

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

## I. PARTICIPANTS

Faculty/Staff			
Name	Title	Institution	Email
Gary A. Eiceman	PI	New Mexico State University	geiceman@nmsu.edu
John A. Stone	Consultant	Queens University	john.stone@chem.queensu.ca
Avi Cagan	Research Professor	New Mexico State University	avicagan@nmsu.edu
Gyoungil-Lee	Senior Associate	New Mexico State University	glee@nmsu.edu
Graduate, Undergraduate and REU Students			
Name	Degree Pursued	Institution	Month/Year of Graduation
Bhupendra Gurung	PhD	New Mexico State University	5/2019
David Emery	BS	New Mexico State University	5/2019

## II. PROJECT DESCRIPTION

### A. Project Overview

Measurements of gas phase ions derived from explosives using either mobility or mass are foundational to explosive trace detectors (ETDs) for use in commercial aviation security. Despite the importance of gas ions of explosives with ETDs, knowledge of such ions was limited and the absence of any quantitative descriptions of the properties of these ions constituted gaps in knowledge. At New Mexico State University (NMSU), methods were developed to measure ion lifetimes and thermochemical parameters of explosive ions in air at ambient pressure and over ranges of temperature. Additionally, decomposition pathways were characterized and compared to ab initio models of ions and decomposition reactions. These discoveries filled gaps in knowledge and provide a foundation for understanding existing ETDs and for designing new embodiments.

### B. State of the Art and Technical Approach

Prior to these studies, there were no literature references on the thermochemical properties of gas ions of explosives. More than forty years of measurements and descriptions of measurements had been made using ion mobility spectrometry and mass spectrometry; consequently, the ionization properties of molecular neutrals of explosives had been established. There was substantial evidence in literature concerning the formation of nitrate from some explosives although the mechanism was unknown [1-2].

The method employed in these studies was dual shutter tandem mobility spectrometry for which prior technology demonstrations of dual shutter operation existed and tandem mobility designs have been described [3-4]. Kinetic studies build upon pioneering work of Ewing, et al. [4] and An, et al. [5]. Essential in this work was the synthesis of and refinements to the combination of all these developments creating a platform where ion kinetics could be measured and rate constants obtained over a range of temperatures. Additionally, pre-fractionation was included to provide defensible measurements regarding interferences from impurities in samples [7-9].

### C. *Major Contributions*

In Year 5, conclusion was made on the measurement of kinetic decomposition of PETN·Cl<sup>-</sup>, constituting the first of a series of thermally labile or improvised explosives. This measurement extended a significant reference work on nitrate esters and others [7-9]. A particular challenge with PETN ions and others, such as peroxides, is their intrinsic instability and a need for kinetic studies to form gas ions from the neutral without significant decomposition of the ion to be studied or decomposition of the neutral from which the ion was derived, and with ion intensities sufficient for a quality determination against levels of noise in the measurements. This necessitated the redesign and redevelopment of an instrument based on the previously successful kinetic IMS studies, but with significantly different approaches and designs for the sample inlet and formation of gas ions. The complexity of ionization of PETN demanded further exploration and controls, which has finally resulted in a complete work suitable (and in process) for publication. Scoping studies with peroxides were made to establish boundary conditions for measurements.

### D. *Milestones*

- A thorough and defensible characterization of the decomposition of ions from PETN was completed and backed by mass analysis.
- *Ab initio* modeling supported a proposed pathway for decomposition.
- A journal article on these discoveries is in progress.
- Technology suitable for studying highly labile explosives and improves explosives was developed and completed with the study of PETN.

### E. *Future Plans (Year 6)*

As a result of the ALERT Biennial Review conducted in March of 2018, this project has been terminated and will not be funded in Year 6. As much as possible, we will complete the investigations currently in progress with the following specific objectives:

- In any future studies by this or another team, we would recommend the addition of a liquid chromatograph to isolate impurities from the authentic substances planned in the same approach used with kinetic IMS studies of volatile explosives where a gas chromatograph was used to remove impurities from measurements.
- We would also recommend a series of studies based on peroxide based explosives and other peroxides to explore and establish the routes of decomposition of explosive related peroxides.

## III. RELEVANCE AND TRANSITION

### A. *Relevance of Research to the DHS Enterprise*

- *Performance of commercial ETDs concerning appearance of mobility spectra and optimization of parameters.* Findings from studies in this project established that each explosive ion exhibited a unique temperature for on-set of thermal decomposition. The selection of a single temperature for a drift tube in an IMS based ETD will result in a range of ion stabilities and thus responses seen in fragments in mobility spectra.
- *Drift tube design in ETDs.* Today, there are more than 10,000 ETDs from several manufacturers distributed within commercial aviation security worldwide. While these instruments are held to a standard, differences in performance exist and can be attributed to design elements for the inlet and the drift tube. The role of ion kinetics and the implications of ion residence in the drift tube complimented the first

relevance; thus, the role of time in the appearance of a spectrum and in the quantitative response was clarified in these studies.

In both of these points of relevance, manufacturers of ETDs should understand with fresh clarity the significance of their choices or decisions on dimensions, electric fields, and operations of ETDs to obtain optimum performance or to understand differences between ETD designs (manufacturers).

#### *B. Potential for Transition*

The fundamental discovery of kinetics and energies of decomposition of gas ions did not translate directly into any technology advance or transfer of technology. Such understandings stimulated thinking and creative developments in other projects where ions were decomposed in strong electric fields and inspired the team at NMSU to develop elsewhere the concept of field induced decomposition of gas ions of explosives.

#### *C. Data and/or IP Acquisition Strategy*

We do not see any IP on fundamental discoveries.

#### *D. Transition Pathway*

See Section III. B. above.

#### *E. Customer Connections*

See Section III. B. above.

### **IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION**

#### *A. Peer Reviewed Journal Articles*

##### **Pending-**

1. Cagan, A., & Eiceman, G.A. "Constituents in headspace vapors of an inert atmosphere over solid Pentaerythritoltetranitrate (PETN) by atmospheric pressure chemical ionization mass spectrometry." Submitted to the *Journal of Propellants, Explosives, and Pyrotechnics*.

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