SAND2014-20292C

Reactions Controlling Thermal Response of FOX-12/RDX Mixtures

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JANNAF 46th CS, 34th APS, 34th EPSS, 28th PSHS Meeting
Small-Scale IM Screening Tests for Gun Propellants
10 December 2014
Albuquerque, NM

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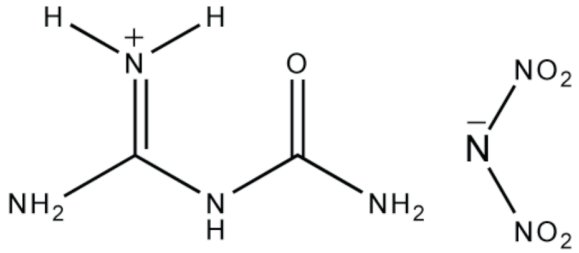
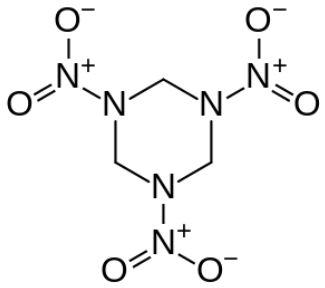
Background: FOX-12 and RDX



N-Guanylurea dinitramide
(FOX-12 / GuDN)



1,3,5-Trinitrohexahydro-*s*-triazine
(RDX)

The Navy is interested in FOX-12 as an additive in gun propellants. Partial replacement of RDX with FOX-12 reduces the sensitivity of gun propellant formulations.

What drives this reduction in sensitivity? Hayden and Behrens (2009) investigated the chemistry of FOX-12/RDX mixtures and determined the major thermal decomposition products of FOX-12 and FOX-12/RDX mixtures. Their data show that RDX decomposes at lower temperatures in the presence of FOX-12, and by a similar process to RDX alone.

New experiments have been conducted to investigate the mechanism of this interaction.

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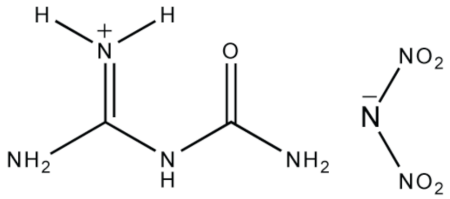
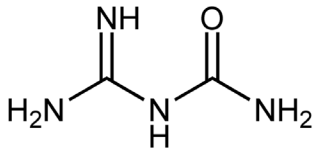
FOX-12 Thermal Decomposition

As shown by Hayden and Behrens, FOX-12 decomposes to form a number of decomposition products:



FOX-12

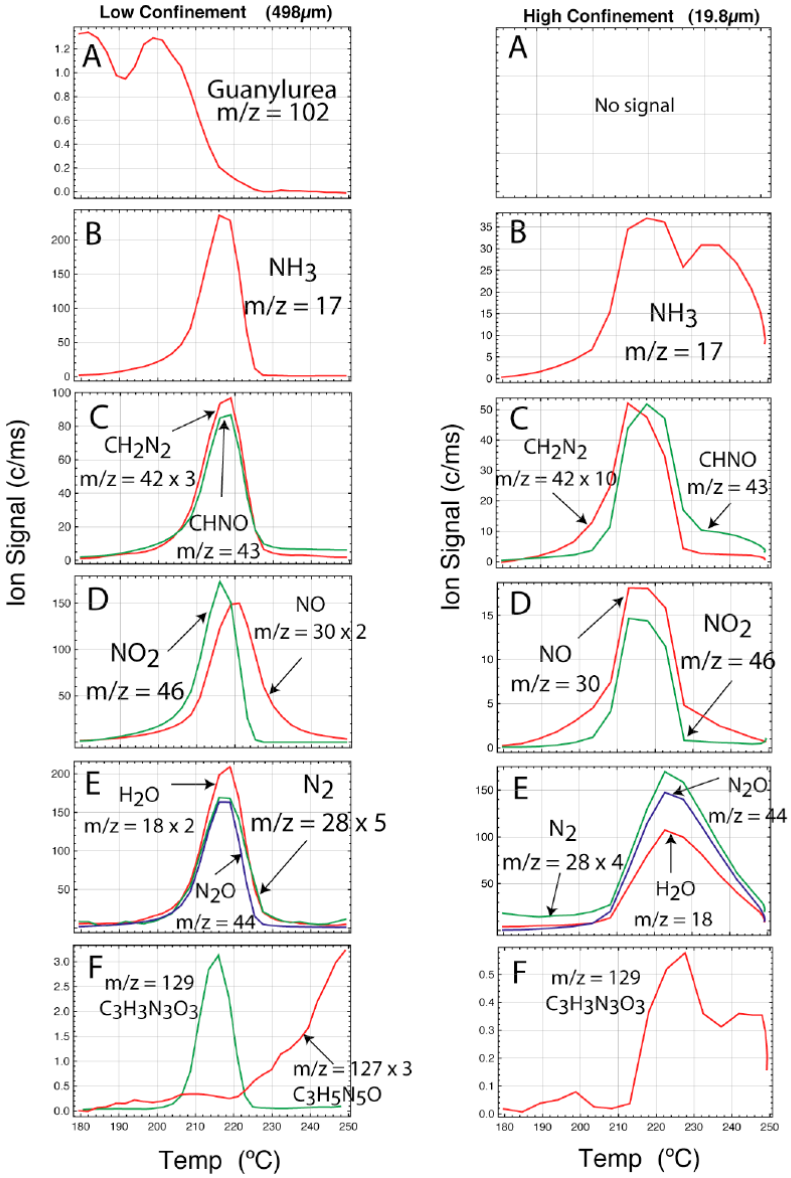


Guanylurea

NH_3, N_2, NO_2, N_2O, NO, H_2O, HOCN, CH_2N_2

$C_3H_3N_3O_3$, $C_3H_5N_5O$

FOX-12 produces a number of small gas-phase molecular products, with some higher molecular weight byproducts.



H. Hayden, R. Behrens, and D. Wiese-Smith, *JANNAF* (2009)

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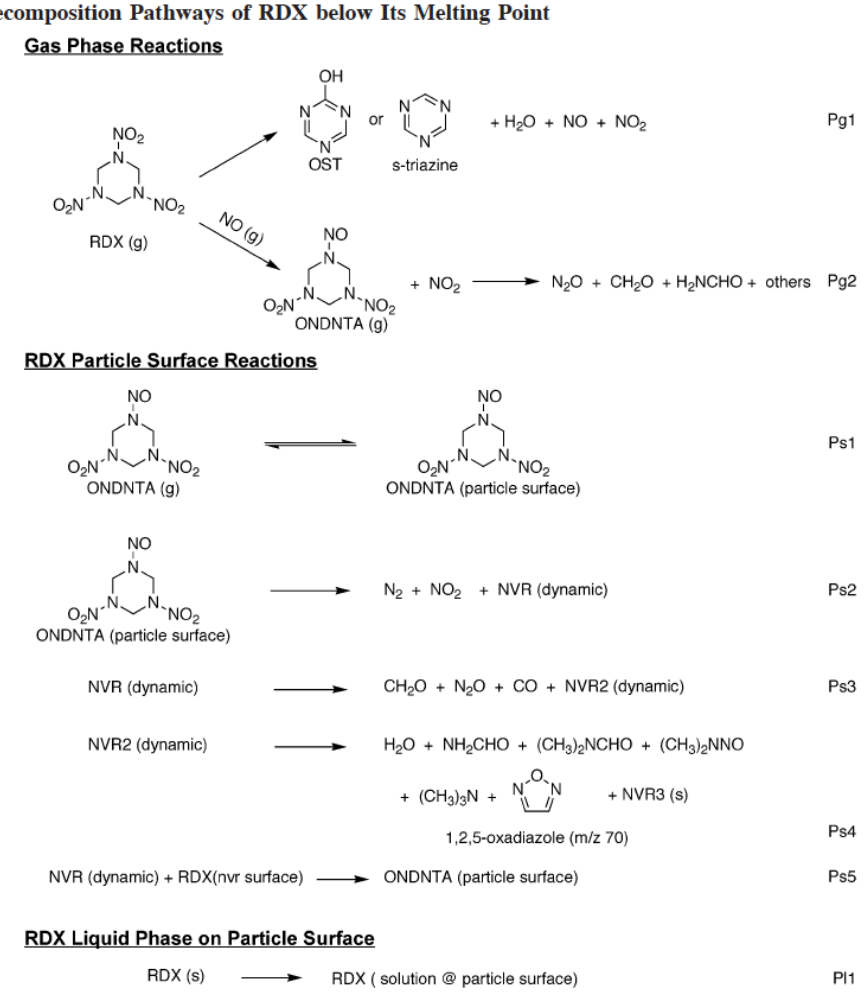
RDX Thermal Decomposition

Solid Phase

RDX is known to decompose by a complex mechanism. Decomposition below the melting point (~200°C) is slow compared to liquid-phase decomposition.

Major solid-phase decomposition products include ONDNTA (1-nitroso-3,5-dinirohexahydro-*s*-triazine), NO_2, N_2, and a nonvolatile residue (NVR). After the NVR has formed, it undergoes further decomposition to produce CH_2O, N_2O, CO, and H_2O at later times.

SCHEME 2. Decomposition Pathways of RDX below Its Melting Point



Maharrey and Behrens, *J. Phys. Chem. A* **109**, 11236 (2005)

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RDX Thermal Decomposition

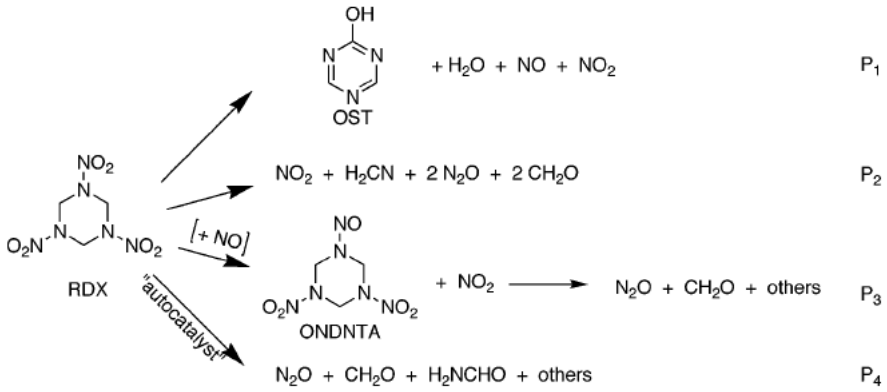
Liquid Phase

RDX is known to decompose by a complex mechanism. Decomposition above the melting point (~200°C) is much faster compared to solid-phase decomposition.

There are multiple pathways; the reaction mechanism is summarized at right.

Major gas phase products include N_2O and CH_2O (formaldehyde). The decomposition process also produces OST (oxy-*s*-triazine).

SCHEME 1. Decomposition Pathways of RDX above Its Melting Point



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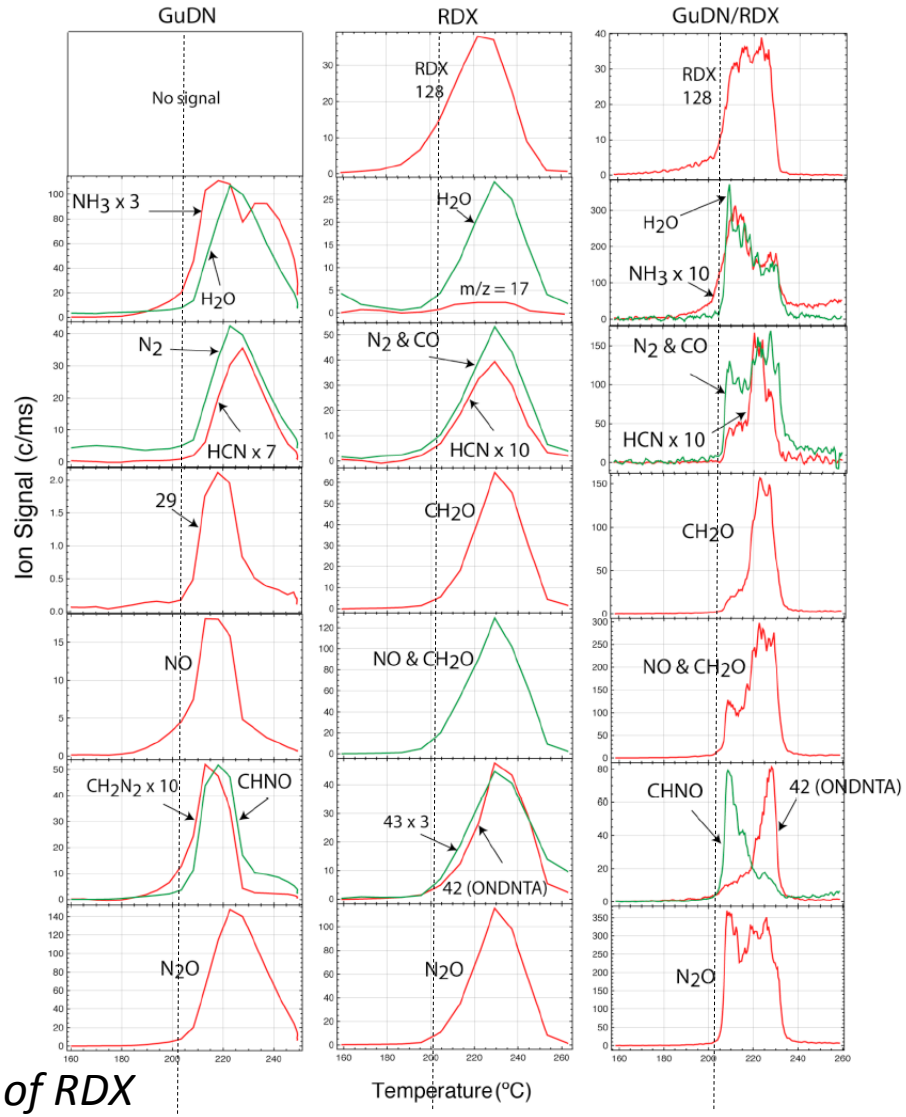
Maharrey and Behrens, *J. Phys. Chem. A* **109**, 11236 (2005)

Decomposition of FOX-12/RDX Mixtures

Hayden and Behrens showed that FOX-12 interacts with RDX, causing both species to decompose at a lower temperature.

The FOX-12/RDX interaction does not appear to substantially alter the nature of RDX's thermal decomposition pathways. It does, however, produce significantly higher amounts of NO and NO_2.

It is suspected that the decomposition products of FOX-12 accelerate decomposition of RDX, but the mechanism is not clear.



Dashed line = m.p. of RDX

H. Hayden, R. Behrens, and D. Wiese-Smith, *JANNAF* (2009)

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Decomposition of FOX-12/RDX Mixtures

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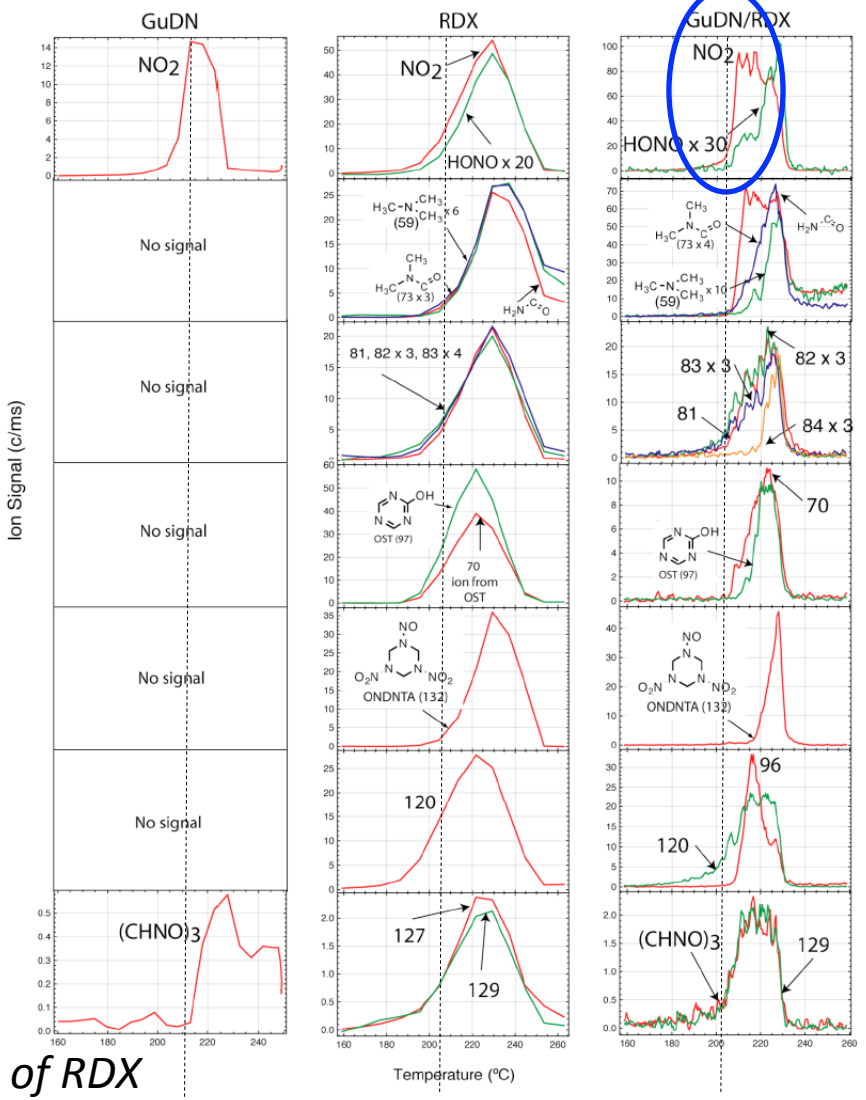
~10x more NO_2



Dashed line = m.p. of RDX

H. Hayden, R. Behrens, and D. Wiese-Smith, *JANNAF* (2009)

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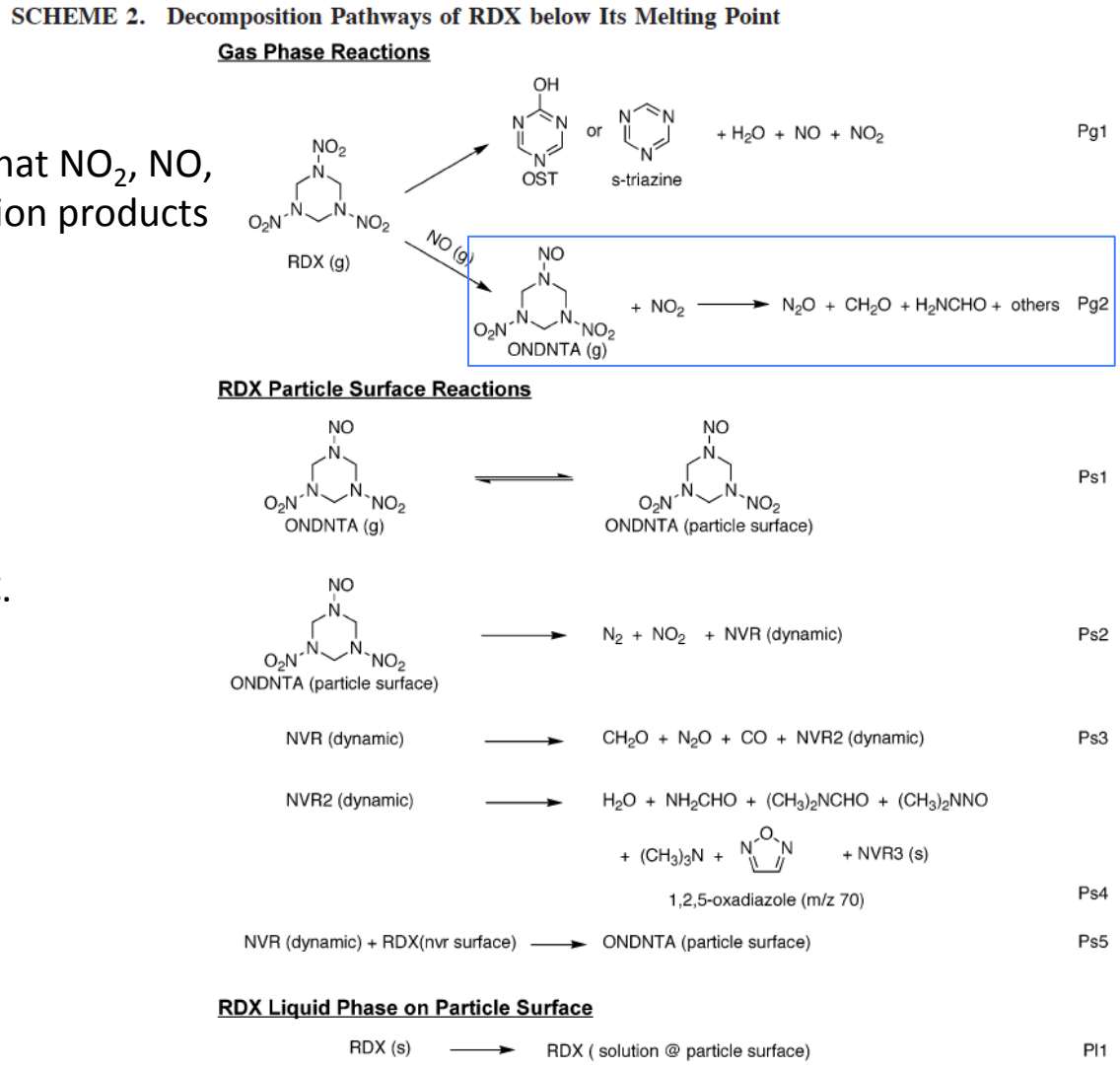
FOX-12/RDX Interaction Mechanism

The data of Hayden et al demonstrate that NO_2, NO, and NH_3 are major reactive decomposition products of FOX-12.

How would these affect RDX?

NO is well-known to easily convert RDX to its mono-nitroso analog, ONDNTA, which decomposes quickly above 165°C.

Decomposition of ONDNTA produces NO_2 and N_2 in the solid-phase decomposition of RDX, and NO_2, N_2O and CH_2O in the liquid-phase decomposition of RDX.



H. Hayden, R. Behrens, and D. Wiese-Smith, *JANNAF* (2009)

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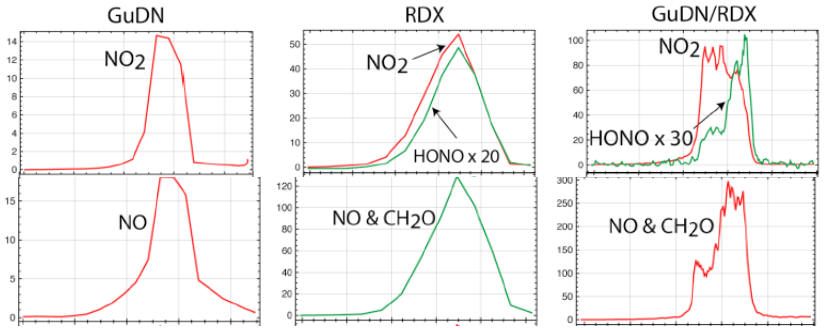
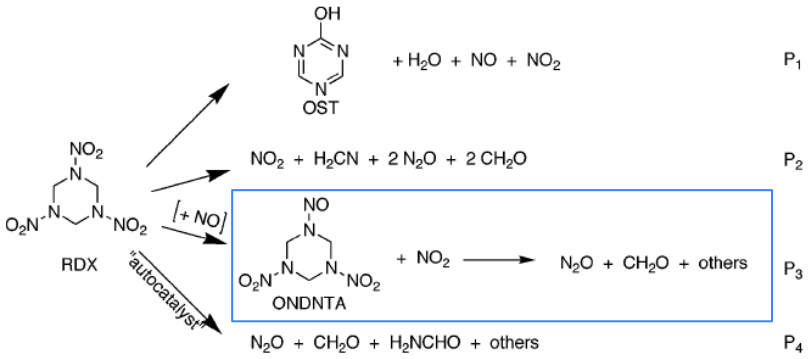
FOX-12/RDX Interaction Mechanism

Given that these products are observed in greater quantities when RDX decomposes with FOX-12, this mechanism appears quite possible.

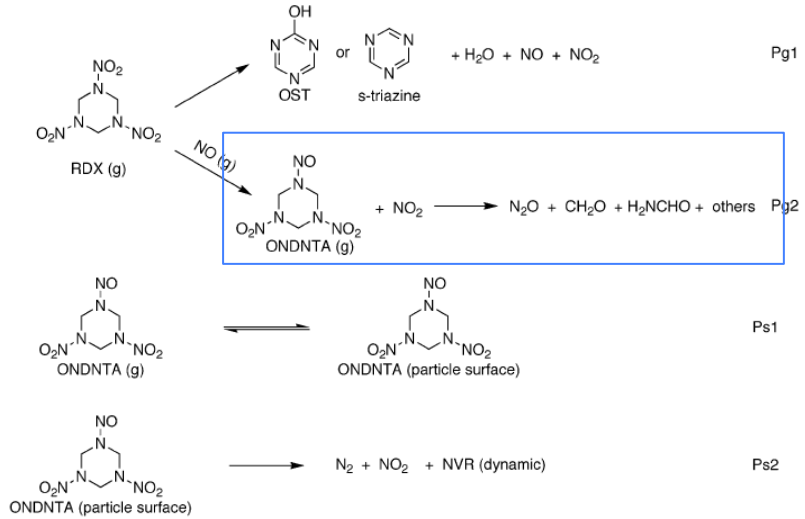
We have designed a new set of experiments to test this hypothesis.



H. Hayden, R. Behrens, and D. Wiese-Smith, *JANNAF* (2009)



Liquid-phase RDX decomposition



Solid-phase RDX decomposition

Maharrey and Behrens, *J. Phys. Chem. A* **109**, 11236 (2005)

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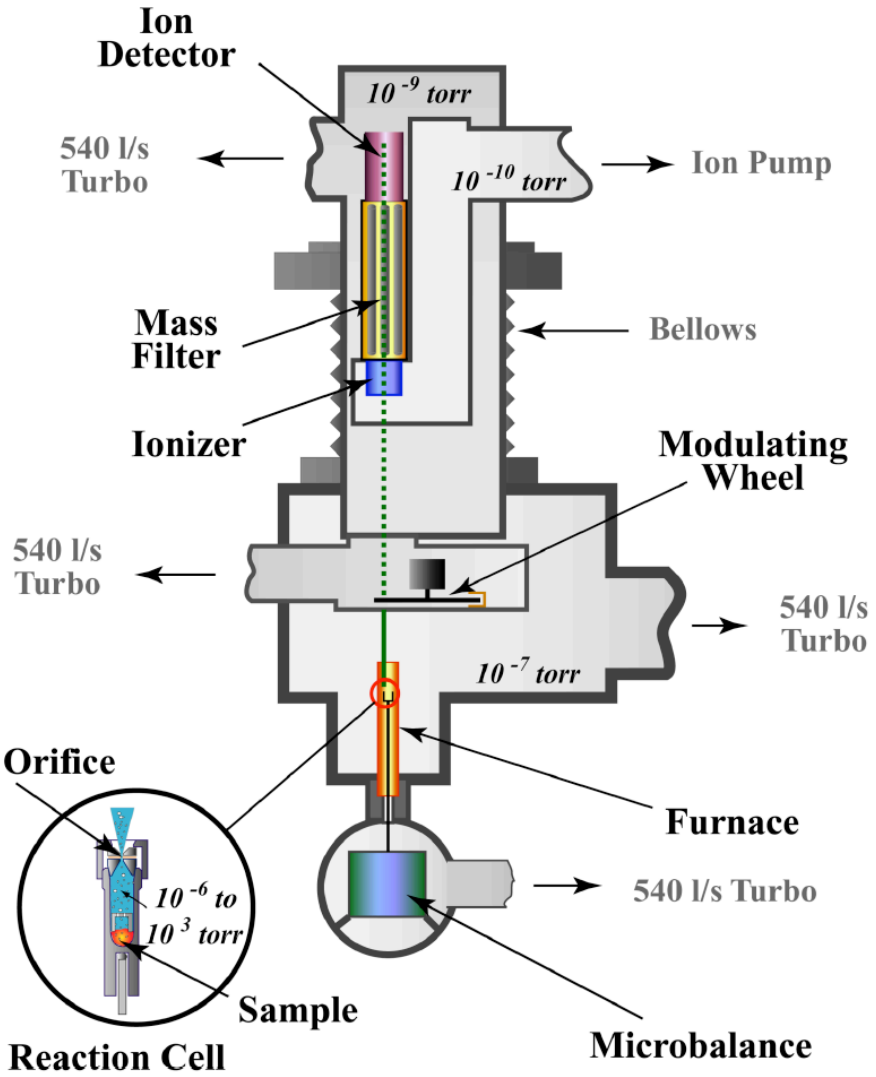
Interaction Between FOX-12 and RDX

Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry

- **Mass spectrum experiments**
  - Samples placed in reaction cell with 20 or 1000 um orifice
  - Programmable temperature control – sample heated from 25°C up to 240°C at 1°C/min
  - Microbalance simultaneously records mass loss (2 µg mass accuracy)
  - Total experiment time 2-10 hours
- **Sample information**
  - FOX-12
    - Guanylurea dinitramide
    - Bofors Lot #20047012
      Received from NSWC Indian Head 2009
  - RDX
    - Insensitive RDX (SIRDX)
    - Holston Lot #0857S00
    - Received from Picatinny Arsenal 2000 and 2014



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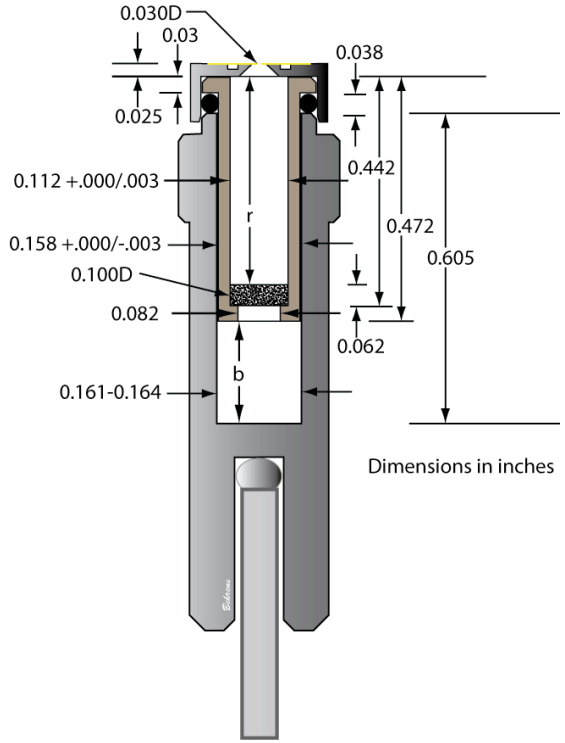
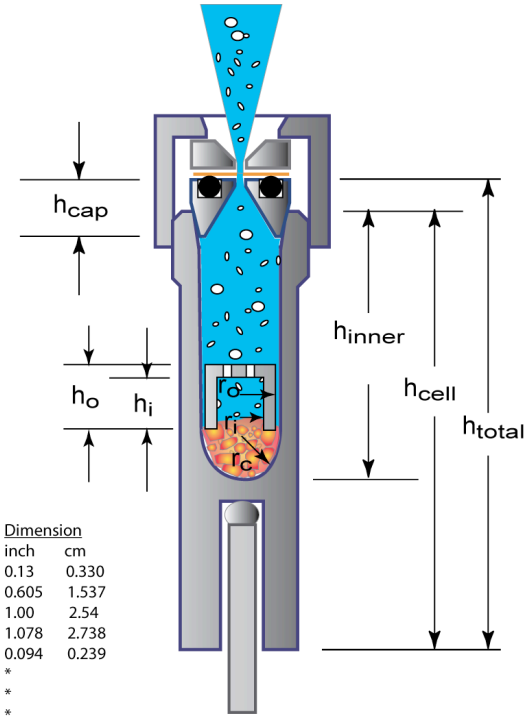
Interaction Between FOX-12 and RDX

Sample Cells

Some experiments use **flow reactor cells** to separate ingredients but allow vapors to interact:



Flow Reactor Cell



Name	Dimension inch	cm
hcap	0.13	0.330
hinner	0.605	1.537
hcell	1.00	2.54
htotal	1.078	2.738
rc	0.094	0.239
ho	*	
r0	*	
hi	*	
ri	*	

Standard Reaction Cell

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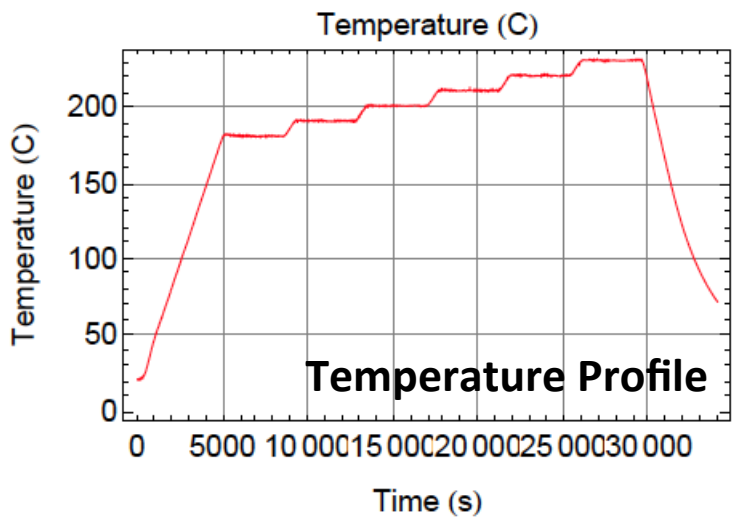
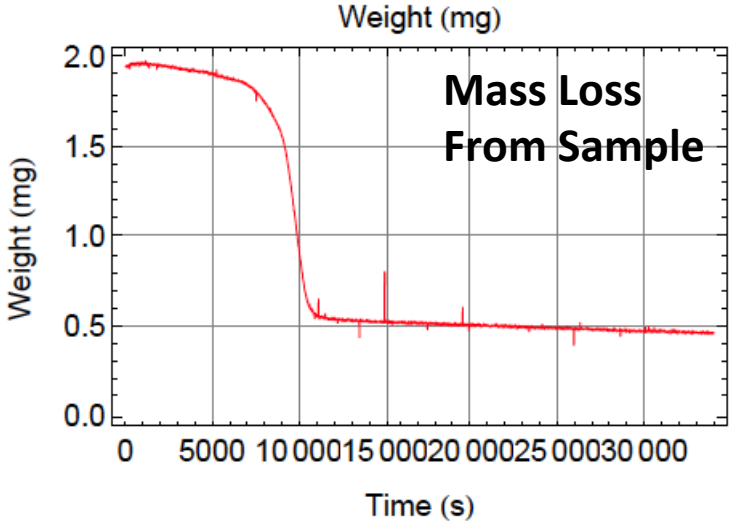
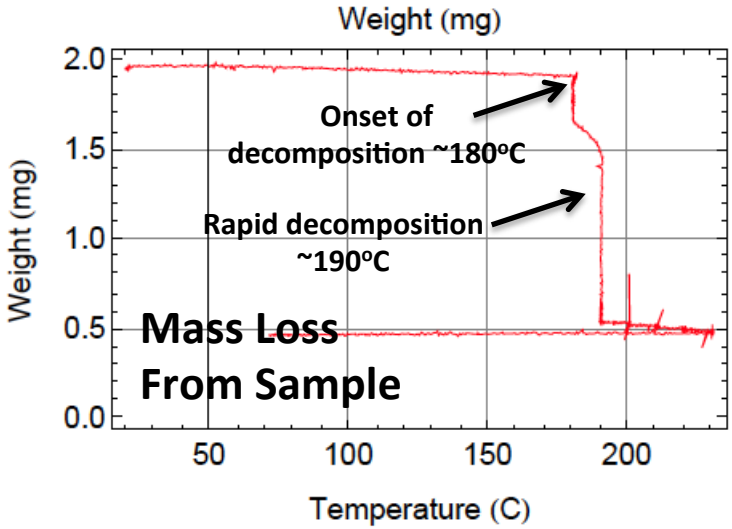
FOX-12 Decomposition





FOX-12 decomposes rapidly at ~190°C.



Standard Reaction Cell Experiment
25 micron orifice
1.87 mg FOX-12

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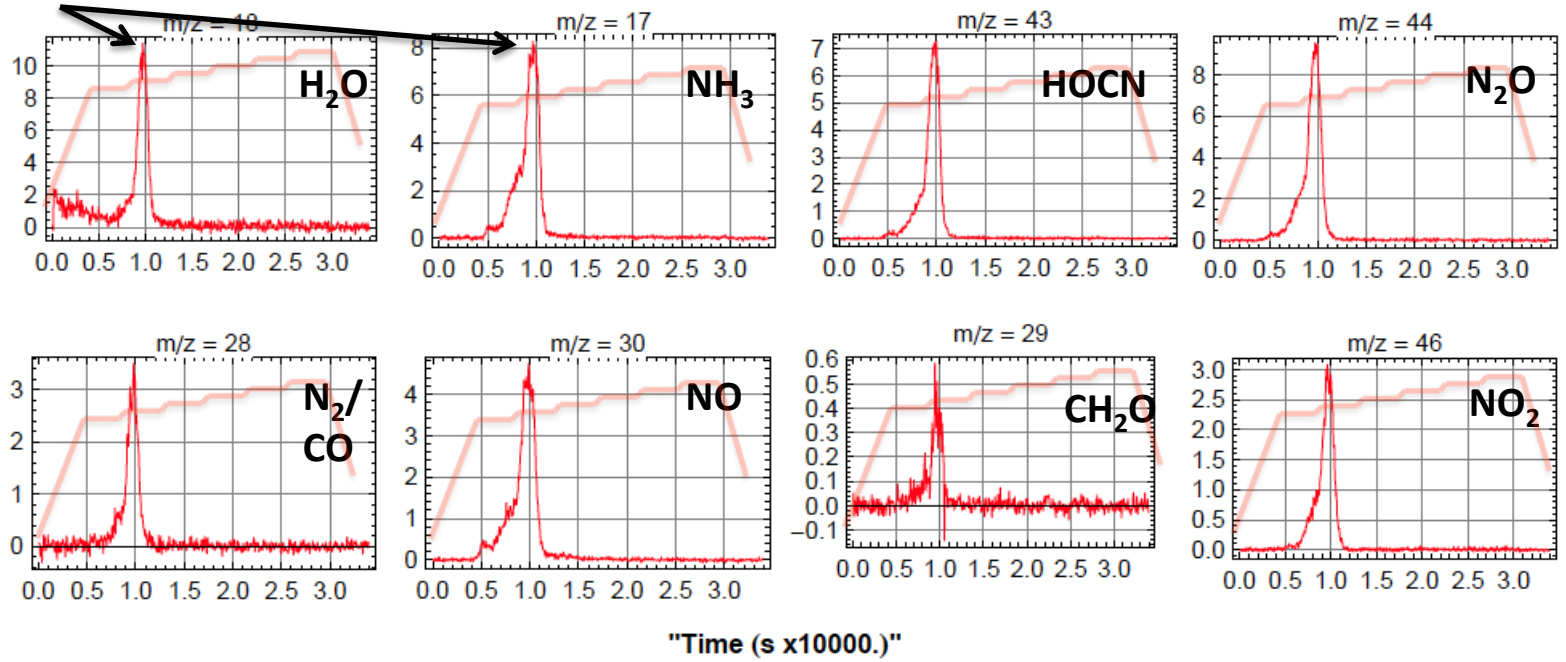
FOX-12 Decomposition

Peak of decomposition
~190°C



FOX-12 decomposes rapidly at ~190°C, producing NO, NO2, N2O, and other small gas products.

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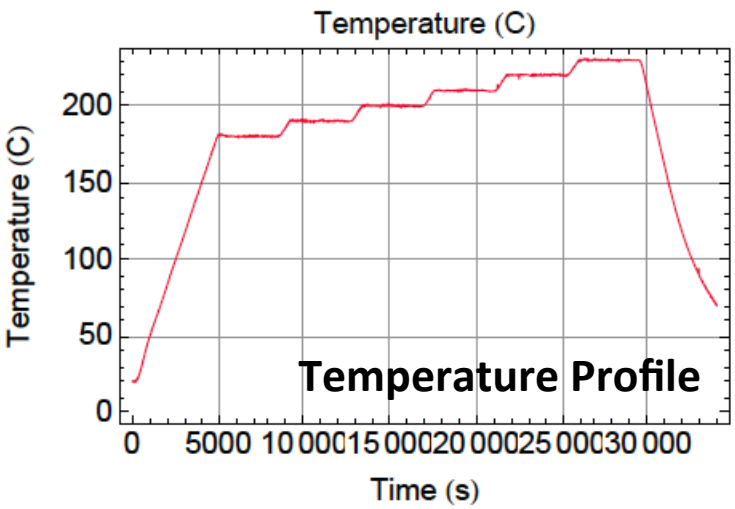
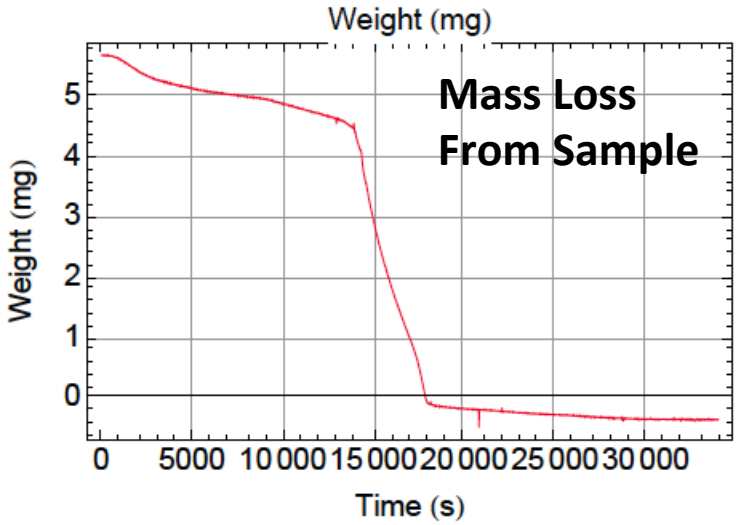
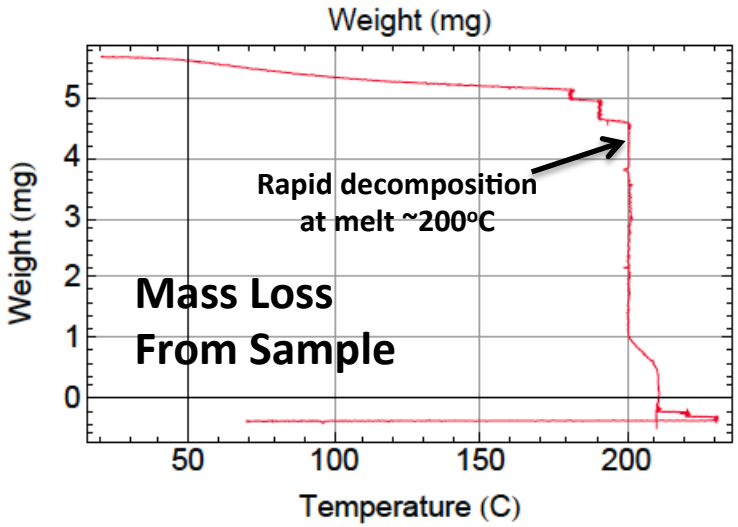
RDX Decomposition







RDX decomposes rapidly at its melting point (~200°C).

Standard Reaction Cell Experiment
25 micron orifice
5.68 mg RDX

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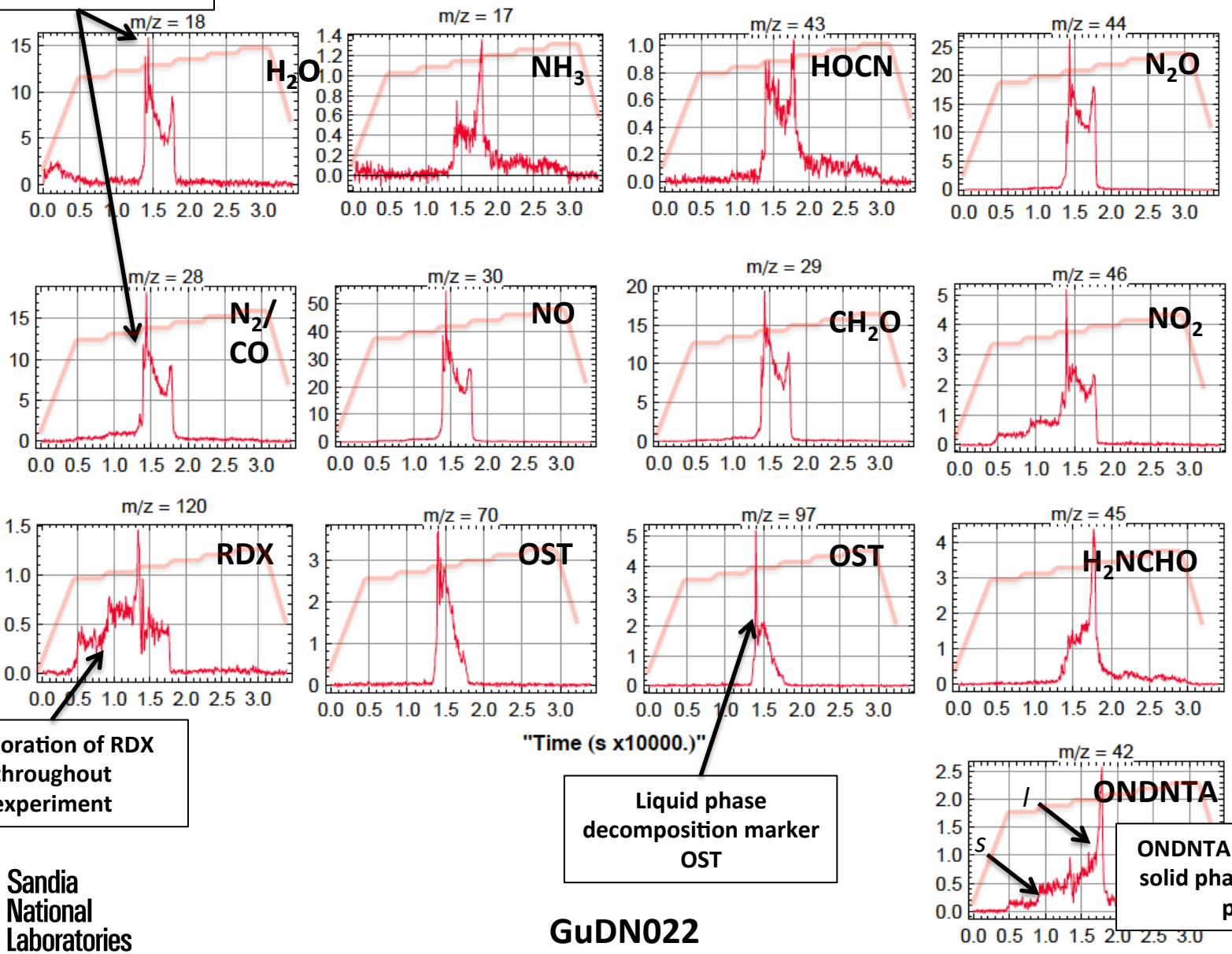
RDX Decomposition



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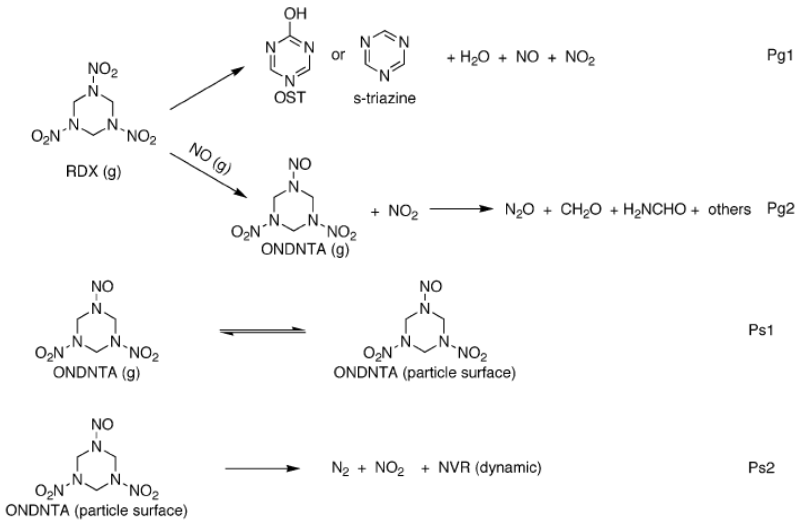
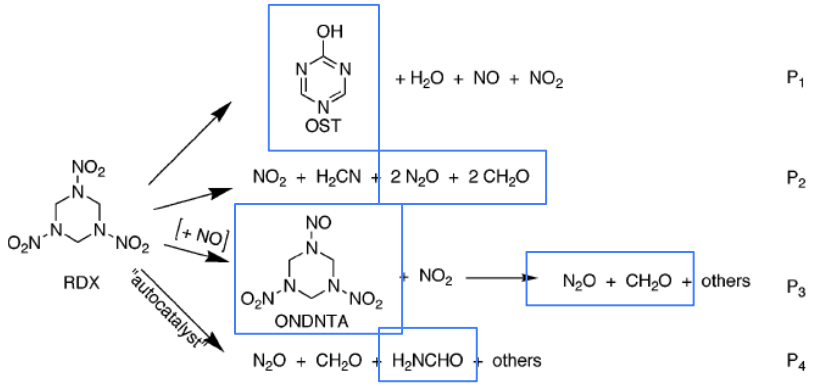
FOX-12/RDX Interaction Mechanism



Solid-phase RDX decomposition



Liquid-phase RDX decomposition

Maharrey and Behrens, *J. Phys. Chem. A* **109**, 11236 (2005)

RDX decomposes rapidly at its melting point (~200°C), producing OST, ONDNTA, N_2O, CH_2O, H_2NCHO, and others.

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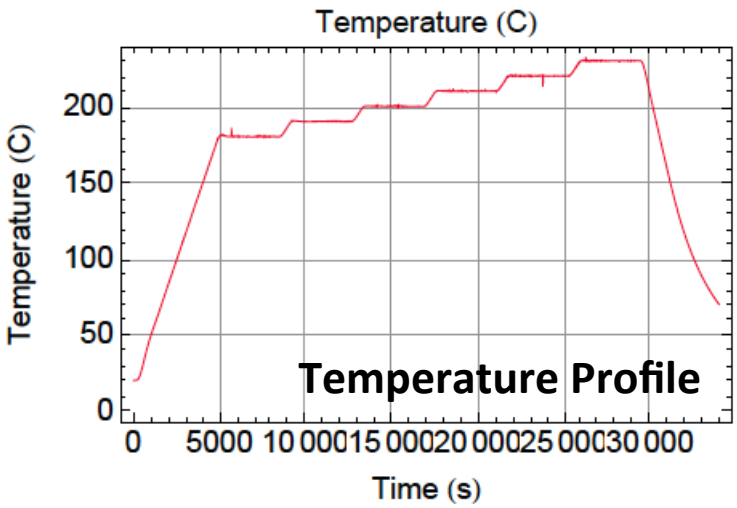
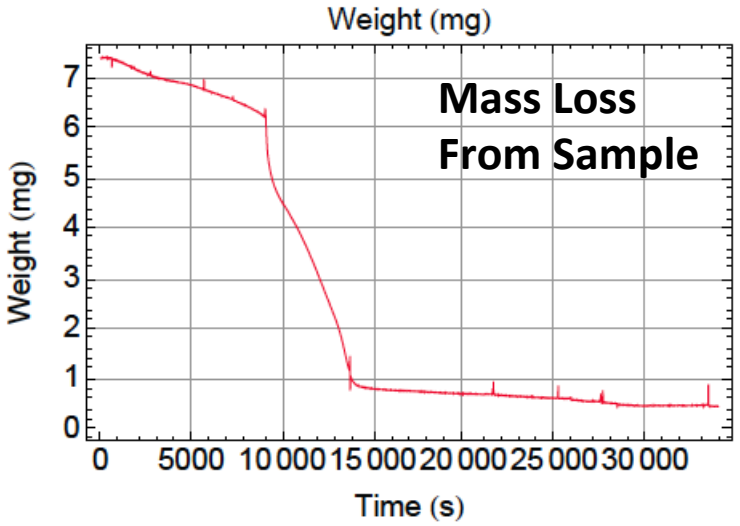
FOX-12/RDX Interaction Experiments





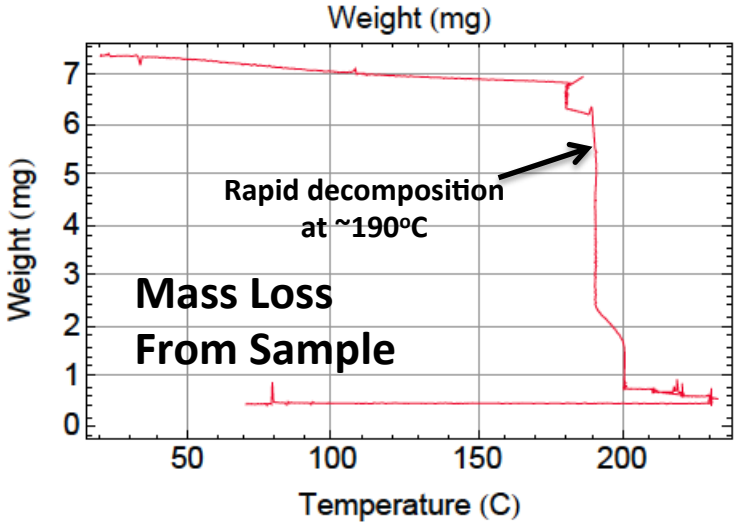
FOX-12/RDX mixture decomposes rapidly at ~190°C – same temperature FOX-12 decomposes

Direct Mix Experiment

25 um gold orifice

1.85 mg FOX-12 (25%), top

5.68 mg IRDX (75%), bottom



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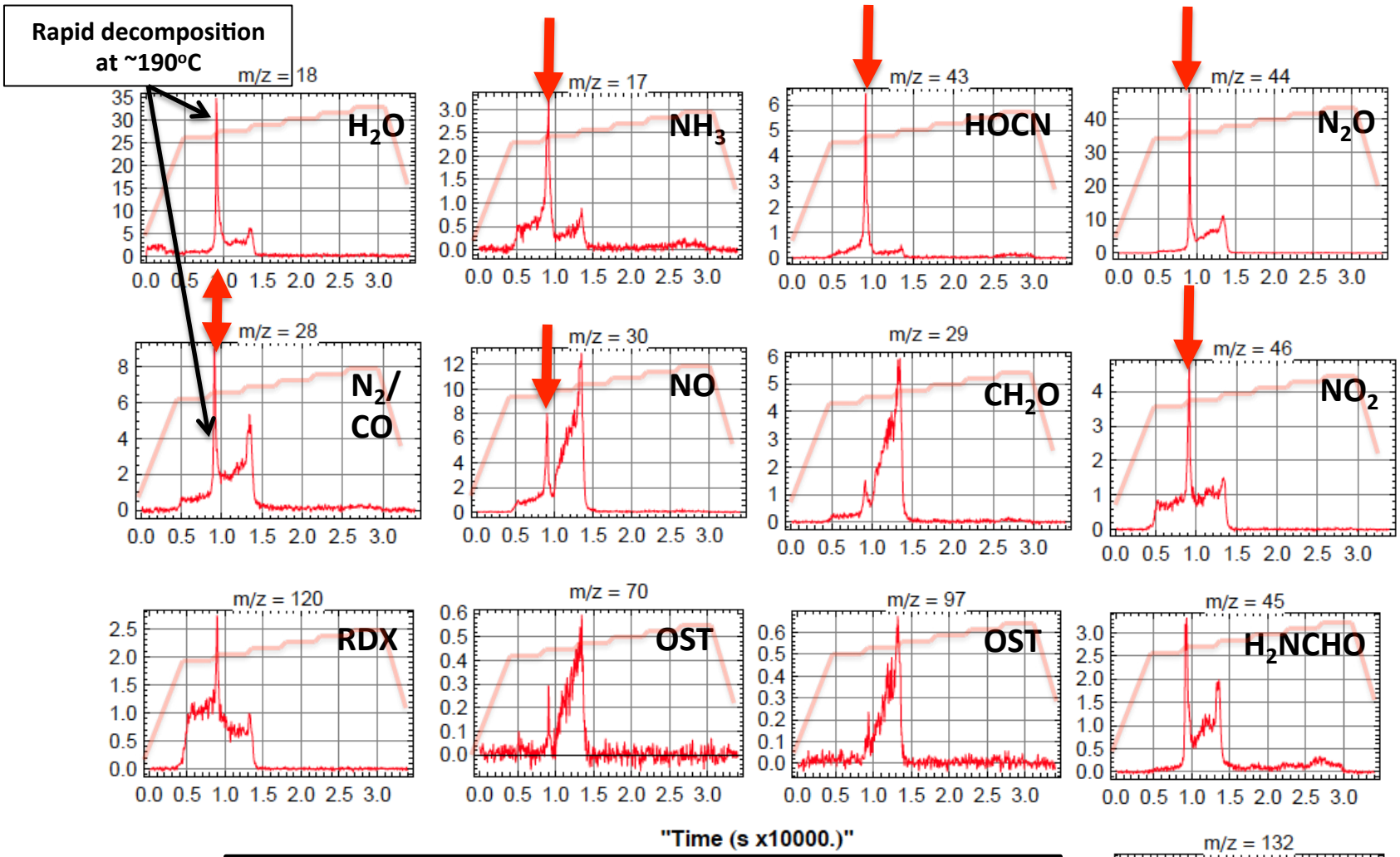
FOX-12/RDX Interaction Experiments



Spike of decomposition products observed at 190°C, followed by RDX decomposition products

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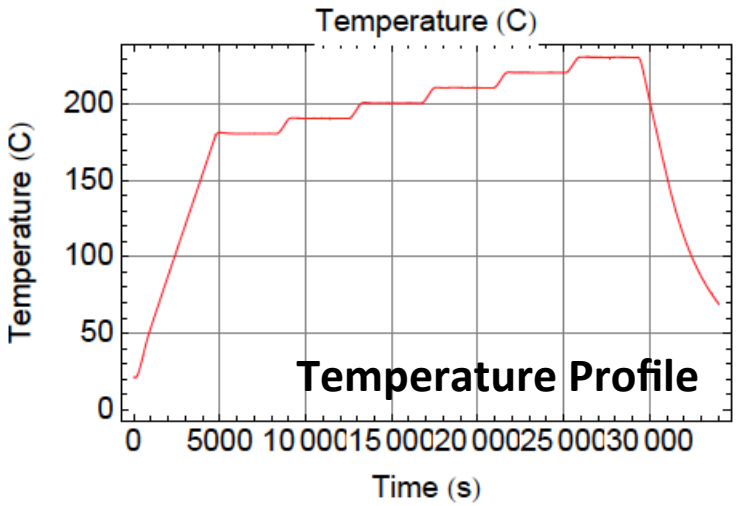
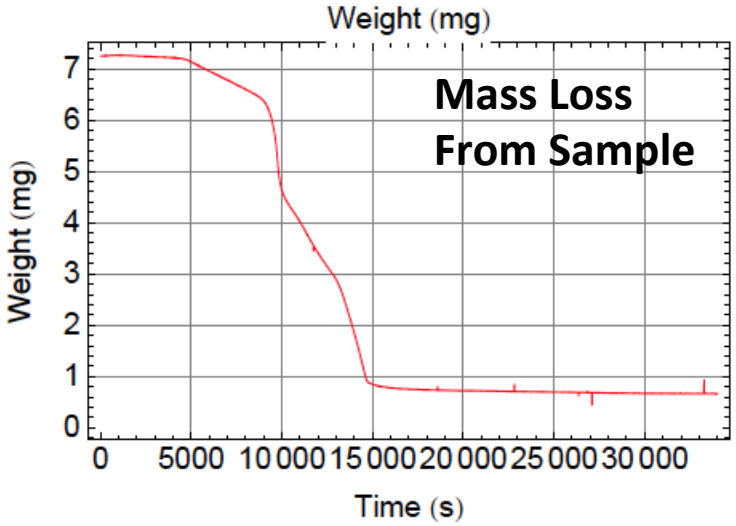
FOX-12/RDX Interaction Experiments





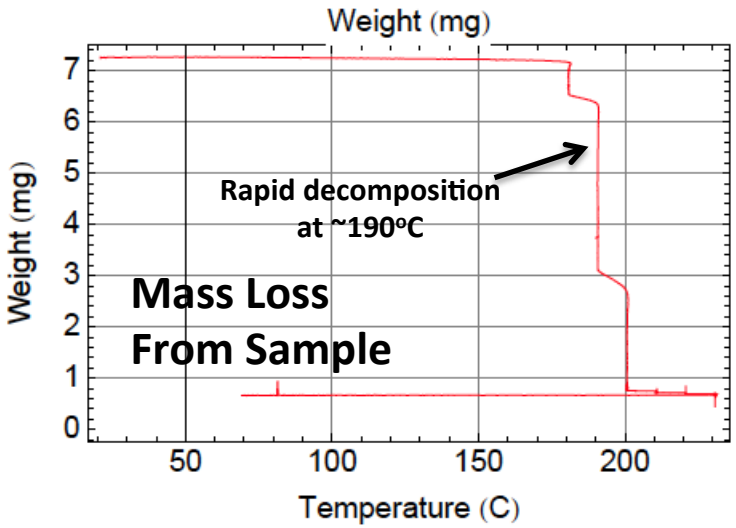
FOX-12/RDX mixture in flow reactor decomposes similarly to mixed powder

Flow Reactor Experiment

37 um alumina orifice

2.72 mg FOX-12 (28%), top

6.84 mg IRDX (72%), bottom



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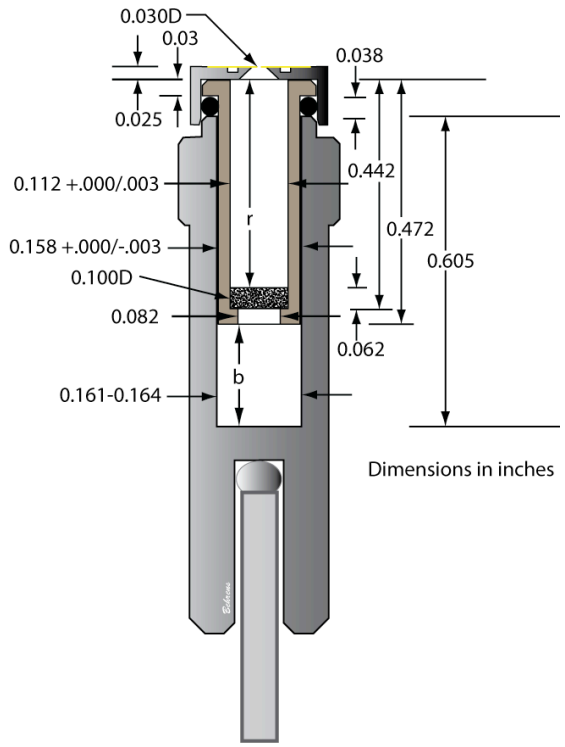
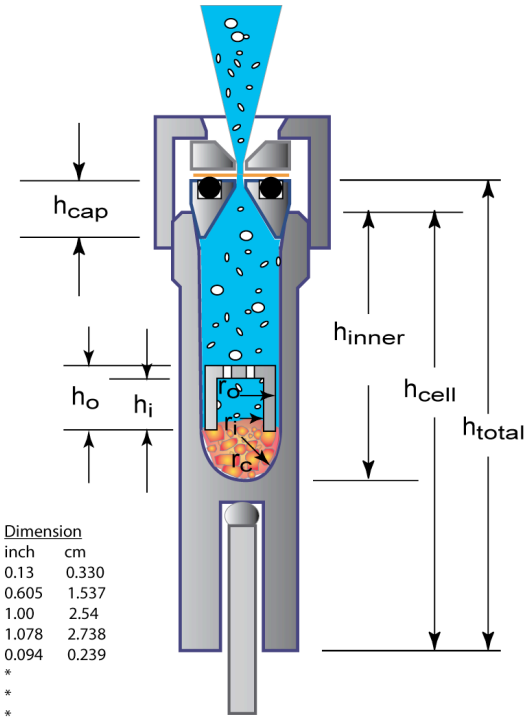
Interaction Between FOX-12 and RDX

Sample Cells





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hcell	1.00	2.54
htotal	1.078	2.738
rc	0.094	0.239
ho	*	
r0	*	
hi	*	
ri	*	

Flow Reactor Cell

No physical contact between FOX-12 and RDX

Standard Reaction Cell

FOX-12 and RDX in intimate contact

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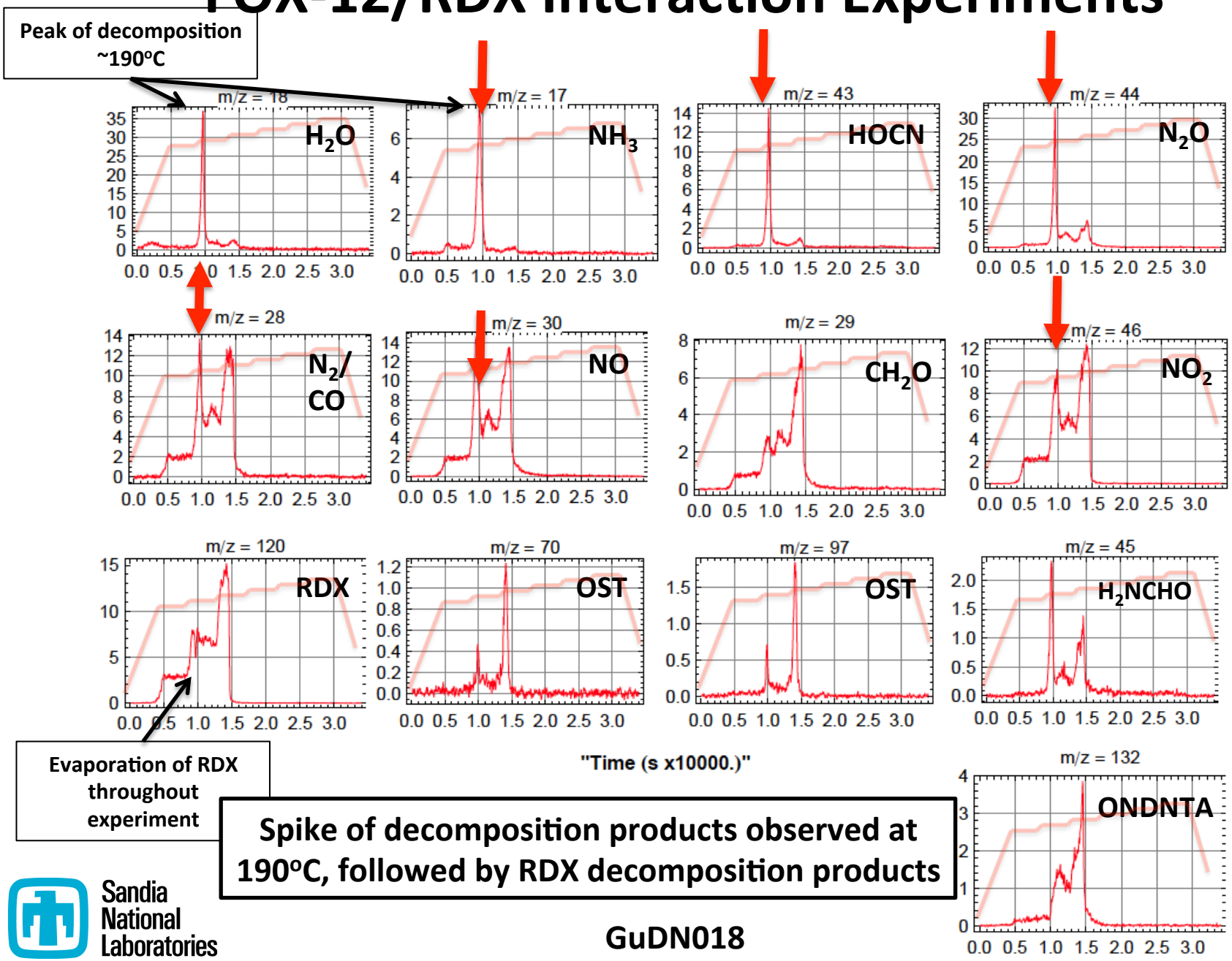
FOX-12/RDX Interaction Experiments



Spike of decomposition products observed at 190°C, followed by RDX decomposition products

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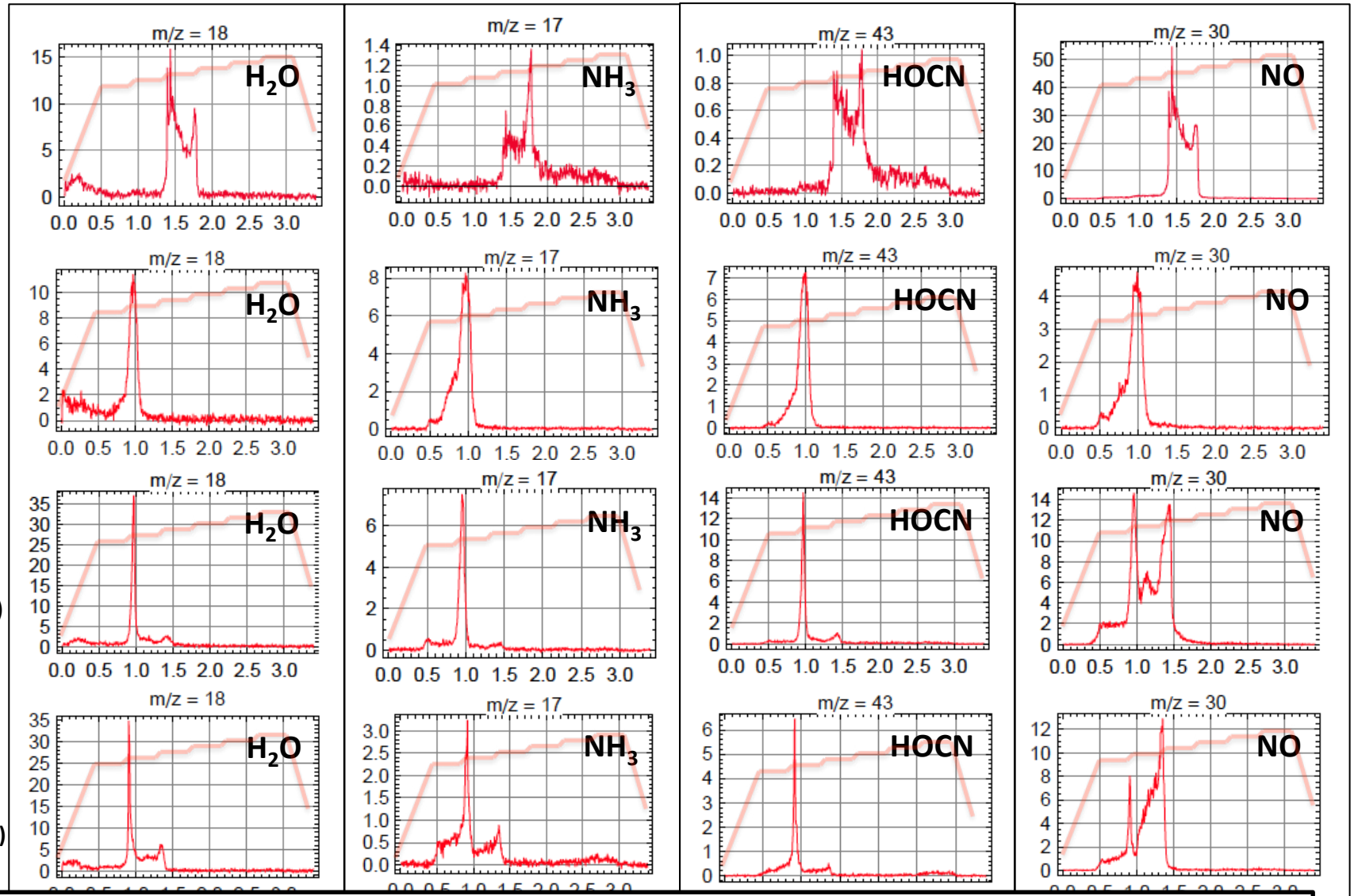
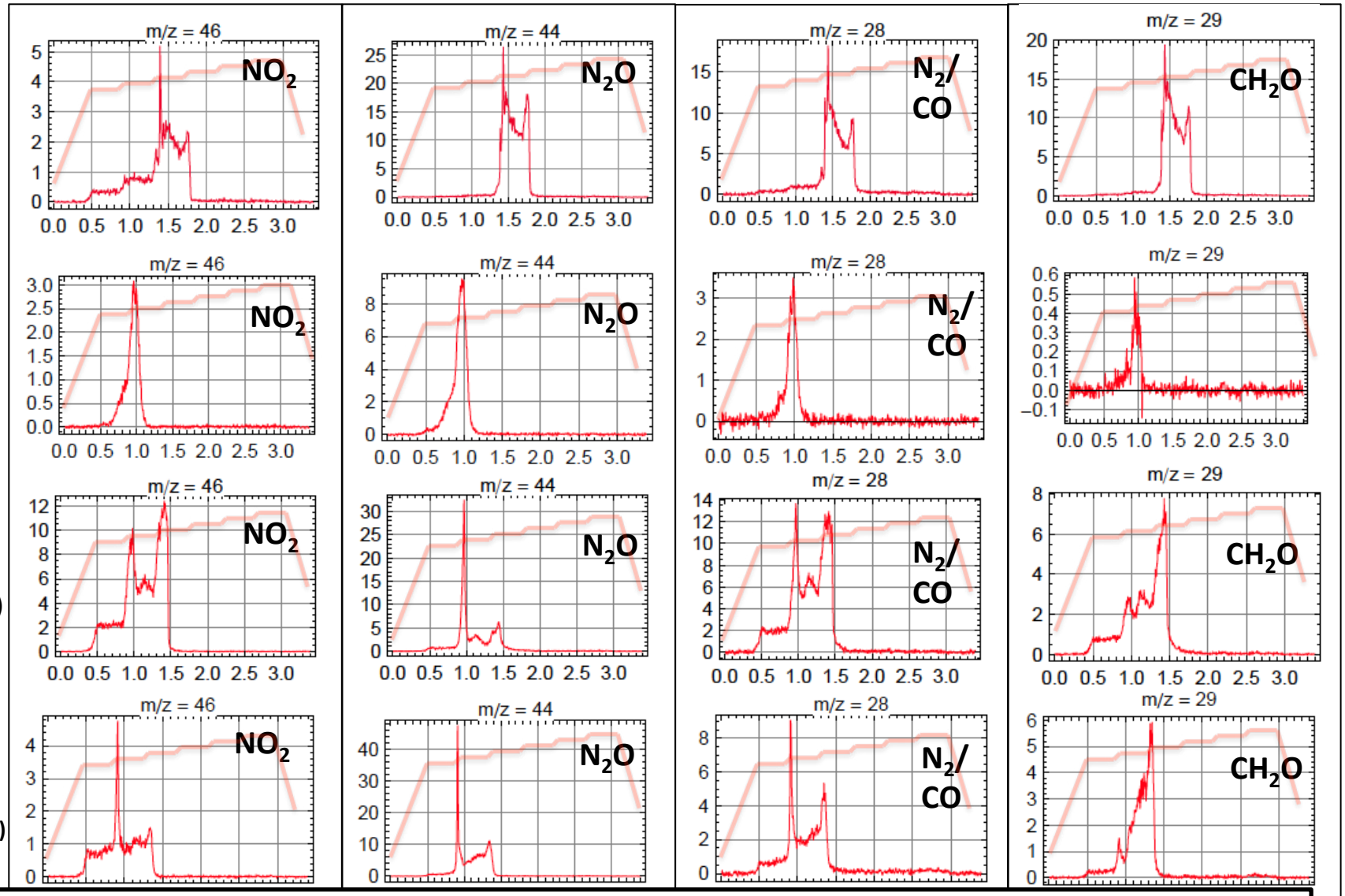
FOX-12/RDX Interaction Experiments



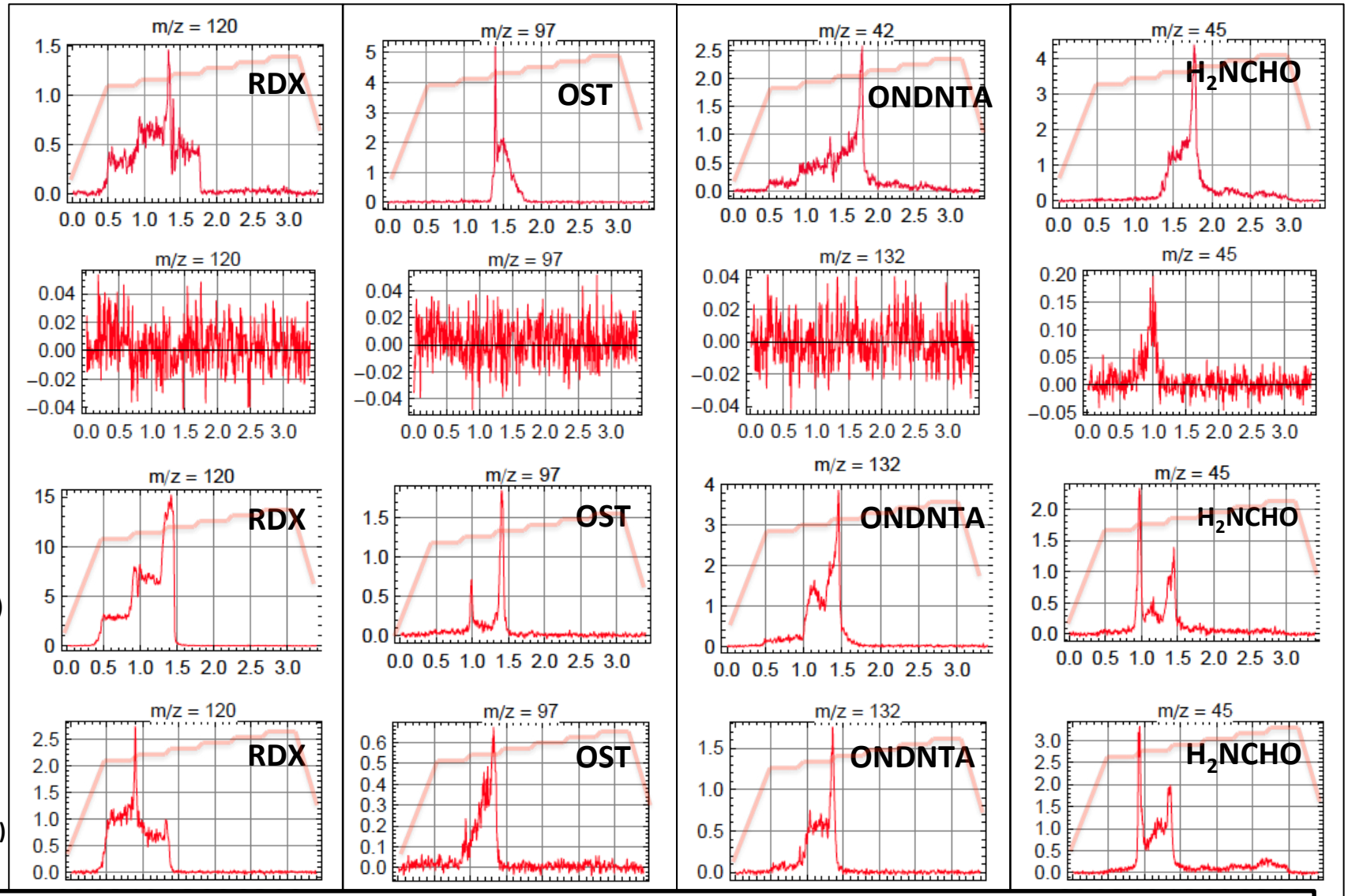
Decomposition of FOX-12+RDX initiates at same temp as FOX-12 alone – for flow reactor and mixed powder

FOX-12/RDX Interaction Experiments



Decomposition of FOX-12+RDX initiates at same temp as FOX-12 – and starts RDX decomposition process

FOX-12/RDX Interaction Experiments



Decomposition of FOX-12+RDX initiates at same temp as FOX-12 – and starts RDX decomposition process

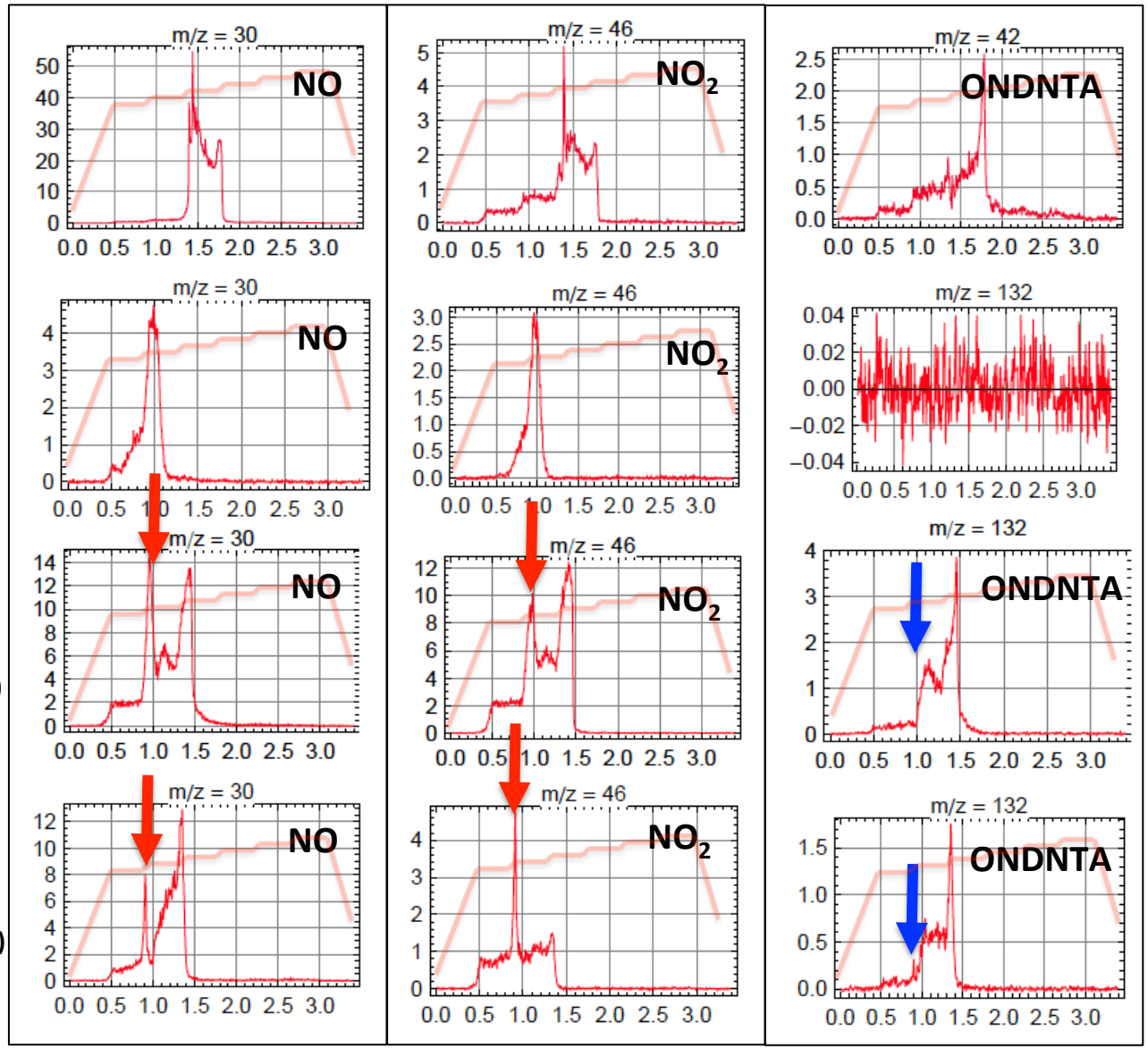
FOX-12/RDX Interaction Experiments

RDX

FOX-12

FOX-12 + RDX (Flow Reactor)

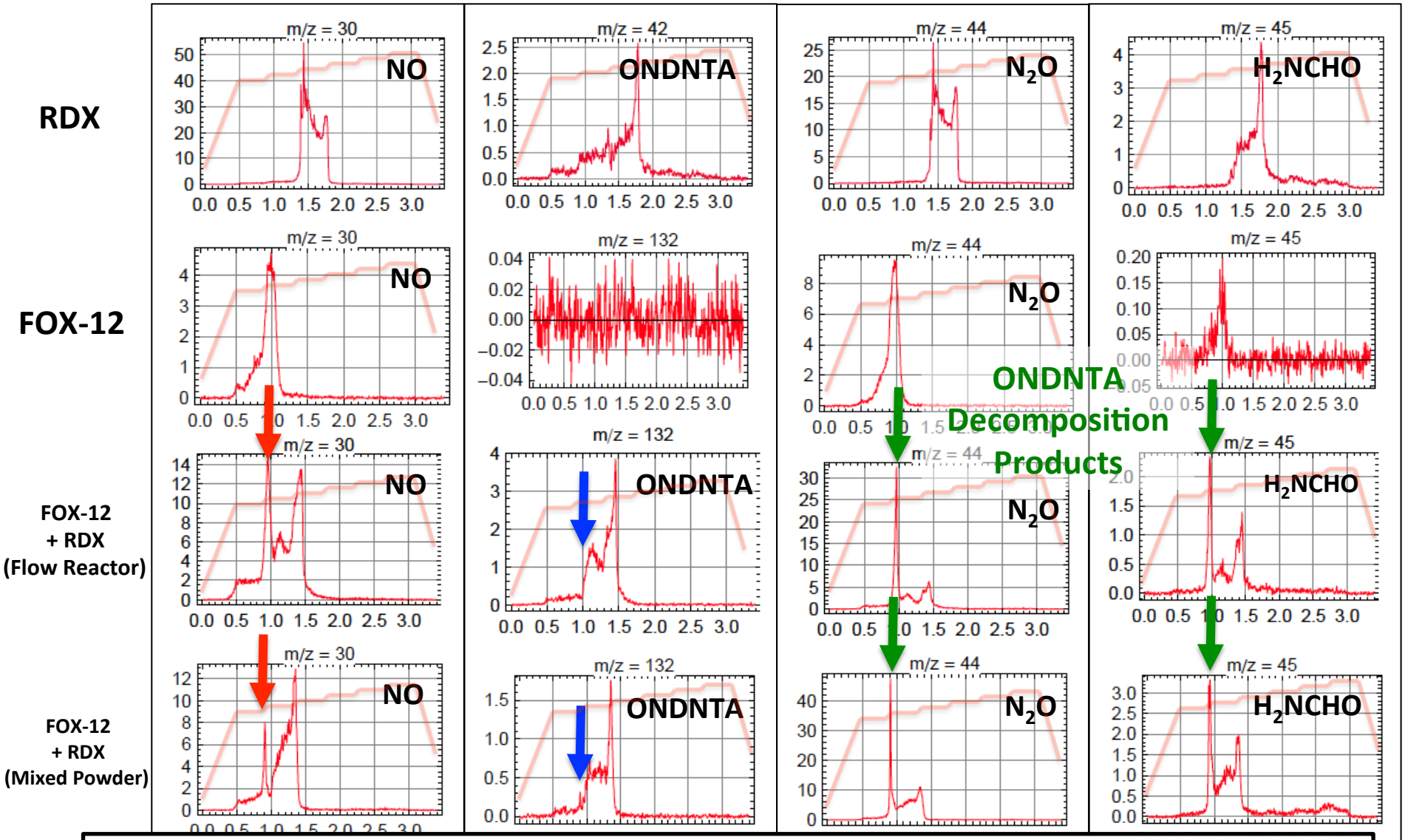
FOX-12 + RDX (Mixed Powder)



Spike in NO and NO_2 from FOX-12 are driving production and decomposition of ONDNTA

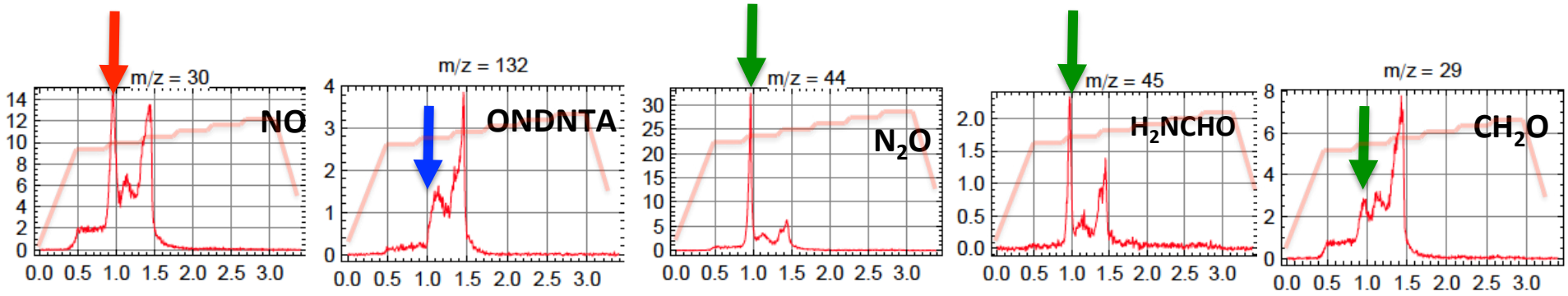
Maximum in NO_x coincides with **minimum in ONDNTA**

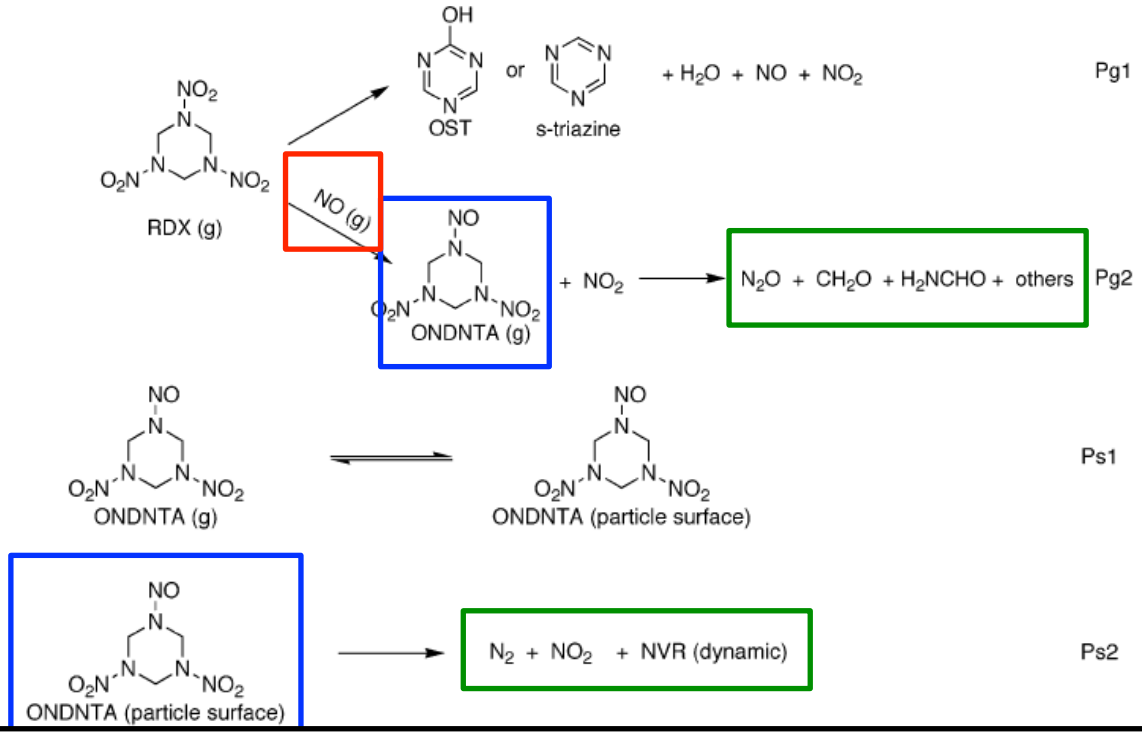
FOX-12/RDX Interaction Experiments



FOX-12 decomposition gases produce ONDNTA, which is rapidly decomposed to N_2O, H_2NCHO, others

FOX-12/RDX Interaction Experiments





FOX-12 decomposition gases produce ONDNTA, which is rapidly decomposed to N_2O, H_2NCHO, others

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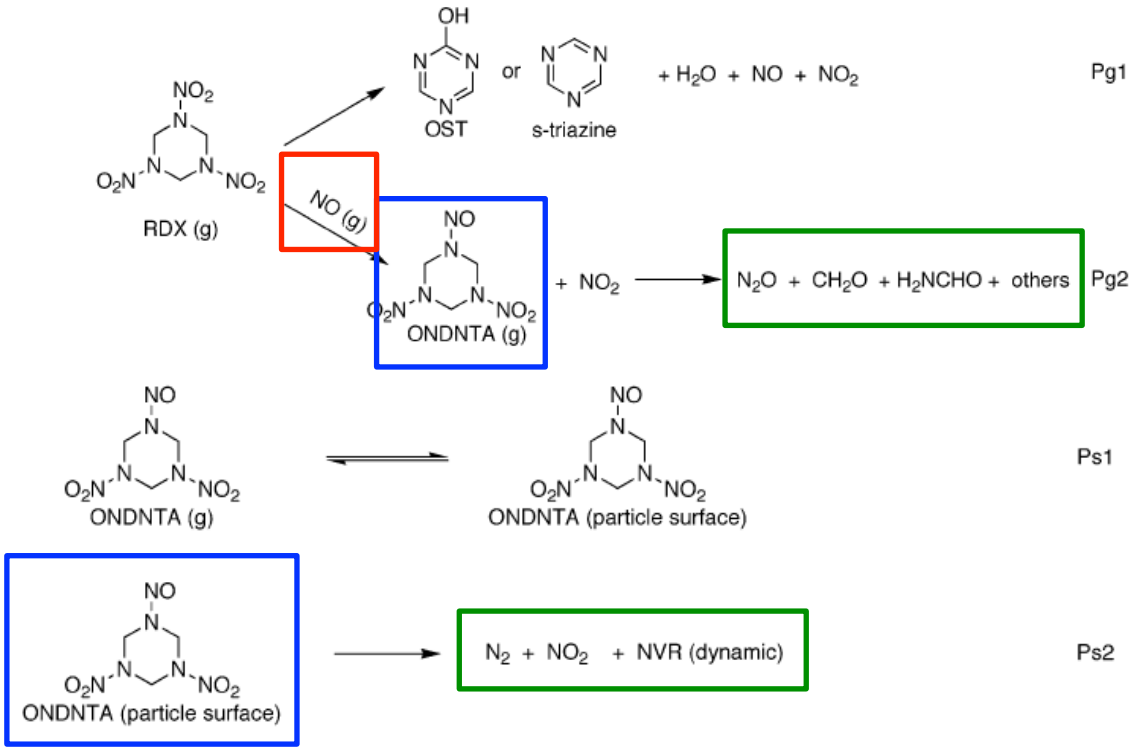


It appears that NO from the FOX-12 decomposition gases convert RDX to ONDNTA, which subsequently decomposes into small gas molecules.

The FOX-12/RDX decomposition process occurs well below the melting point of RDX, when decomposition of pure RDX becomes rapid.

Conclusions

- A variety of experiments have been conducted to examine the mechanism of chemical interaction that reduces thermal sensitivity of FOX-12 and RDX mixtures

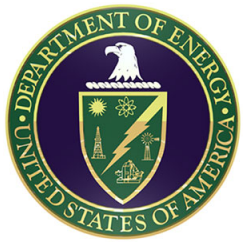
- **Decomposition of FOX-12/RDX mixtures initiates at temperatures similar to FOX-12 decomposition and below normal RDX decomposition.** The interaction occurs while RDX is still solid.

- **The decomposition process is similar whether FOX-12 and RDX are directly mixed (intimate contact) or physically separated, indicating that a gas-surface reaction drives the interaction between the two compounds**, and initiates decomposition of RDX at temperatures where it normally decomposes very slowly.

- Decomposition products from FOX-12 coincide with a minimum in production of ONDNTA and a maximum in ONDNTA decomposition products, consistent with FOX-12 decomposition gases driving conversion of RDX to ONDNTA and rapid reaction of ONDNTA into gas phase products.

- **Gas-phase decomposition products of FOX-12 appear to initiate decomposition of RDX at temperatures where it would ordinarily decompose very slowly.**

Questions?

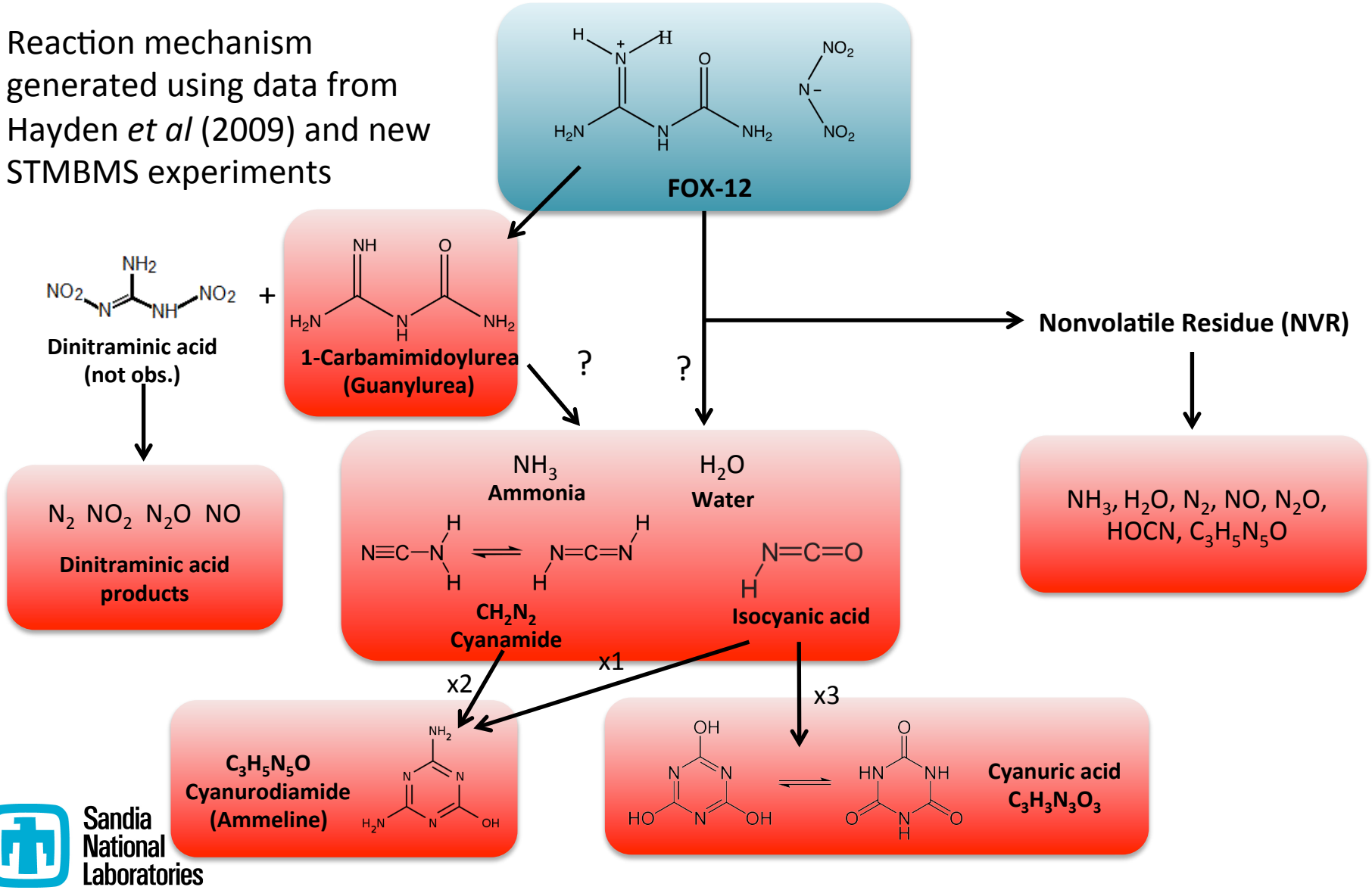


Thank you to:

US DoD/DOE Joint Munitions Program
Deneille Wiese-Smith (SNL/CA)
Ken Chavez (SNL/NM)
Leanna Minier (SNL/NM)

New FOX-12 Decomposition Mechanism

Reaction mechanism generated using data from Hayden *et al* (2009) and new STMBMS experiments



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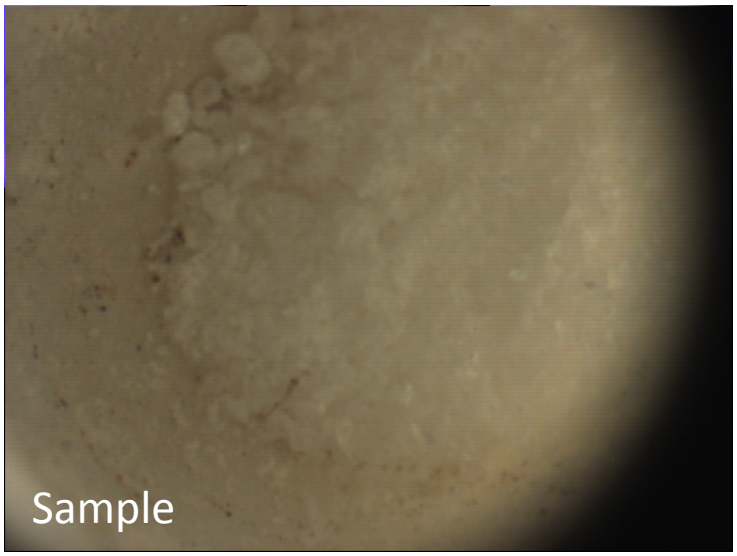
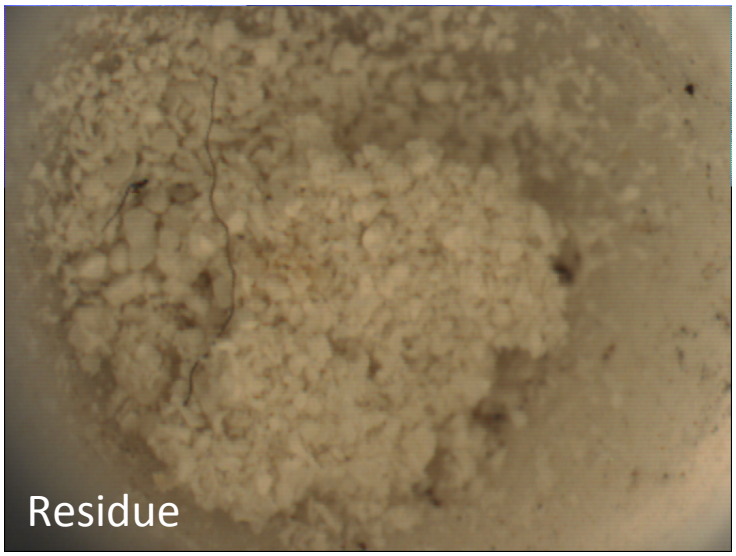
FOX-12 Decomposition

Before/after microscope images of sample and residue





0.46 mg residue

Standard Reaction Cell Experiment
25 micron orifice
1.87 mg FOX-12

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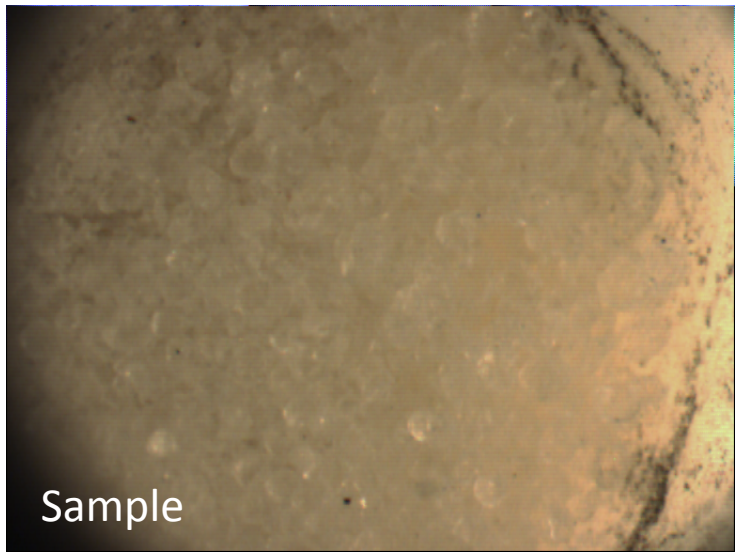
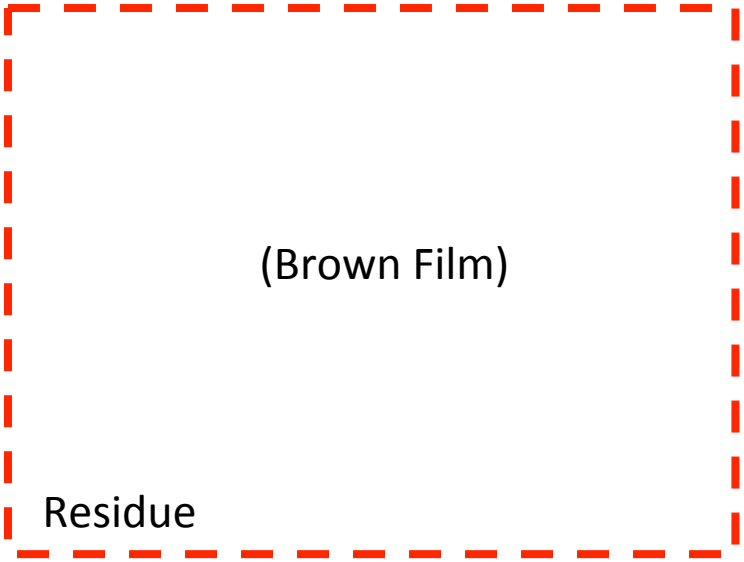
RDX Decomposition

Before/after microscope images of sample and residue





Residue wt. unknown (small)

Standard Reaction Cell Experiment
25 micron orifice
5.68 mg RDX

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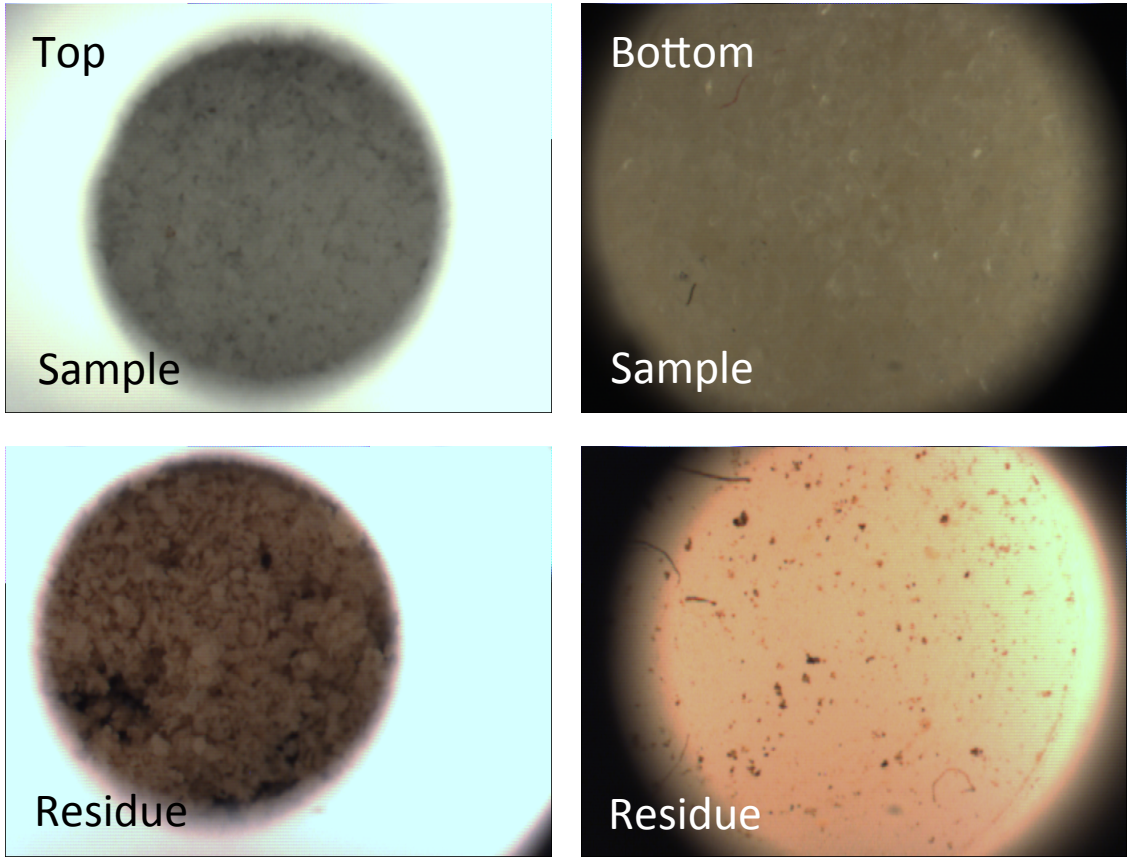
FOX-12/RDX Interaction Experiments

Before/after microscope images of sample and residue



0.61 mg residue (primarily in top)

Flow Reactor Experiment
37 um alumina orifice
2.72 mg FOX-12 (28%), top
6.84 mg IRDX (72%), bottom

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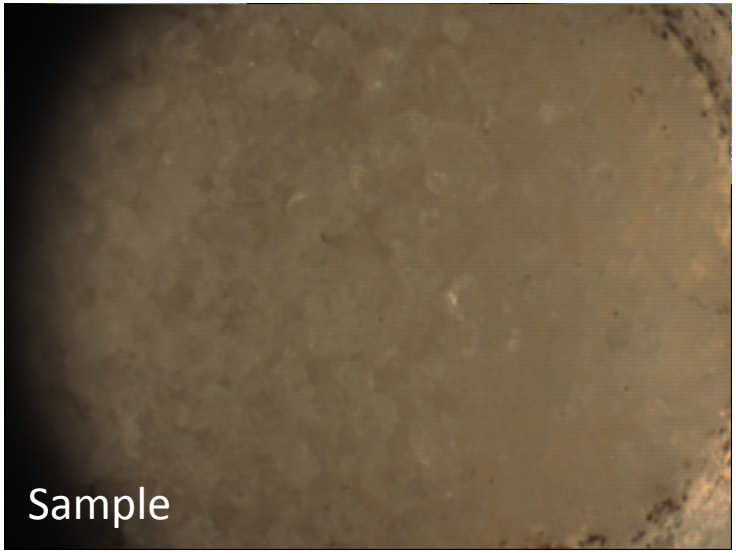
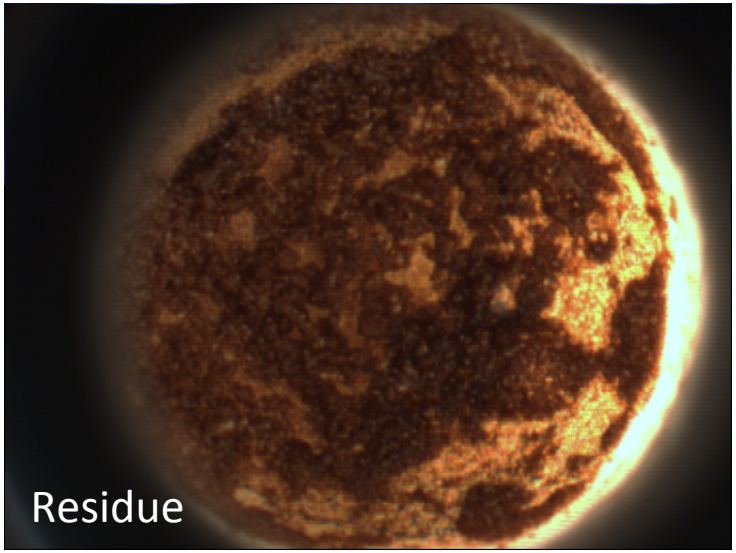
GuDN018

FOX-12/RDX Interaction Experiments

Before/after microscope images of sample and residue





0.45 mg residue

Direct Mix Experiment
25 um gold orifice
1.85 mg FOX-12 (25%), top
5.68 mg IRDX (75%), bottom

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Experiments on FOX-12

Several experiments are available from our data archives:

GuDN001: Decomposition of FOX-12; thermal ramp, high confinement.
GuDN002: Decomposition of FOX-12; thermal ramp, low confinement.
GuDN003: FTICR on FOX-12; thermal ramp, low confinement.
GuDN004: FTICR on FOX-12; thermal ramp, high confinement.
GuDN005: Isothermal decomposition of FOX-12; 205^{o}C, low confinement.
GuDN006: Isothermal decomposition of FOX-12; 205^{o}C, high confinement.
GuDN008: FTICR on FOX-12; isothermal at 200^{o}C, low confinement.
GuDN009: FTICR on FOX-12; isothermal at 200^{o}C, high confinement.
GuDN011: Decomposition of FOX-12; thermal ramp, high confinement.
GuDN012: Decomposition of FOX-12; thermal cycling, low confinement.
GuDN013: Decomposition of FOX-12; isothermal steps, low confinement.
GuDN015: FTICR on FOX-12; thermal ramp, low confinement.
GuDN016: Isothermal decomposition of FOX-12; 205^{o}C, medium confinement.

Experiments on FOX-12/RDX

Several experiments are available from our data archives:

GuDN010: Decomposition of FOX-12/RDX; thermal ramp, high confinement.
GuDN014: Decomposition of FOX-12/RDX; isothermal steps, high confinement.

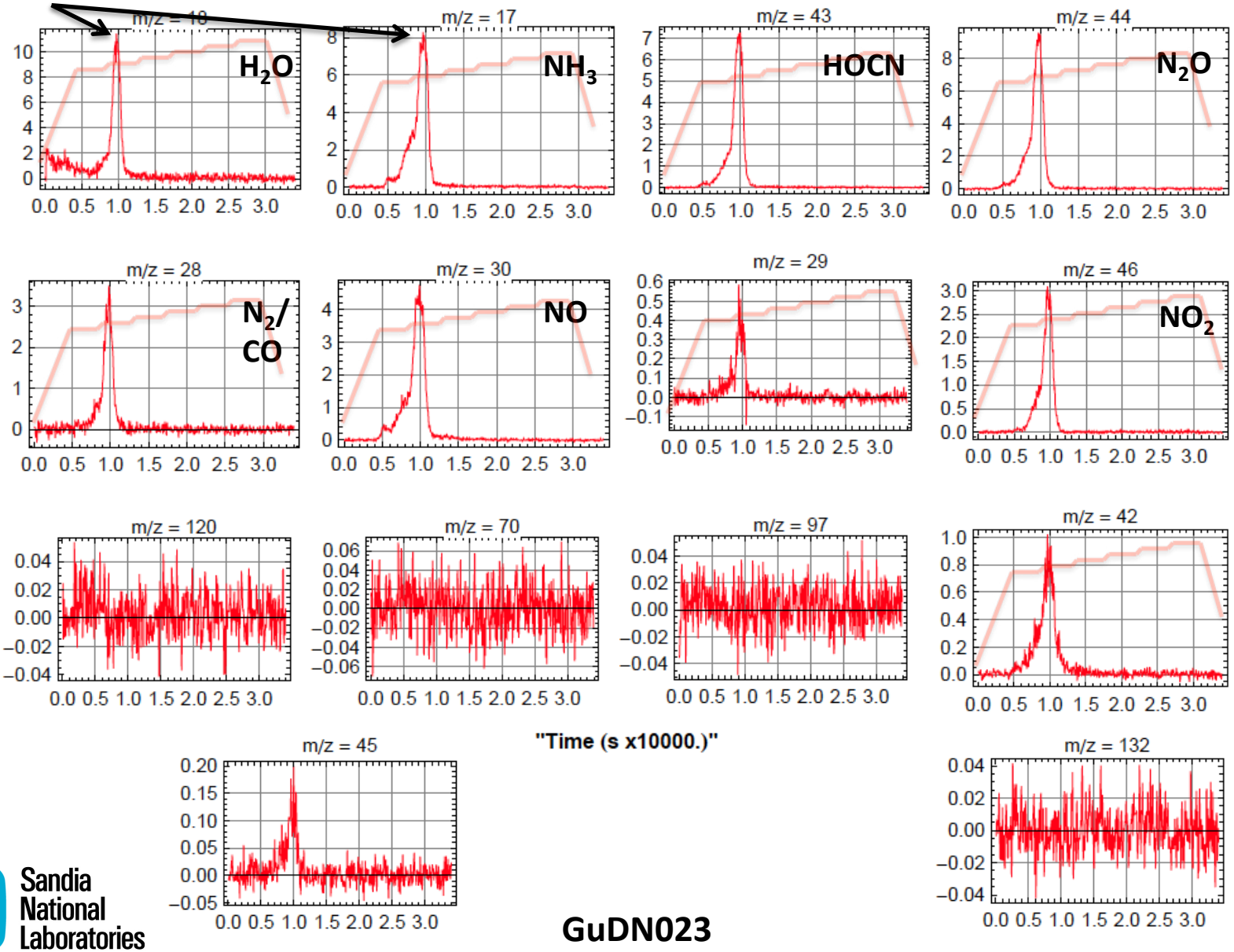
New Experiments on FOX-12/RDX

We have conducted several new experiments on FOX-12/RDX mixtures:

GuDN017: Flow reactor experiment using FOX-12/RDX; isothermal steps, medium confinement.
GuDN018: Flow reactor experiment using FOX-12/RDX; isothermal steps, high confinement.
GuDN019: Analog of GuDN017 with direct mix; isothermal steps, medium confinement.
GuDN020: Analog of GuDN019 without FOX-12; isothermal steps, medium confinement.
GuDN021: Analog of GuDN018 with direct mix; isothermal steps, high confinement.
GuDN022: Analog of GuDN021 without FOX-12; isothermal steps, high confinement.
GuDN023: Analog of GuDN021 without RDX; isothermal steps, high confinement.
GuDN024: Analog of GuDN021 but rapid heating to 180^{o}C then slow to 250^{o}C, high confinement.
GuDN025: Analog of GuDN021 with mil-spec RDX; isothermal steps, high confinement.

FOX-12 Decomposition

Peak of decomposition
~190°C



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GuDN023