Combustion of Energetic Materials

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Chemical Kinetics and Flame Structure of Energetic Materials
What are molecular and homogeneous energetic materials

• These are the “premixed” systems of energetic materials
  – Kinetically limited, not diffusion

• Monomolecular (single molecular)
  – Pure materials and plastic bonded
    • Small amount of binder is neglected

• Molecularly mixed materials
  – Double based and triple base
Aliphatics

- Aliphatic organic compounds belong to the alkane, alkene, and alkyne classes of compounds
- Both open chained and cyclo aliphatic groups
- The major sources of oxidizer are from the nitro (-NO₂), nitrite (-ONO), nitrate (-ONO₂), and nitramine (-NH-NO₂) groups

Nitromethane

\[
\text{H}_3\text{C} - \text{N}^+\text{O}^- \\
\text{O} \\
\]

Methylnitrite

\[
\text{H}_3\text{C} - \text{O} - \text{N} = \text{O} \\
\]

Methylnitrate

\[
\text{H}_3\text{C} - \text{O} - \text{N}^+\text{O}^- \\
\]

Nitroguanidine, NQ

\[
\text{N} - \text{NO}_2 \\
\text{H}_2\text{N} - \text{C} - \text{NH}_2 \\
\]

Nitroglycerine, NG

\[
\text{O} - \text{N}^+\text{O}^- - \text{O} - \text{N}^+\text{O}^- - \text{O} - \text{N}^+\text{O}^- \\
\]

Pentaerythritoltetranitrate, PETN
Cycloaliphatics

- These are also nitramines
- Very commonly used in propellants and explosives
- They are really not flat. In fact, they can have different configurations, which give different crystal structures, which are different solid phases

\[
\begin{align*}
\text{Cyclotrimethylene} & \quad \text{Trinitramine, RDX} \\
\text{Cyclohexylnitramine} & \quad \text{Tetranitramine, HMX}
\end{align*}
\]
Aromatics

• Oxygen added by -NO₂ groups mainly

Trinitrobenzene, TNB

Trinitrotoluene, TNT

Triaminotrinitrobenzene, TATB

(Good performance and sensitivity, but difficult to make - expensive)

(The standard for insensitivity)
Inorganics

• Inorganic compounds do not have hydrocarbon backbones forming the basis of the molecules
• Usually are ionic acids or bases, or salts

Ammonium nitrate, AN, NH$_4^+$NO$_3^-$

Potassium chlorate, KClO$_3$

(hard to use as a propellant or explosive, but very inexpensive, and chlorine free)

Ammonium perchlorate, AP, NH$_4^+$ClO$_4^-$

Potassium perchlorate, KClO$_4$

(common composite propellant oxidizer)

Also azides, e.g., lead azide

(can explode alone with strong impact, less prone to decompose under UV than KClO$_3$)
Some Newer Energetic Materials

Ammonium dinitramide, ADN

\[
\begin{pmatrix}
\text{O}^2- & \text{N}^+ & \text{N}^+ & \text{O}^2- \\
\text{N}^- & \text{O}^- & \text{O}^- & \text{N}^+ \\
\end{pmatrix}
\quad \text{NH}_4^+
\]

Hydroxylammonium nitrate, HAN, \( \text{NH}_3\text{OHNO}_3 \)

\[
\begin{pmatrix}
\text{H} & \text{H} & \text{N} & \text{O} & \text{H} \\
\end{pmatrix}^+ 
\quad \begin{pmatrix}
\text{O}^2- & \text{N}^+ & \text{O}^2- \\
\end{pmatrix}^{-}
\]

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane, CL-20

Octanitrocubane

5-Nitro-1,2,4-triazol-3-one, NTO

1,3,3-Trinitroazetidine, TNAZ
High-Nitrogen Energetic Materials

Focus is on HN ring systems with known chemistries

tetrazole

azo

azide

tetrazine

furazan

azoxy, N-oxide

tetraaza pentalene
High-Nitrogen Energetics Exhibit Unusual Properties

• Explosive Performance vs Sensitivity rule does not follow. AAzF, DAAF
• High Burn Rates with Low Pressure Sensitivity (DAATO3.5, 100 atm, 6 cm/s, n=0.275)
• Detonate despite having no oxygen DHT/DAAT
• Burn rapidly without visible flame DHT/BTATz
• High Hydrogen also DHT/TAGzT
Reactions and Energetics of Decomposition

• **Simple bond fission**

\[
BDE = \Delta H_{f,298}^0 (A) + \Delta H_{f,298}^0 (B) - \Delta H_{f,298}^0 (A - B)
\]

\[
BDE (C−NO_2) > BDE(C−NO), \ BDE(N−NO_2) \sim BDE(N−NO)
\]

\[
BDE(C−NO_2) \sim BDE(C−ONO), \ BDE(N−NO_2) > BDE(N−ONO)
\]

By comparing bond strengths, one finds CH$_3$ONO and CH$_3$ONO$_2$ decompose by breaking the O-N bond rather than the C-\(\ddot{O}\) bond.

• **Bond fission of radicals**

Energy required to break a bond in a radical species can differ from the \(BDE\) – must consider a barrier to dissociation in addition to the \(BDE\).

The \(BDE\) for removing the radical species from a radical adduct generally less than the corresponding \(BDE\) for the stable species.

• **Concerted decomposition**

Alternative decomposition process is a concerted process in which the activation energy is lower than any of the individual bonds.

Trioxane \(\hat{\bigcirc} \hat{\bigcirc} \hat{\bigcirc} (− CH_2O −)_3 \rightarrow 3 \text{CH}_2\text{O}; \ \text{RDX} \rightarrow 3 \text{CH}_2\text{NNO}_2\)

• **Complex fission – five centered HONO elimination**

• **Autocatalytic- radical attack on energetic materials**

• **Water assisted reactions**
## Bond Dissociation Energies for Various Nitro, Nitroso, Nitrite, and Nitrate Species in kcal/mol

<table>
<thead>
<tr>
<th>Nitroso Compounds</th>
<th>Nitro Compounds</th>
<th>Nitrite Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–NO</td>
<td>H–NO2</td>
<td>H–ONO</td>
</tr>
<tr>
<td>50.3</td>
<td>73.4</td>
<td>78.3</td>
</tr>
<tr>
<td>CH3–NO</td>
<td>CH3–NO2</td>
<td>CH3–ONO</td>
</tr>
<tr>
<td>37.6</td>
<td>58.9</td>
<td>57.3</td>
</tr>
<tr>
<td>NH2–NO</td>
<td>NH2–NO2</td>
<td>NH2–ONO</td>
</tr>
<tr>
<td>49.4</td>
<td>51.4</td>
<td>32.9</td>
</tr>
<tr>
<td>HO–NO</td>
<td>HO–NO2</td>
<td>HO–ONO</td>
</tr>
<tr>
<td>50.2</td>
<td>46.8</td>
<td>17.1</td>
</tr>
<tr>
<td>CH3O–NO</td>
<td>CH3O–NO2</td>
<td>CH3NH–ONO</td>
</tr>
<tr>
<td>43.5</td>
<td>39.9</td>
<td>29.3</td>
</tr>
<tr>
<td>CH2H–NO</td>
<td>CH2H–NO2</td>
<td>(CH3)2N–ONO</td>
</tr>
<tr>
<td>22.1</td>
<td>37.1</td>
<td>28.1</td>
</tr>
<tr>
<td>CH3NH–NO</td>
<td>CH3NH–NO2</td>
<td>CH2N–ONO</td>
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<tr>
<td>48.7</td>
<td>50.6</td>
<td>22.1</td>
</tr>
<tr>
<td>CH2CH–NO</td>
<td>CH2CH–NO2</td>
<td>CH2CH–ONO</td>
</tr>
<tr>
<td>51.0</td>
<td>70.2</td>
<td>68.5</td>
</tr>
<tr>
<td>C2H5–NO</td>
<td>C2H5–NO2</td>
<td>C2H5–ONO</td>
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<tr>
<td>38.5</td>
<td>60.8</td>
<td>59.3</td>
</tr>
<tr>
<td>NH2CHCH–NO</td>
<td>NH2CHCH–NO2</td>
<td>CHO–ONO</td>
</tr>
<tr>
<td>60.6</td>
<td>78.2</td>
<td>60.0</td>
</tr>
<tr>
<td>CHO–NO</td>
<td>CHO–NO2</td>
<td></td>
</tr>
<tr>
<td>29.2</td>
<td>49.8</td>
<td></td>
</tr>
<tr>
<td>NH2O–NO</td>
<td>(CH3)2N–NO2</td>
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</tr>
<tr>
<td>17.1</td>
<td>45.9</td>
<td></td>
</tr>
<tr>
<td>HOO–NO</td>
<td>NH2CHCH–NO2</td>
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</tr>
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<td>25.5</td>
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<tr>
<td>CH3NHO–NO</td>
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<td>12.1</td>
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<tr>
<td>CH2CHO–NO</td>
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<tr>
<td>15.5</td>
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</table>

**Nitrate Compounds**

<table>
<thead>
<tr>
<th>H–ONO2</th>
<th>105.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3–ONO2</td>
<td>83.7</td>
</tr>
</tbody>
</table>

From Melius, 1989
Comparison of decomposition energetics of NO$_2$ bond breaking and HONO elimination for CH$_3$ONO$_2$, CH$_3$NHNO$_2$, CH$_3$CH$_2$NO$_2$, and CH$_2$=CHNO$_2$

- The top energy value represents the bond dissociation energy for NO$_2$ bond fission
- The middle energy value represents the barrier height for the 5-centered elimination of HONO
- The bottom energy represents the heat of dissociation for formation of HONO
Reaction of CH$_3$NHNO$_2$ + H

From Melius, 1989
Reaction diagrams for the water catalyzed concerted reaction for the conversion of nitramine, NH$_2$NO$_2$, to N$_2$O+H$_2$O through the intermediate *aci* form, HNN(O)OH

- In the first concerted mechanism, the H from the nitramine shifts to the water molecule while the H on the water shifts to the O of the nitramine, forming the *aci* molecule.
- In the second step, the *aci* molecule is converted to N$_2$O and H$_2$O by again having the H bonded to the N shifting to the water molecule while the H on the water molecule is shifted to the OH group of the *aci* molecule.

From Melius, 1989
Gas-Phase Experiments and Model Development

**Necessary and Sufficient Experiments**

- Coupled Combustion Chemistry Transport & Heat Release
- Diffusion and Premixed Flames

**Combustion Chemistry**

- Shock Tubes
- Flow Reactors
- Static Reactors

**Isolated Species and Reactions**

- Rate Constant Measurements
- Product Detection

**Model / Theory**

- 1-D Gas Phase Model Simulation & Validation
  - Transport and Heat Release Added to Elementary Chemistry

- 0-D Gas Phase Model Simulation & Validation
  - Complex Chemistry Only

- Semi-Empirical Theory
  - Rate Constant Estimates
  - Critical Data Analysis
  - Thermochemistry

**Microscopic to Macroscopic**

- Multiple and Complementary Diagnostics

**Sensitivity Analysis**
Gas-Phase Chemistry Mechanisms

Hydrocarbon Combustion Chemistry

- CH₄ / O₂
- CH₃OH / O₂
- CH₂O / O₂
- CO / H₂O / O₂
- H₂ / O₂

- C₃H₈ / O₂
- C₂H₆ / O₂

Nitrate Ester / Nitramine Combustion Chemistry

- C₂H₆ / NO₂ / N₂O
- CH₄ / NO₂ / N₂O
- HCN / NO₂ / N₂O
- NH₃ / NO₂ / N₂O

- H₂ / NO₂ / N₂O
- CH₃NO₂

ADN
Gas-Phase Submodel Development

Flow reactor studies of a CH$_4$/N$_2$O/N$_2$ mixture reacting at 3.3 atm and 1153 K

Flow reactor studies of N$_2$O decomposition at 6 atm and 1123 K
Initial Conditions: 100% gaseous CH₃NO₂, Tᵢ = 1100 K; Pᵢ = 7.25 atm
Constant Volume Nitromethane Combustion - Species

Initial Conditions: 100% gaseous CH$_3$NO$_2$, T$_i$ = 1100 K; P$_i$ = 7.25 atm

From Melius, 1995
Nitromethane First Stage Chemistry

**Carbon Mechanism**

\[
\begin{align*}
\text{CH}_3\text{ONO} & \xrightarrow{+ \text{NO}_2} \text{CH}_3 + \text{NO}_2 \\
\text{CH}_3\text{ONO} & \xrightarrow{+ \text{M}} \text{CH}_3 + \text{NO}_2 \\
\text{CH}_3\text{NO}_2 & \xrightarrow{+ \text{M}} \text{CH}_3 + \text{NO}_2 \\
\text{CH}_3\text{NO}_2 & \xrightarrow{+ \text{OH}} \text{CH}_3 + \text{OH} \\
\text{CH}_3\text{OH} & \xrightarrow{+ \text{H}} \text{CH}_2\text{OH} \\
\text{CH}_3\text{OH} & \xrightarrow{+ \text{CH}_3} \text{HCO} \\
\text{HCO} & \xrightarrow{+ \text{NO}_2} \text{CO} \\
\text{CH}_4 & \xrightarrow{+ \text{H}} \text{CH}_2\text{O} \\
\text{CH}_2\text{O} & \xrightarrow{+ \text{CH}_3} \text{HCO} \\
\end{align*}
\]

**Nitrogen Mechanism**

\[
\begin{align*}
\text{CH}_3\text{ONO} & \xrightarrow{+ \text{M}} \text{NO}_2 + \text{NO} \\
\text{CH}_3\text{ONO} & \xrightarrow{+ \text{CH}_3} \text{NO}_2 + \text{NO} \\
\text{CH}_3\text{NO}_2 & \xrightarrow{+ \text{M}} \text{NO}_2 + \text{NO} \\
\text{NO}_2 & \xrightarrow{+ \text{H}} \text{NO} \\
\text{NO} & \xrightarrow{+ \text{HCO}} \text{HNO} \\
\text{HNO} & \xrightarrow{+ \text{HNO}} \text{N}_2\text{O} \\
\text{N}_2\text{O} & \xrightarrow{+ \text{M}} \text{N}_2 \\
\end{align*}
\]

From Melius, 1995
Nitromethane Intermediate (Dark Zone) Stage Chemistry

Carbon Mechanism

\[
\begin{align*}
CH_4 & \rightarrow CH_3 \\
CH_3 & \rightarrow CH_3NO \quad + NO \quad + H \\
CH_3NO & \rightarrow H_2CNOH + M \\
H_2CNOH & \rightarrow HCN + M \\
H_2CN & \rightarrow HCN + M \\
CH_3OH & \rightarrow CH_2OH + OH \\
CH_2OH & \rightarrow CH_2O + H \\
CH_2O & \rightarrow HCO + H \\
HCO & \rightarrow CO + OH \\
CO & \rightarrow CO_2 + OH
\end{align*}
\]

Nitrogen Mechanism

\[
\begin{align*}
NO & \rightarrow HCN + CH_3 \\
H_2CN & \rightarrow HCN + M
\end{align*}
\]

From Melius, 1995
Nitromethane Second Stage Chemistry

Carbon Mechanism

Nitrogen Mechanism from HCN

Nitrogen Mechanism from NO

From Melius, 1995
Flame Structure of a Double-Base Propellant

I. **Preheat Zone**: heating of propellant occurs without chemical reaction

II. **Solid-phase reaction zone**: Thermal decomposition begins by CO–NO₂ bond breaking

III. **Fizz Zone**: NO₂ and aldehydes react with other gaseous species to produce NO, CO, H₂, and CO₂

IV. **Dark (induction) zone**: slow oxidation reaction of the products formed from the fizz zone. The dark zone is considered isothermal with nearly negligible thermal and mass diffusion.

V. **Luminous flame zone**: Final products are formed and remainder of heat released
Effect of pressure on flame structure of double base propellant

- As pressure is increased, the rates of reaction in the fizz, dark, and luminous flame zones increase.
- The reaction in the dark zone is more sensitive to $p$ than the other zones.

\[ \begin{array}{c|c|c|c}
   p(\text{MPa}) & 1 & 2 & 3 \\
   r_b(\text{mm/s}) & 2.2 & 3.1 & 4.0 \\
\end{array} \]

From Kubota, Propellants and Explosives, 2002

\[ \begin{array}{c|c}
   \text{NC} & 53.0 \\
   \text{NG} & 40.5 \\
   \text{DEP} & 4.0 \\
   \text{2NDPA} & 2.5 \\
\end{array} \]

\[ H_{\text{exp}} = 4.36 \text{ MJ/kg} \]
Flame Structure of Double Based Propellants

- Condensed phase mechanisms are often neglected due to the lack of their understanding.
- In addition to possible vaporization, initial condensed phase decomposition is assumed to occur at the surface.
- A pyrolysis law relates the surface temperature to the rate of reaction, e.g., Zenin (1980) from empirical studies developed the following pyrolysis law for DB propellants:

\[ m'' \left( \text{g/m}^2 - s \right) = 1.8 \times 10^3 \exp \left( - \frac{5000}{T(K)_{s}} \right) = r_b \rho_p \]

- Various types of thermolysis experiments where the surface is heated in a low temperature (and often low pressure) gas environment are used to measure the species composition evolving from the surface.
Flame Structure of Double Based Propellants-cont’d

• The condensed phase of very few simple ingredients, such as RDX, and a few simple binary mixtures, have been studied

• Detailed gas-phase processes, including complex elementary reaction mechanisms, heat transfer, and multicomponent diffusion have been used in one and two dimensions to study the flame structure and burning rate behavior.

• One example is the work of Miller and Anderson (2000) who have developed detailed models to study flame structure and predict burning rates of multi-ingredient DB propellants
Comparison of calculated burning rate of a JA2 propellant with measured data

JA2 propellant example:
60% by wt NC
15% by wt NG
25% by wt DEGDN

Mole fractions of Condensed-Phase Decomposition Products at Propellant Surface:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO2</td>
<td>0.2771</td>
</tr>
<tr>
<td>HONO</td>
<td>0.0579</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>0.0211</td>
</tr>
<tr>
<td>HCO</td>
<td>0.1050</td>
</tr>
<tr>
<td>CH2O</td>
<td>0.2415</td>
</tr>
<tr>
<td>CH2</td>
<td>0.0919</td>
</tr>
<tr>
<td>CH3</td>
<td>0.0140</td>
</tr>
<tr>
<td>CH4</td>
<td>0.0070</td>
</tr>
<tr>
<td>CO</td>
<td>0.1574</td>
</tr>
<tr>
<td>H</td>
<td>0.0271</td>
</tr>
</tbody>
</table>

Miller and Anderson (2000)
Comparison of measured and calculated temperature and NO mole fraction profiles for a JA2 propellant at $T_i = 294$ K

Miller and Anderson (2000)
Thermal Decomposition Mechanisms of RDX

- *Homolytic cleavage of an N-N bond* to form NO₂ plus a residual molecule RDR (H₂CNNO₂)₂(H₂CN), which subsequently decomposes to form various products

- *Concerted decomposition of the ring* to form three methylene nitramine molecules (MN; H₂CNNO₂)

- *Successive HONO elimination* to form three HONO and 1,3,5 triazine (TAZ, C₃H₃N₃), with subsequent decomposition to three HCN molecules
Decomposition of RDX at High Temperatures


\[ \text{#n (ΔE) : Position, Order, and Energy of Chain Bond Breaking (Energy in kcal/mole)} \]
Potential Energy Profile for RDX Thermal Decomposition via Homolytic N-NO$_2$ Bond Cleavage

TS – Transition State
INT – Intermediate Species
MN – Methylene nitramine (CH$_2$NNO$_2$)
MNH - CH$_2$NHCHNNO$_2$ radical
RDR – RDX after losing one NO$_2$
RDRO – RDR with the C-N ring opened

Prod1: RDX$\rightarrow$NO$_2$+HCN+MN+MNH + $\Delta H_{r1}$ (=64.5 kcal/mol)

Prod2: RDX$\rightarrow$NO$_2$+2MN+CH$_2$N+ $\Delta H_{r2}$ (=75.8 kcal/mol)

Prod3: RDX$\rightarrow$2NO$_2$+MN+CH$_2$NCHNH + $\Delta H_{r3}$ (=44.3 kcal/mol)

From Chakraborty et al., 2000)
Potential Energy Profile for RDX Thermal Decomposition via HONO Elimination

Prod1: RDX $\rightarrow$ 2HONO + MN + 2HCN + $\Delta H_r1$ (=24.8 kcal/mol)

Prod2: RDX $\rightarrow$ 3HONO + 3HCN + $\Delta H_r2$ (=14.2 kcal/mol)

From Chakraborty et al., 2000)
## Condensed Phase Chemical Kinetic Studies

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simultaneous thermogravimetric modulated beam mass spectroscopy (STMBS)</td>
<td>$10^{-2}$ K/s</td>
</tr>
<tr>
<td>R. Behrens - Sandia</td>
<td></td>
</tr>
<tr>
<td>T-jump/FTIR</td>
<td>$10^3$ K/s</td>
</tr>
<tr>
<td>T. Brill - U Delaware</td>
<td></td>
</tr>
<tr>
<td>Confined Rapid Thermolysis</td>
<td></td>
</tr>
<tr>
<td>S. Thynell – Penn State</td>
<td></td>
</tr>
<tr>
<td>Pulsed laser heating / thermal quench</td>
<td>$10^7$ K/s</td>
</tr>
<tr>
<td>C. Wight - U Utah</td>
<td></td>
</tr>
</tbody>
</table>
Measured $\text{N}_2\text{O/NO}_2$ ratio after 10 s at 5 atm Ar from T-jump/FTIR spectroscopy of HMX and RDX

after Brill, 1995
Condensed-Phase Reaction Mechanisms


\[
\begin{align*}
4(3) \text{(CH}_2\text{O + N}_2\text{O)} & \quad (-29 \text{ kcal/mol}) \quad 1 \\
\text{HMX(RDX)} & \\
4(3) \text{(HCN + HONO)} & \quad (28 \text{ kcal/mol}) \quad 2 \\
\text{CH}_2\text{O + NO}_2 & \rightarrow \text{CO + NO + H}_2\text{O} \quad (-44 \text{ kcal/mol}) \quad 3
\end{align*}
\]

<table>
<thead>
<tr>
<th>RDX Thermal Decomposition Rate Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>


Global 10 step condensed phase reaction mechanism obtained by inverse-based iterative fitting
Thermal Decomposition of Liquid Phase RDX

- Elementary reactions identified using *ab initio* quantum chemistry methods including density functional theory
- Liquid phase reactions are simulated using the conductor-like polarizable continuum for solvation with water as solvent

P1: HONO elimination

P2: N-NO₂ homolysis

Patidar and Thynell, Combustion & Flame, Vol. 178, April 2017
Thermal Decomposition of Liquid Phase RDX

P3: Reaction with NO and formation of ONDNTA

P4: Prompt oxidation via HONO and ONNO₂ addition

P5: Hydrogen abstraction via NO₂

Patidar and Thynell, Combustion & Flame, Vol. 178, April 2017
Thermal Decomposition of Liquid Phase RDX

- Confined rapid thermolysis/FTIR spectroscopy, where 0.5mg of RDX is heated at 2000K/s to 548 K at 1 atm
- HONO elimination is more significant than N-NO₂ homolytic cleavage in liquid phase
- HONO elimination is followed by ring opening instead of successive HONO elimination

From Patidar and Thynell, Combustion & Flame, Vol. 178, April 2017, pp. 7–20; Khichar, Patidar and Thynell, 10th National Combustion Meeting, April 23-26, 2017; results on HMX decomposition is also presented at the 10th National Combustion Meeting.
Temperature Profiles in Various Flame Zones and Condensed-Phase Regions of Nitramine Monopropellant

Formation of NO\textsubscript{2} and HCN favored at higher temperature

Formation of N\textsubscript{2}O and CH\textsubscript{2}O favored at lower temperature.

Luminous flame zone

Dark zone

Primary reaction zone

Carbonaceous layer

Foam layer

Condensed phase reaction region

Crystal phase transition region

Inert heating region

RDX
Modeling of RDX Combustion

- Numerical models have included detailed chemical kinetics and transport phenomena in the gas-phase and thermal decomposition and subsequent reactions in the condensed phase
- Formation of gas bubbles in the subsurface layer to molecular degradation and evaporation has also been included
- Model for RDX Combustion by Liau and Yang
RDX Monopropellant Deflagration
Effect of Pressure

\[ T_{\text{initial}} = 293 \text{ K} \]
Calculated temperature Profiles of Self-Sustained RDX Combustion at Various Pressures
Comparisons of Calculated and Measured Major Species Concentrations at P=0.5 atm

(a) Calculated results of Liau and Yang (1995)

(b) Measured data of Korobeinichev et al. (1985)
Effect of Pressure on Foam Layer Thickness, Surface Temperature, and Void Fraction for RDX Deflagration

(a) Foam layer thickness

(b) Surface temperature and void fraction
Temperature Sensitivity Calculations

- HMX $\sigma_p$ increases dramatically at low pressure
- RDX $\sigma_p$ increases slightly at low pressure
- AP $\sigma_p$ constant
- Washburn HMX condensed phase model includes Marangoni surface tension effect

Washburn & Beckstead 2006
Typical Solid Composite Propellant Mixture

~12% Binder (HTPB)
~18% Aluminum
~70% Oxidizer

- Very heterogeneous burning surface
- Dimensions don’t allow direct combustion measurements
- Crystals are not round - irregular shapes

- Fine oxidizer ~1-15 μm (bacteria to talcum powder)
- Aluminum ~ 20-50 μm
- Medium oxidizer ~ 20-90 μm (white blood cell to hair)
- Coarse oxidizer ~ 200-400 μm (fine to medium beach sand)
Hierarchical Approach Applied

Start with the simplest systems and work up, with validations at each step

• 1-D Monopropellant: Single ingredient
  – Gas phase and condensed phase chemistry development
  – Surface regression models

• 1-D Composite propellant: Add chemical complexity without spatial complexity
  – Chemistry interaction

• 1-D Counterflow: Add diffusion flame, but remain 1-D
  – Chemistry with fluid dynamics
  – Oxidizer with binder decomposition product chemistry
Hierarchical Approach – cont’d

• 2-D Sandwich and axisymmetric: Idealized diffusion flame in 2-D
  – Multidimensional flames
  – Full fluid dynamic coupling
  – Surface regression interactions

• 2-D with realistic packing: Diffusion flame interactions and evolving surface geometry
  – Simulation of oxidizer/binder distribution
  – Platform for development of reduced chemical models

• 3-D with realistic packing: Full propellant system
  – Propellant design tool
Why Kinetics Based Models Necessary

- $I_{sp}$ and $T_f$ easily calculated from thermodynamics, but...
- *Kinetics* controls *critical* ballistic properties
  - Burning rate, pressure exponent, $T$ sensitivity, ignition and transient combustion, combustion instability, cookoff, DDT
- *Must* know ballistics to design rocket motor
  - *Only 33% error in burning rate can lead to 300% overpressure and catastrophic failure of system*
  - *Pressure exponent critical to system design, for example*...
    - Mesa for operational stability or high exponent for pintle throttllability
- *Global Models Inadequate*
  - Don’t uncover real kinetic mechanism
  - Can’t predict combustion instability, ignition, DDT etc.
  - Can’t help design new propellants based on new materials
AP Propellant Properties

• AP is very atypical oxidizer
• Widely used oxidizer
• Significantly increased burning rates relative to pure AP
• Significant particle size effect
  – Smaller particles → faster rate
• 30% excess O₂
• 1.3 hazard classification
  – PDL ~ 20 atm
  – ΔHₖ -71 kcal/mol
• Chlorine chemistry
  – HCl products

Composite AP-based solid propellants use a bimodal distribution of particle sizes for increasing propellant density and controlling burning rate.

Microscale flame structure above a bimodal composite AP propellant. Represented here are the (1) monopropellant flame, (2) pseudo-premixed flame, (3) final diffusion flame, and (4) leading-edge flame.

AP Decomposition Kinetics and Monopropellant Deflagration

- Chen and McQuaid (2014 JANNAF CS Meeting) have developed the most recent gas-phase mechanism consisting of 788 reaction rate expressions and 105 species.

- The condensed phase mechanism remains uncertain. Most recently, Zhu and Lin (J. Phys. Chem. C 112 (2008) 14481) proposed a dissociative sublimation mechanism of crystal NH₄ClO₄(c) that involves a NH₃...HClO₄(g) complex.

  \[
  \text{NH}_4\text{ClO}_4(\text{c}) \leftrightarrow \text{NH}_4\text{ClO}_4(\text{s}) \leftrightarrow \text{NH}_3...\text{HClO}_4(\text{g}) \leftrightarrow \text{NH}_3(\text{g}) + \text{HClO}_4(\text{g})
  \]

  where \( \text{NH}_4\text{ClO}_4(\text{s}) \) corresponds to a relaxed surface of the crystal.
Propellant Surface and Sub-Surface

• Condensed phase and interface/surface phenomena is the least understood
  – The surface reaction zone is very thin, multiphase, and has a steep temperature gradient
• Several studies used cinephotomicrography to observe burning surface, then sample was quenched and examined using scanning electron microscopy
• Other studies used fast thermolysis and FTIR to measure decomposition products
• Typically microthermocouples are embedded within propellant sample at various distances from the surface to measure thermal response of propellant
• Need information on condensed phase reactions, AP phase changes and binder decomposition before reaching the burning surface
1-D Diffusion Flame

- 1D counter-flow configuration
  - Oxidizer + binder chemical interaction without spatial complexity
  - 1D flame allows rapid turn around 1D model
  - Enormous expansion of length scale
    - Sandwich flame standoff 100 microns
    - Counter-flow standoff 5 mm

2D Gaseous Fuel AP Diffusion Flames

• With kinetics finalized via 1D counter-flow flames, extended model and experiment to 2D geometry
• Started with simplicity of the same gaseous fuel (methane or ethylene) as 1D work
• Axisymmetric (experiment and modeling)
  – Small fuel hole in center of big domain of AP Drilled hole in AP pellet
  – 990 μm down to 60 μm
  – O-ring seal to AP cylinder
  – CH₄ fed below at desired rate
  – CH₄ exit velocity was 9.75 m/sec peak, parabolic flow

Effects of pressure and particle size on burning rate

- Premixed limit represents maximum rate for given AP%
- Burning rate vs. particle size curve shifts up and to the left
- Premixed cutoff size decreases with pressure
  - %AP in homogenized binder decreases with pressure

3D Modeling of Heterogeneous Propellants

• Over the past two decades, parallel computing has become a staple of engineering calculations, with multidimensional simulations of heterogeneous propellants following this trend

• Jackson and Buckmaster carried out first three dimensional simulation of solid propellant in 2000

• Random packing algorithms are used to generate the microstructure of a heterogeneous propellant and an unsteady solid gas numerical code for the combustion problem
Random Packing Algorithm for Generating Realistic Microstructures

A number of random packing algorithms have been developed for energetic materials (see T.J. Jackson, AIAA Journal 50, 5 (2012) 993.)

Validation of the packing codes are carried out by comparing first-order (volume fraction) and second order statistics to those of surrogate propellants as well as actual AP based propellants using x-ray tomography

- 10,002 particle pack that models the Miller M24 pack (R.R. Miller, AIAA 1982-1096)
- Gray spheres have diameters in the range 5-15 μm, blue spheres have diameters 16-42 μm, and red spheres have diameters 46-211 μm
- Void regions correspond to binder
- Domain is cubic with periodic boundaries, and only those particles with centers inside cube are shown

From T.L. Jackson, AIAA Journal 50, 5, May 2012, 993
Chemistry for Heterogeneous Propellants

- The inclusion of elementary kinetics (hundreds of species) for the gas-phase is well beyond the scope of today’s most powerful supercomputers; and the condensed phase chemistry remains generally poorly understood.

- Simple global kinetic schemes are adopted, and the challenge is identification of the appropriate parameters for the kinetics.

- In the context of AP/HTPB propellants, a three step model, familiar from the BDP model is used, characterized by an AP diffusion decomposition flame, primary diffusion flame, and secondary diffusion flame.

\[
\begin{align*}
AP & \xrightarrow{R_1} P_d \quad \text{(AP products)} \\
AP + HTPB & \xrightarrow{R_2} P_{pdf} \\
HTPB + P_d & \xrightarrow{R_3} P_{sdf}
\end{align*}
\]

- Based on the 2D single particle AP/HTPB modeling results, the mechanism was modified to a 4-step reaction that included a premixed binder flame above the homogenized AP/HTPB mixture.

From T.L. Jackson, AIAA Journal 50, 5, May 2012, 993
Premixed Binder

- Assume fine AP and HTPB form homogeneous mixture
  - Experimentally supported
  - AP/HTPB react in premixed, laminar reaction zone
  - Limits numerical resolution (Shorter runtime)
AP/HTPB composite propellant burning as a function of pressure

As pressure increases, the premixed flames draws closer to the surface, resulting in a faster burning rate, and the stand-off distance of the diffusion flame increases, decreasing the flame’s contribution to burning rate and increasing the surface topology

From Gross et al. Comb. Flame 160 (2013) 982
Surface topography and temperature level surfaces for a sample 3D propellant burning at 20 atm

Shown is the instantaneous 3D combustion field for an 18 wt% Al, 54wt% AP propellant

The spheres above the propellant surface are aluminum particles, colored according to their surface temperatures

For submicron aluminum, modeling has been performed where the submicron aluminum is homogenized into the binder

- Studies with aluminum particles are limited
- Studies are necessary that consider surface tension, ignition, phase change, agglomeration, collision, sintering, radiation for proper understanding

From T.L. Jackson, AIAA Journal 50, 5, May 2012, 993