R2-A.2: Stability of Gas Ions of Explosives in Air at Ambient Pressure

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II. PROJECT DESCRIPTION

A. Project Overview

Central to the function of the most widely-used explosive trace detector (ETD) technology, and to future technology, are gas phase ions created from explosives when introduced into these detectors. Until this project, no systematic database existed on the ion lifetimes or thermochemical values for these gas ions, typically-chloride adducts for most explosives, or protonated monomers for some others. Knowledge of these fundamental terms informs understandings of performance for current ETDs and of boundaries of behaviors needed in designs for new embodiments of ETDs.

In prior work with familiar explosives (trinitrotoluene (TNT), ethylene glycol dinitrate (EGDN), nitroglycerin (NG), and others), thermochemical values and ion lifetimes were determined and several categories of behavior were observed [1-3]. These included simple thermal decomposition over a range of temperatures, relatively complex decomposition, and limited or no decomposition. In subsequent studies with improvised explosives or what could be called specialized explosives (pentaerythritol tetranitrate (PETN), high melting explosive (HMX), hexamethylene triperoxide diamine (HMTD), peroxides), complexities were observed during the formation of the gas ions, blocking further ion characterization.

The project achievements in Year 4 include:

- In 2017, the first successful studies of these “difficult-to-characterize (DTC)” explosives were completed with the new technology, which was designed, built and, applied in this year. This new kinetic instrument is based on ion mobility spectrometry (IMS) but includes a method to deliver explosives into a reactive region (to form gas ions) directly before the kinetic analysis region, minimizing losses of ion signal intensity.
- The chloride adduct of PETN was evaluated between 156 to 177 °C, and decomposition was determined with standard enthalpy of decomposition of 81 kJ/mole using the new instrument.
- The decomposition of PETN*Cl- proceeded through a nitrate displacement, releasing NO₃⁻ as the product.
(ion) of decomposition. Mass analysis of gas ions is in progress in support of the kinetic IMS studies.

- Another ion of PETN, to be presumed as the nitrate adduct (PETN\(\cdot\)NO\(_3\)), was observed as stable as far as measured to 210 °C. This is consistent with prior findings with nitrate esters, where nitrate adducts were stable beyond the experimental parameters of the kinetic IMS.

- Peroxides present highly complex mixtures, and efforts to evaluate these are under development with attention directed largely to pre-separation of complex mixtures in combination with the kinetic IMS.

One preliminary result with peroxides is a seemingly high stability of the protonated monomers or protonated products of peroxides, such as TATP and others. This is in strong contrast, if validated in Year 5, with common understandings of the original explosives substances as neutral solids or gases.

**B. Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address**

The two major weaknesses identified during the Year 2 Biennial Review were the relevance of the work to the broader community of explosives investigators and a path to use the studies for future advances in ETD development. These were addressed in the follow ways:

1. We have clarified that studies of gas ions of explosives are relevant to current ETD technology (e.g. IMS) and perhaps the promising method of atmospheric pressure ionization-mass spectrometry (API-MS). Fundamental studies inform users and developers of both technologies.

2. Presentations and publications have been made on our studies, and industry has been invited into discussion.

3. Several discussions have arisen and new concepts have been extended from the core understandings of this project, meaning our work confirms and supports ideas developed in parallel with our efforts in the field.

**C. State of the Art and Technical Approach**

There is no other team worldwide contributing to the mostly-empty table of thermochemical values for gas ions of explosives, and there is, as of yet, no other experimental approach to obtain enthalpy and entropy of decomposition of gas ions of explosives in air at ambient pressure [1-3]. Recently a team at Florida International University has used trapped ion mobility spectrometry to explore ion decomposition with favorable result at much reduced pressures [4]. The state of the art in gas phase ion decomposition at ambient pressure in air or nitrogen was established at New Mexico State University (NMSU) over the past six years, and further advancements were made this year with the development of a new instrument suited for the study of improvised explosives. Additionally, the prior instrument was refitted and upgraded to measure in positive ion mode for temperatures approaching 250 °C for studies with peroxides.

This work is somewhat isolated to our efforts, however several prior explorations or observations exist. This includes studies of temperature’s effect on the response of ETD or IMS instruments to explosives [5, 6]. Although ion mobility spectrometers are widely used in DHS efforts with defense of commercial aviation, there is surprisingly little exploration of the foundations of response.

**D. Major Contributions**

During the past year, the conditions for measuring thermochemical parameters of gas ions for DTC explosives were developed and refined. In this, a nebulizer was used to convert explosives that were once solutions into vapors with high-speed flash vaporization, which was fast enough and cool enough to deliver molecules of explosives into a reaction region at ambient pressure. This reaction region was 1 to 10 mm from the ion shutters that initiate the kinetic mobility measurements. The close proximity of the ionization region to the mobility drift regions permitted, along with the heated nebulizer concept, strong intensity for ion adducts of
PETN, HMX, and HMTD. The schematic in Figure 1 shows this innovation, where a nebulized sample is passed over the ion shutter and mixes with reactant ions arising in the radioactive source (grey rectangle).

![Diagram of drift tube for fast vaporization of thermally labile explosives (PETN) with rapid ionization and analysis near the first ion shutter.](image)

Figure 1: Diagram of drift tube for fast vaporization of thermally labile explosives (PETN) with rapid ionization and analysis near the first ion shutter.

The entire drift tube was placed in a custom-built oven (see Fig. 2), and measurements were made with PETN dissolved in a solvent. Experimental findings in Figure 3 (on the next page) are shown from dual shutter isolation of the PETN adduct ion with chloride (pending mass analysis confirmation) with spectra shown at several temperatures from 156 to 177 °C.

![Photograph of side flow kinetic IMS with dual shutters for determination of thermochemical parameters of gas ions of explosives which have otherwise been too unstable to measure.](image)

Figure 2: Photograph of side flow kinetic IMS with dual shutters for determination of thermochemical parameters of gas ions of explosives which have otherwise been too unstable to measure.
The spectra show classic patterns for ion decomposition, with an elevated base line between the adduct of PETN and an ion of higher mobility (smaller drift time). This is the evidence of ion decomposition in the kinetic IMS instrument, and the baseline slope provides a measure of the rate constant for ion decomposition. The rate constant obtained as several temperatures provides data points for an Arrhenius plot (see Fig. 4), which is the first ever for a chloride adduct of PETN.

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Figure 3: Mobility spectra of the chloride adduct of PETN (mass analysis pending) at several temperatures. The spectra are uncorrected in drift behavior for temperature. All show the loss of intensity for the PETN adduct with temperature (20 to 22 ms), and the increase in intensity for a fragment ion peak (14 to 17 ms). The fragment ion peak is thought to be NO₃⁻ that is produced from chloride displacement reactions and was observed widely for nitro esters.

Figure 4: Arrhenius plot for the decomposition of chloride adduct of PETN in air at ambient pressure. The decomposition proceeds through a chloride substitution reaction releasing a nitrate anion.
The plot shows reasonable fit to a line from triplicate measurements, and the standard enthalpy change obtained experimentally (Fig. 5) is consistent with other chloride displacement reactions with a release of nitrate.

![Standard enthalpy change for dissociation reaction (measured) (ΔH°)]

\[
\Delta H^\circ = E_a + RT \\
= (77858.95 + 8.314*440) \text{ J/mol} \\
= 81517.11 \text{ J/mol} \\
\approx 81 \text{ kJ/mol}
\]

Pre-exponential factor (A) = \(1.75 \times 10^{11} \text{ s}^{-1}\)

Figure 5: Calculation of standard enthalpy from energy of dissociation (activation, \(E_a\)) from Figure 4, adjusted for \(R\) and \(T\).

Results from ab initio modeling of the decomposition of PETN is shown in Figure 6, where the dissociation energy is 87 kJ/mole, under 10% relative difference from the 81 kJ/mole experiment. Nonetheless, prior studies with other explosives have seen a 5% relative difference or better. Mindful that this substance has required more than a year of study and the development of a new instrument, we are reasonably content with the match between modeling and experimentation.

![Dissociation enthalpy ΔH°=.03315 au = 87 kJ/mol](image)

Figure 6: Findings from ab initio modeling of the chloride substitution reaction for a chloride adduct of PETN releasing \(\text{NO}_3^-\).

Other ion peaks can be seen in mobility spectra for PETN and one ion peak preceding the presumptive chloride adduct after dual shutter isolation to study decomposition (shown in Fig. 7 on the next page). The two spectra suggest limited or no significant ion decomposition based on intensity for the ion peak (here thought to be the nitrate adduct of PETN) and on the limited distortion of the baseline preceding the ion peak. This too is completely consistent with nitrate esters where the nitrate adducts were not decomposed at tempera-
tures shown or at 210 °C. This is consistent with ab initio modeling of a simple nitrate dissociation which was determined as 139 kJ/mole.

Studies with HMX and HMTD showed very high thermal stability to 210 °C, and the drift tube shown in Figure 2 is undergoing minor refurbishment to reach temperatures of ~250 °C. Studies with peroxides are on-going using the original kinetic IMS developed in Years 1 to 3, which has been modified slightly to reach 250 °C in positive ion polarity.

E. Milestones

The major milestones reached in Year 4 were:

1. Determine and document lifetimes for ions from pentaerythritol tetranitrate (PETN), hexamethylene triperoxide diamine (HMTD), triacetone triperoxide (TATP), RDX, and possible others previously unmeasurable in a vapor phase inlet, such as the gas chromatograph.
   a. The first characterization of the decomposition of gas ions (chloride adduct) for PETN with supporting modeling using ab initio calculation of enthalpy of reaction.
   b. The discovery that PETN chloride adducts, as gas ions at ambient pressure in air, decompose to nitrate anions as seen with nitrate esters.
   c. One ion of PETN, presumed to be nitrate adduct pending mass analysis, was stable to 210 °C without evidence of thermal decomposition.

2. Refine technology to accept several ion sources including an electrospray ion source and an atmospheric pressure photoionization (APPI).
   a. We completed the building of a new IMS kinetic instrument, described above. This has been a success and was used in studies of HMX and HMTD (see below).

3. Examine some of the “problem” explosives which fit into one of four categories of: 1) Too unstable; 2) Too stable; 3) Too complex chemically; and 4) Too unstable to be vaporized by heat. These chemicals will be characterized using improvisation on existing instrumentation.
a. A discovery that gas ions of HMX and HMTD are stable to 210 °C in air at ambient pressure.
b. Ions of a butyl peroxide were studied found stable to temperatures above 210°C.
c. The surprising stability of the ions of peroxides necessitated modifications of the original kinetic IMS to operate in positive ion polarity to 250 °C. This was done and measurements are on-going.

F. Future Plans

In Year 5, we intend to:

1. Develop a simple version of the instrument in Figure 2 and attach it to a mass spectrometer for mass analysis of ions of PETN from 150 to 250 °C. When these measurements are completed, the findings for PETN will be published.
2. The instrument in Figure 2 will be refurbished to reach 250 °C, and the stability of gas ions of HMX and HMTD will be explored between temperatures of 200 and 250 °C.
3. Peroxides are currently under study, though challenged by the purity of samples. The formation of gas ions will become a central focus toward obtaining thermochemical values and ion lifetimes for organic peroxides, including TATP, as a chemical family.

In Year 6, we intend to translate these findings into designs of ETDs in which ion stability is utilized as a second dimension of selective response.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

Relevance #1: Until studies were made at NMSU on the stability of gas ions of explosives at ambient pressure, knowledge of and interpretation of mobility spectra with baseline distortions and the appearance of nitrate from chloride adducts of certain explosives existed at the level of conjecture only. Studies from Years 1 to 4 established quantitative tables of thermochemical values for gas ions of explosives and revealed the foundations of ion chemistry for these substances. Mobility spectra can now be understood, and the performance from various vendors (drift tube designs) can be compared and described from a thorough description of ion chemistry of explosives. These understandings extend directly to API-MS and future designs for API-MS instruments.

Relevance #2: We have discovered that gas ions for explosives exhibit stability, as a family, over a very broad range of temperatures. NG adduct ions decompose near 100 °C while adducts of PETN decompose above 150 °C, and some compounds (TNT, HMX) exhibit stability as chloride adducts (or simple products such as M-1 anions) at temperatures over 200 °C. This range of behaviors informs us that no single ETD will provide optimum response for all explosives with a given fixed temperature; ions of some explosives will be decomposed from the molecular adduct and others will remain as M*Cl⁻ species. Analytical performance with IMS-based ETDs will therefore be distinctive for each explosive, as dependent on the temperature of the measurement.

B. Potential for Transition

We anticipate that understandings developed here may inspire and inform new measurement concepts for ETDs. Innovations in technology, such as advances in drift tube design and operation, have occurred with the confidence drawn from these fundamental discoveries. While not immediately related to the discoveries here, understandings and experiences from this project have inspired possible designs now in testing, such as drift tubes which have reactive stages.
C. **Data and/or IP Acquisition Strategy**

We do not expect any IP to be developed directly from the measurements of thermochemical values and discoveries of thermal decomposition of gas ions. We anticipate that the understandings and discovered behaviors here will be foundational in the development of new ETDs; however, pursuing IP based on such influences is seen as unreliable for claiming IP rights.

D. **Transition Pathway**

These discoveries fit broadly into understandings of the stability of ions at a fundamental level. One industrial sponsor of technology in our laboratory, while independent of our efforts on thermal decomposition of gas ions is broadly pursuing the concept of a reactive IMS. While these activities benefit from fundamental understandings, the innovations arise for industry funding and could not be directly associated to this project’s IP (see comments above).

E. **Customer Connections**

One company in Spain, SEADM, has patented concepts that are consistent with our discoveries and our fundamental understandings although there were no collaborations or discussions with the NMSU team before they patented their concept 2014. During 2017, we met the company and encouraged their efforts using findings from this project. They have begun developing technology for baggage screening based on reactive IMS concepts.

IV. **PROJECT ACCOMPLISHMENTS AND DOCUMENTATION**

A. **Education and Workforce Development Activities**

1. **Student Internship, Job, and/or Research Opportunities**
   a. Students in the research team have been equipped with experiences and capabilities that are highly specialized and useful in the development and operation of ETDs. These capabilities arise from daily and weekly accomplishment under the PI's supervision.

B. **Peer Reviewed Journal Articles**

Pending-


C. **Other Proceedings**


V. REFERENCES


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