place to Work for a Place That’s Hot!
Edwards AFB Accolades too Many
But, e.g., Visit the URLs......


http://www.militarymuseum.org/EdwardsAFB.html

Murphy's Laws

“If anything can go wrong, it will”
Phrase born in 1949, EAFB
Capt. Edward A. Murphy
Engineer working on AF Project MX981
How much sudden deceleration
a person can stand in a crash

Chuck Yeager

First human to officially break the sound barrier
October 14, 1947, EAFB
Flew the experimental Bell X-1
A rocket-engine powered airplane
Mach 1 at an altitude of 45,000 ft

EAFB’s success is KSC’s success!
Our Partners in Propulsion
Research & Technology Development
# Rocket Propulsion for the 21st Century (RP21) Goals

## Boost and Orbit Transfer Propulsion

<table>
<thead>
<tr>
<th>Goal</th>
<th>2017</th>
<th>2027</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce Stage Failure Rate* (RP)</td>
<td>75%</td>
<td>75%</td>
<td>Baseline (B)</td>
</tr>
<tr>
<td>Improve Mass Fraction (Solid)</td>
<td>18%</td>
<td>38%</td>
<td>5%</td>
</tr>
<tr>
<td>Increase ISP % (Solid/Liquid* (RP))</td>
<td>2%/0%</td>
<td>5%/4%</td>
<td>1%/B</td>
</tr>
<tr>
<td>Increase Thrust to Weight % (Liquid, (RP))</td>
<td>103%</td>
<td>103%</td>
<td>10%</td>
</tr>
<tr>
<td>Reduce Engine Turn Time(Reusable)</td>
<td>&lt;8hrs</td>
<td>&lt;4hrs</td>
<td>B</td>
</tr>
<tr>
<td>MTBO/MTBR (Missions, Liquid)</td>
<td>50/100</td>
<td>50/100</td>
<td>10%</td>
</tr>
<tr>
<td>Decrease Motor Health State Uncertainty</td>
<td>20%</td>
<td>50%</td>
<td>10%</td>
</tr>
</tbody>
</table>

## Spacecraft Propulsion

<table>
<thead>
<tr>
<th>Goal</th>
<th>2017</th>
<th>2027</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase Efficiency (ET/ES/EM)</td>
<td>15%/15%</td>
<td>65%/35%</td>
<td>B/B/B</td>
</tr>
<tr>
<td>Decrease EP System Dry Mass (ET/ES/EM)</td>
<td>0%/50%</td>
<td>75%/90%</td>
<td>B/B/25%</td>
</tr>
<tr>
<td>Decrease Flexible Prop System Wet Mass</td>
<td>35%</td>
<td>65%</td>
<td>B</td>
</tr>
<tr>
<td>Increase Chemical Prop. Density Isp</td>
<td>5%</td>
<td>15%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Decrease Chemical Prop. Dry Mass</td>
<td>10%</td>
<td>40%</td>
<td>B</td>
</tr>
</tbody>
</table>

## Tactical Propulsion*

<table>
<thead>
<tr>
<th>Goal</th>
<th>2017</th>
<th>2027</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase Total Impulse (RS&amp;Smokey/MS)</td>
<td>20%/33%</td>
<td>35%/45%</td>
</tr>
<tr>
<td>4 Pulse motors</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- RS/Smokey Total Impulse Penalty</td>
<td>10/Mf</td>
<td>0</td>
</tr>
<tr>
<td>- Minimum Smoke Increase Total Impulse</td>
<td>5%</td>
<td>25%</td>
</tr>
<tr>
<td>Increase Density Isp</td>
<td>5%</td>
<td>7%</td>
</tr>
</tbody>
</table>

## Additional Backup goal information exists

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In-Space Propulsion (RQRS) R&D Basic Science to Flight Demo

Sustainment

Hall Effect Thruster (HET)
- XR-5A thrusters

Resiliency

High Power (>100 kW class) EP (FRCs)
- Extremely low mass, high thrust
- multimode compatible

Superiority

AF-M315E Transition (GPIM)
- Replacement of hydrazine with higher performance non-toxic propellant
- Customer: NASA/AF/Industry
- Developing family of thrust levels ¼ to 20 lbf

Densified Ionic Liquid Electrosprays (DILE)
- Cube sat applications
- Extremely high efficiency, scalable thrust

Next-gen Adv Biprop Thruster (ABT)
- More performance
- Vol-limited spacecraft

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STEM Students
How to Work at AFRL EAFB?

- **Ph.D**
  - NRC Post-doc

- **Graduate Students**
  - AF SFFP
  - AFIT
  - SMART
    - [http://www.asee.org/fellowship-programs/graduate](http://www.asee.org/fellowship-programs/graduate)
  - USAFA
    - [http://afsffp.sysplus.com/SFFP/contact/usafa-colorado-springs-co.aspx](http://afsffp.sysplus.com/SFFP/contact/usafa-colorado-springs-co.aspx)

- **Under Graduate Students**
  - Pathways
    - [https://www.usajobs.gov/GetJob](https://www.usajobs.gov/GetJob)
  - **Student-teachers**
    - STAR
      - [http://starteacherresearcher.org/sites.html](http://starteacherresearcher.org/sites.html)
Our Interest in Combustion Kinetics of Bipropellants

- Understand Auto-ignition Chemistry
  - Occurs at Low Temperature-Pressure Conditions

- Understand Fuel Pyrolysis
  - Competes With Oxidation

- Understand Fuel Oxidation
  - Competes With Pyrolysis

- Construct Comprehensive Reaction Kinetics Models
  - Discover Other Auto-igniting Bipropellant Systems

Improve Propulsion Capabilities Over the Current State-of-the-art CH$_3$NHNH$_2$/N$_2$O$_4$
Why Quantum Chemical Reaction Kinetics Studies?

- **Only Option When Experiments are not Possible or Limited**
  - Combustion Conditions of P & T too Extreme to Probe

- **Accuracy \((E_a)\) can be as Good or Better Than Experiments**
  - Thermochemical Accuracy Possible
  - Ideal for Branching Ratio Predictions for Closely Competing Reactions

- **Can be a Cost Effective Alternate to Experiments**
  - Hardware & Software Efficiencies Improving Constantly

- **A Balanced Approach to Kinetics Calculations Recommended**

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N\textsubscript{2}H\textsubscript{3} + NO\textsubscript{2} Reaction Kinetics

### Perspective

- **Radical Chemistry Modelling**
  - N\textsubscript{2}H\textsubscript{4}/NO\textsubscript{2} Auto-ignition

- **Recent Works**
  - **Only Theoretical Studies**
    - See Raghunath et al., *Adv. Quantum Chem.*, 69, 253 (2014)..............$k_{298 \text{K}, 1\text{atm}} = (2.3 \times 10^{-11})$
    - See Daimon et al., *Sci. Tech. Energetic Materials*, 74, 17 (2013)...........$k_{298 \text{K}, 1\text{atm}} = (1.6 \times 10^{-14})$?
    - See Daimon et al., *J. Propul. Power*, 30, 707 (2014)...................$k_{298 \text{K}, 1\text{atm}} = (1.9 \times 10^{-11})$
      

  - CH\textsubscript{3}NNH\textsubscript{2} + NO\textsubscript{2} $\rightarrow$ Products, $k = (2.2 \times 10^{-13})$
  - trans-CH\textsubscript{3}NHNH + NO\textsubscript{2} $\rightarrow$ Products $k = (1.4 \times 10^{-12})$
  - cis-CH\textsubscript{3}NHNH + NO\textsubscript{2} $\rightarrow$ Products $k = (1.2 \times 10^{-12})$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}

- **This work** (submitting for publication)
  - Pulsed Laser Photolysis - Flow Tube Mass Spec Experiments
    - First Experimental Determination
  - *Ab initio* Chemical Kinetics
    - Rice–Ramsperger–Kassel–Marcus Theory and Master Equation Simulations: $k(E,J)$

---

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Pulsed Laser Photolysis
Flow Tube Apparatus
# N$_2$H$_3$ Source & Flow Tube Chemistry

\[
\begin{align*}
\text{N}_2\text{H}_4 + \text{hv} & \rightarrow \text{N}_2\text{H}_3 + \text{H} & \sigma_{\text{193 nm}} = 450 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1} \\
\text{NO}_2 + \text{H} & \rightarrow \text{NO} + \text{OH} & k_2 = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
\text{N}_2\text{H}_4 + \text{H} & \rightarrow \text{N}_2\text{H}_3 + \text{H}_2 & k_3 = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
\text{N}_2\text{H}_4 + \text{OH} & \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O} & k_4 = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
\text{N}_2\text{H}_3 + \text{NO}_2 & \rightarrow \text{N}_2\text{H}_2 + \text{HONO} & k_5 \\
\text{N}_2\text{H}_3 + \text{NO}_2 & \rightarrow \text{other products} & k_6 \\
\text{HONO} & \rightarrow \text{loss} & k_7 = 1 \text{ s}^{-1} \\
\text{N}_2\text{H}_3 & \rightarrow \text{loss} & k_8 = 10 \text{ s}^{-1} \\
\text{H} & \rightarrow \text{loss} & k_9 = 10 \text{ s}^{-1} \\
\text{OH} & \rightarrow \text{loss} & k_{10} = 10 \text{ s}^{-1} \\
\end{align*}
\]

\[
\begin{align*}
[N\text{ONO}] &= (k_5[N\text{O}_2][N_2\text{H}_3]_o)[e^{k_7 \cdot t} - e^{k' \cdot t}] / (k' - k_7) \\
k' &= (k_5 + k_6)[\text{NO}_2] + k_8 \\
[N\text{H}_4] &= 5 \times 10^{14}, [\text{H}] = 5 \times 10^{12}, [\text{NO}_2] = 1 \times 10^{13} \text{ to } 5 \times 10^{13} \text{ molecule cm}^{-3}
\end{align*}
\]
Typical [HONO] Temporal Profile

Second-order Plot

\[ k_{298 \text{ K, 2 Torr } N_2} = (1.23 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
Temperature Dependence of \( \text{N}_2\text{H}_3 + \text{NO}_2 \) Reaction

\[
(k_5 + k_6)_{2\text{-Torr-N}_2} = (2.36 \pm 0.47) \times 10^{-12} \exp((520 \pm 350)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]
Ab initio Quantum Chemistry Approaches for N₂H₃ + NO₂ Reaction

- Previous Work used Single-reference Methods (e.g. CCSD(T))
- However, Reaction is not a Simple H-abstraction Process
- There is Strong Electron Repulsion Between N and O-atoms
- The Significant Multi-reference Character of the Wavefunction in the TSs for Addition and Bond Breaking With Loose Geometries Needs Proper Treatment
- Here in addition, we Apply CASPT2 With Dunning’s Augmented Correlation Consistent Basis Set to Characterize the PES
Potential Energy Surface for $\text{N}_2\text{H}_3\text{NO}_2$ Adduct Formation

Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pVTZ
CCSD(T)/cc-pV\textsuperscript{$\infty$}Z

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Potential Energy Surface for N$_2$H$_3$ONO Adduct Formation

Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pV$\infty$Z

CCSD(T)/cc-pV$\infty$Z
TSs and Complex Structures Involved in $\text{N}_2\text{H}_3$ Addition to $\text{NO}_2$

- Pseudo-planar 6-member ring structure
- $\text{NO}_2$ interaction With 2 H-atoms of $\text{N}_2\text{H}_3$
- TS Stabilization Two H-bonds formed

- Pseudo-planar 5-member ring structure
- One H-bond
- Loose geometry

- Planar 4-member ring structure
- Loose geometry
Rice–Ramsperger–Kassel–Marcus (RRKM) Theory Together With Multi-well Master Equation Simulations Carried out to Compute the Phenomenological Thermal Decomposition Rate Coefficients (Klippenstein and Co-workers, VARIFLEX, Version 2.0)

\[ \Delta E_{\text{down}} = 125 \times \left(\frac{T}{300}\right)^{0.85} \text{ cm}^{-1} \] Energy Transfer Model Used

TST With Rigid-rotor Harmonic-oscillator Assumption Including Tunneling Corrections Used to Calculate High-pressure Limit

Good Agreement With Experiment Observed
Branching Rate Coefficients (2 Torr N₂) & High Pressure Limit Versus T

![Graph showing branching rate coefficients and high pressure limit versus 1000/T(K).]

- $k$ (cm³ molecule⁻¹ s⁻¹)
- 10⁻¹⁰ to 10⁻²⁴
- $1000/T(K)$ range from 0.0 to 4.0
- NH₂NHNO₂, high pressure limit
- NH₂NHNO₂
- trans-N₂H₂+trans-HONO
- cis-N₂H₂+trans-HONO
- NH₂NNO₂H
- Expt., 298-348 K, 2 Torr N₂

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Branching Rate Coefficients (1 Atm \(N_2\)) & High Pressure Limit Versus \(T\)

![Graph showing branching rate coefficients versus temperature](image)
CH₃NH
Perspective

- CH₃NHNH₂ (Bipropellant Fuel)
  - Pyrolysis and Oxidation Compete in Combustion Processes
    - Facile Bond Breaking: CH₃NHNH₂ → CH₃NH + NH₂
      - Previously, NH₂ Monitored, Li et al., Combustion Flame, 161, 16, (2014)
      - However, Fate of CH₃NH not Well Understood
        - Important for Kinetics Modelling Simulations

- CH₃NH (Decomposition, Source of H-atoms?)

  CH₃NH → TS1 → CH₃ + NH
  → TS2 → CH₂=NH + H
  → TS3 → CH₂NH₂

  CH₂NH₂ → TS4 → CH₂=NH + H

  CH₃NH → TS5 → CH₃N + H
  → TS6 → CH₂=N + H₂

- This work
  - Multi-reference *ab initio* Methods Used to Characterize Bond Breaking Processes
  - RRKM and Multi-well Simulations Carried out to Compute Reaction Rates
CH₃NH Dissociation

PES

CASPT2 Theory for N-H and C-N Bond Breaking
RRKM and Multi-well Simulations for CH$_3$NH Decomposition

Dominant Channel:
CH$_3$NH $\rightarrow$ TS2 $\rightarrow$ CH$_2$=NH $+$ H
\[ \text{CH}_3\text{NHNH}_2 + \text{H} \rightarrow \text{TS}_7 \rightarrow \text{CH}_3\text{NNH}_2 + \text{H}_2 \]

\[ \rightarrow \text{TS}_8 \rightarrow \text{trans-CH}_3\text{NHNH} + \text{H}_2 \]

\[ \rightarrow \text{TS}_9 \rightarrow \text{cis-CH}_3\text{NHNH} + \text{H}_2 \]

\[ \rightarrow \text{TS}_10 \rightarrow \text{CH}_2\text{NHNH}_2 + \text{H}_2 \]
Conclusions

- **N₂H₃ + NO₂ Reaction Kinetics**
  - Fast addition reaction
  - Direct detection of HONO product confirmed
  - Weak -ve temperature dependence of rate coefficient (k) seen
  - Multi-reference methods employed to accurately determine stationary energies of the PES
  - Calculated k in agreement with experiment

- **CH₃NH Decomposition**
  - CH₂=NH + H channel dominates

- **CH₃NHNH₂ + H Reaction Kinetics**
  - Agreement seen in absolute rate coefficient between theory and experiment
  - Theory provides insight regarding at which site H-abstraction dominates

- High-level *ab initio* quantum chemical calculations and direct *real-time* kinetics measurements can provide unparalleled-details regarding the nature of the reaction mechanism of a chemical system of interest
Acknowledgements