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Reactive Processes In Energetic Materials

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Reactive Processes in Energetic Materials

This project develops the scientific tools for understanding the reactive chemistry that drives explosives, propellants, and pyrotechnics.

Explosives

Current Materials: FOX-7, CL-20, DNAN, HNS, LLM-201, RDX, HMX

Formulations: PBXN-111, PBXN-109, IMX-101, IMX-104

Propellants

Current Materials: AP, AP/HTPB

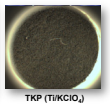
Formulations: AP/Al/HTPB Rev. Cure HTPB

Pyrotechnics

Current Materials: TKP ($Ti/KClO_4$), THKP ($Ti_2/KClO_4$)

FOX-7

AP/Al/HTPB



TKP ($Ti/KClO_4$)

Our work is focused in 6 areas:

Safety and IM Properties
What conditions cause violent reaction?
Can we mitigate violence?

Shock Initiation and Thermal Ignition
Can we predict when materials will initiate or ignite?

Aging
Do reactions at ambient temperature change performance or properties over time?
How can we predict changes in materials?

Interactions Between Ingredients and at Interfaces
How do energetic and inert ingredients interact to affect performance and IM properties?

New Energetic Compounds
Understanding the properties of new energetic materials

Modeling Reactive Processes in Energetic Materials
How can we describe reactions and physical changes in complex materials?

Energetic Materials: Chemically-Driven Systems

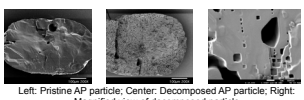
Energetic Materials are complex chemical systems and are difficult to characterize using conventional chemical techniques, requiring new and comprehensive strategies.

- Most chemical understanding comes from gas phase or dilute solutions
- Reactions in EM are rarely A → B reactions
- We do not generally understand the chemistry that controls phenomena of interest

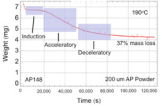
- Reactions involve:
  - Multiple steps
  - Hard to observe species
  - Fast events
  - Multiple phases
  - Transport-limited reactions
  - Morphology, particle size effects

Example: Ammonium perchlorate thermal decomposition

Ammonium perchlorate undergoes partial decomposition (~30%) and stops, leaving microporous material with same gross morphology



Left: Pristine AP particle; Center: Decomposed AP particle; Right: Magnified view of decomposed particle



R1: $NH_4ClO_4(cr) \longleftrightarrow NH_3(g) + HClO_4(g)$

R2: $NH_4ClO_4(cr) \longrightarrow H_2O(v^*) + O_2(v^*) + HCl(v^*) + N_2O(v^*) + NO_2(v^*) + Cl_2(v^*) + NH_4ClO_4(m.s.)$

R3: $NH_4ClO_4(cr) \xrightarrow{\Delta E_a} NH_4ClO_4(sub)$

R4: $H_2O(+\Delta E) + O_2(v^*) + HCl(v^*) + N_2O(v^*) + NO_2(v^*) + Cl_2(v^*) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g)$

R5: $NH_4ClO_4(sub) \longleftrightarrow NH_3(g) + HClO_4(g)$

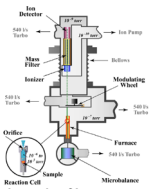
R6: $NH_4(sub) + HClO_4(sub) \rightarrow NH_4ClO_4(m.s.) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g) + NH_4ClO_4(m.s.)$

R7: $NH_3(g) + HClO_4(g) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g)$

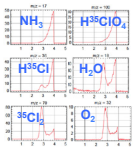
Time-Resolved Mass Spectrometry

We use time-resolved mass spectrometry to characterize reaction chemistry at moderate temperatures

- Programmable thermal controller heats sample from 25ºC – 1100ºC
- Microbalance records mass loss (10 µg to 1 g mass range with 2 µg accuracy)
- Inert reaction cell with variable confinement (1 mTorr to 10 atm)



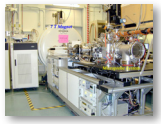
Schematic of Instrument



Quantitative ion signals allow determination of reaction products and mechanism

High-Precision Mass Spectrometry

We use Fourier-transform mass spectrometry to uniquely determine chemical formulas of observed species



- **High mass resolution (m/Δm = 60,000-1,000,000)**
  Ions with same nominal mass can be easily separated
  $^{12}C^{16}O$ = 27.99491,
  $^{14}N_2$ = 28.00614,
  ^{28}Si = 27.9769 amu
- **High mass accuracy (< 1 ppm)**
  Unambiguous determination of molecular formula
- **High molecular weight capability**
  Up to 30,000 Daltons – polymers, binders, residues, etc.

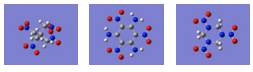
Example: PETN

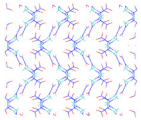
- Molecular weight: 316.01386 amu
- There are 236 C,H,N,O compounds with mass 316.01386 ± 0.3 amu
- There is only ONE C,H,N,O compound with mass 316.01386 ± 0.001 amu
- Its formula is $C_5H_8N_4O_{12}$

PETN

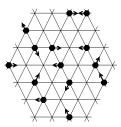
Reaction Modeling

We are developing theoretical models to understand shock-induced and thermal reactions in energetic materials.





Quantum chemical modeling of shock-induced reactions at the molecular scale

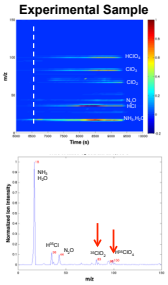


Multiscale modeling of thermal reactions

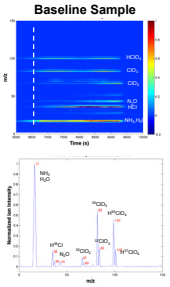
Understanding IM Response

Working with NAWC/China Lake, we have helped understand the improved IM (cookoff) properties of new experimental propellants.

Experimental Sample



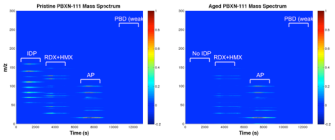
Baseline Sample



The data shown here indicate much lower evolution of perchloric acid in the experimental sample, indicating more effective absorption of reactive species by binder.

Aging of Energetic Formulations

Working with NSWC/Indian Head, we have helped understand reactions that occur in AP/Al/RDX/HTPB explosive formulations during accelerated aging.

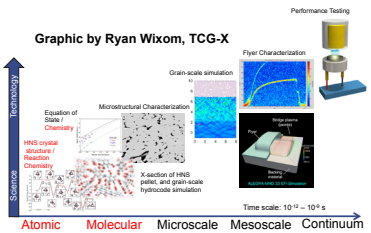


Data shown here indicate loss of plasticizer as primary change that occurs during accelerated aging of PBXN-111, with minor changes in RDX, AP, and HTPB. Results are being used to develop predictive models of natural aging.

Developing Predictive Models of Shock Initiation

Working with colleagues at SNL/NM, we study reactions computationally on the molecular scale to determine the conditions needed to initiate reactions under shock conditions relevant to Sandia explosive components.

Graphic by Ryan Wixom, TCG-X



Results from molecular scale are fed up to higher scales, allowing predictive modeling of explosive components.

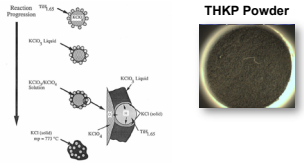
Enabling Predictive Modeling of Thermal Ignition

Working with colleagues at SNL/NM, we have helped develop predictive time-to-ignition models of TKP pyrotechnic powder, used in Sandia explosive components.

The chemistry that drives thermal reactions of energetic materials, such as thermal ignition, is difficult to quantify. As a result, thermal ignition events (intentional or unintentional) are difficult to predict.

We have used our mass spectrometry tools to explicitly quantify the reactive chemistry that drives thermal ignition of energetic materials. We show here an example of thermal ignition in titanium/potassium perchlorate pyrotechnic.

In this work, we determined the set of reactions that are important to ignition, and distilled that reaction mechanism down to a small set of key reactions that can be input to a macroscopic initiation model.



THKP Powder

Ti / $KClO_4$ ignition is a multi-step process, involving multiple chemical reactions, transport of species between micron-sized particles, and phase changes.

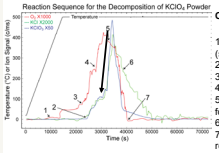
Full Reaction Mechanism

$KClO_4(s,rh) \leftrightarrow KClO_4(s,cu)$ [309°C]
$KClO_4(s) \rightarrow KClO_3(s) + O(g)$
$KClO_3(s) \rightarrow KClO_3(l)$ [356°C]
$KClO_4(s) + KClO_3(l) \rightarrow (KClO_4 + KClO_3)_{(s\text{solution})}$
$KClO_3 \rightarrow KCl(s) + \frac{3}{2}O_2(g)$
$4KClO_4 \rightarrow 3KClO_4 + KCl$
$2KClO_4 + O \rightarrow K_2O(s) + 2ClO_3(g) + O_2(g)$
$ClO_3(g) + O(g) \rightarrow ClO_4(g) + O_2(g)$
$O(g) + O(g) \rightarrow O_2(g)$
$Ti(s) + O_2(g) \rightarrow TiO_2(s)$

Reduced Reaction Mechanism

$KClO_3(s) \rightarrow KCl(s) + 2O_2(g)$
$Ti(s) + O_2(g) \rightarrow TiO_2(s)$

Generation of reactive oxygen from decomposition of $KClO_4$ is the main driver of thermal ignition



Oxygen release process:

1. Oxygen loss from KClO4 (slow)
2. Formation of KClO3
3. Liquefaction
4. Rapid release of O2
5. Depletion of O2, formation of KCl
6. Solidification
7. Termination of oxygen release

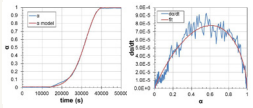
$$\frac{d\alpha_1}{dt} = f_1(\alpha_1)k_1(t) = C_1\alpha_1^{n_1}A_1\exp\left(\frac{-E_{a_1}}{RT}\right)$$

$$\frac{d\alpha_2}{dt} = [O_2(t)]f_2(\alpha_2)k_2(t) = [O_2(t)]C_2(1/\alpha_2)^{n_2}A_2\exp\left(\frac{-E_{a_2}}{RT}\right)$$

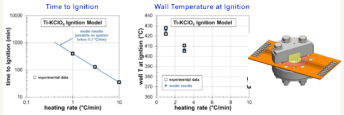
Reaction Model
Oxygen release process
Shrinking core/ thickening shell for Ti oxidation

$$\alpha_2 = \left[\mathrm{Ti}(s)\right]_0 - \left[\mathrm{Ti}(s)\right] / \left[\mathrm{Ti}(s)\right]_0$$

$$\alpha_1 = \left[\mathrm{KClO_4}(s)\right]_0 - \left[\mathrm{KClO_4}(s)\right] / \left[\mathrm{KClO_4}(s)\right]_0$$



Finite-element simulations Courtesy of W. Erikson, SNL/NM)



Finite-element model of thermal ignition:
Aluminum casing is heated (thermal source), heats EM. Model includes heat transport from case and reactions in each finite element. Extent of reaction in each element is followed. Code correctly predicts time to ignition in small-scale tests.

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