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Gas phase ion chemistry of an ion mobility spectrometry based explosive trace detector elucidated by tandem mass spectrometry[☆]

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ABSTRACT

The gas phase ion chemistry for an ion mobility spectrometer (IMS) based explosive detector has been elucidated using tandem mass spectrometry. The IMS system, which is operated with hexachloroethane and isobutyramide reagent gases and an ion shutter type gating scheme, is connected to the atmospheric pressure interface of a triple quadrupole mass spectrometer (MS/MS). Product ion masses, daughter ion masses, and reduced mobility values for a collection of nitro, nitrate, and peroxide explosives measured with the IMS/MS/MS instrument are reported. The mass and mobility data together with targeted isotopic labeling experiments and information about sample composition and reaction environment are leveraged to propose molecular formulas, structures, and ionization pathways for the various product ions. The major product ions are identified as [DNT-H]⁻ for DNT, [TNT-H]⁻ for TNT, [RDX+Cl]⁻ and [RDX+NO₂]⁻ for RDX, [HMX+Cl]⁻ and [HMX+NO₂]⁻ for HMX, [NO₃]⁻ for EGDN, [NG+Cl]⁻ and [NG+NO₃]⁻ for NG, [PETN+Cl]⁻ and [PETN+NO₃]⁻ for PETN, [HNO₃+NO₃]⁻ for NH₄NO₃, [NO₂]⁻ for DMNB, [HMTD-NC₃H₆O₃+H+Cl]⁻ and [HMTD+H-CH₂O-H₂O₂]⁺ for HMTD, and [(CH₃)₃CO₂]⁺ for TATP. In general, the product ions identified for the IMS system studied here are consistent with the product ions reported previously for an ion trap mobility spectrometer (ITMS) based explosive trace detector, which is operated with dichloromethane and ammonia reagent gases and an ion trap type gating scheme. Differences between the explosive trace detectors include the [NG+Cl]⁻ and [PETN+Cl]⁻ product ions being major ions in the IMS system compared to minor ions in the ITMS system as well as the major product ion for TATP being [(CH₃)₃CO₂]⁺ for the IMS system and [(CH₃)₂CNH₂]⁺ for the ITMS system.

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1. Introduction

A recent research effort has focused on elucidating the gas phase ion chemistry inherent to ion mobility spectrometry based explosive trace detectors (ETDs) using mass spectrometry [1–3]. The underlying objective of the research has been to attain a fundamental understanding of the ambient pressure ionization pathways

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that govern the operating principles of the ETD equipment and to leverage that knowledge to advance the effectiveness of current and next generation systems. To date, the research effort has entailed interfacing two widely deployed ETDs, namely an ion trap mobility spectrometer (ITMS) manufactured by Morpho Detection Inc. and an ion mobility spectrometer (IMS) manufactured by Smiths Detection Inc., to triple quadrupole mass spectrometers (MS/MS).

While both the ITMS/MS/MS and IMS/MS/MS instruments have been demonstrated to accurately measure the mass-to-charge ratios (m/z), collision-induced dissociation pathways, and reduced mobility (K_0) values for the ion species formed in the respective ETD systems, this data has only been reported for a comprehensive list of explosives using the ITMS/MS/MS instrument. Because ambient pressure ionization pathways are sensitive to any variation in reaction environment, including temperature, reagent gas composition, and ion gating strategy, it is erroneous to assume that data from the ITMS based instrument can be unconditionally extrapolated to the IMS based instrument [4–11]. For example, the ITMS based instrument

implements dichloromethane and ammonia reagent gases in addition to an ion trap type gating scheme, whereas, the IMS based instrument implements hexachloroethane and isobutyramide reagent gases in addition to an ion shutter type gating scheme.

With the aim of directly and comprehensively characterizing the gas phase ion chemistry inherent to reaction environment in the IMS based ETD system, product ion masses, daughter ion masses, and reduced mobility values for a collection of nitro, nitrate, and peroxide containing explosives have been measured using the IMS/MS/MS instrument. This data along with proposed molecular formulas, structures, and ionization pathways for the various product ions are reported, with closing discussion focused on examining similarities and differences between the ITMS and IMS based instruments.

2. Materials and methods

2.1. Instrumentation

All new data presented here was acquired using either an unmodified benchtop IMS based ETD (Model 400B Smiths Detection Inc.) or a IMS based ETD (Model 400B Smiths Detection Inc.) interfaced to a SCIEX API 2000 triple quadrupole mass spectrometer (see Fig. S1 and Table S1 in supplementary material) [1,12,13]. Electric field strengths, timings, pressures, temperatures, gas flows, reagent chemicals, and internal calibrants for both the negative and positive polarity operation of the IMS system are summarized in Table 1. The IMS system is composed of a thermal desorber attached to a stainless steel housing containing a reaction region with ^{63}Ni β -radiation source, an electrostatic ion shutter gate, an ambient pressure counter-flow drift region, and a Faraday plate detector [1,13]. During the operation of the IMS system, the thermal desorber is maintained

Table 1
Operating parameters for the benchtop IMS based ETD and the IMS based ETD attached to the API 2000 triple quadrupole mass spectrometer.

Polarity	Negative ion mode		Positive ion mode	
	Value	Unit	Value	Unit
Electric field strengths				
Drift region	257	V/cm	228	V/cm
Timings				
Ion gate pulse width	200	μs	200	μs
Ion gate repetition period	30	ms	30	ms
Pressures				
Reaction region/drift region	760	Torr	760	Torr
Temperatures				
Desorber	205	$^{\circ}\text{C}$	205	$^{\circ}\text{C}$
Inlet	240	$^{\circ}\text{C}$	285	$^{\circ}\text{C}$
Reaction region/drift region (housing)	115	$^{\circ}\text{C}$	225	$^{\circ}\text{C}$
Reaction region/drift region (gas)	111	$^{\circ}\text{C}$	217	$^{\circ}\text{C}$
Gas flows				
Sample gas ^a	250	cm^3/min	250	cm^3/min
Drift gas ^a	300	cm^3/min	300	cm^3/min
Reagents and calibrants				
Reagent chemical	Hexachloroethane		Isobutyramide	
Internal calibrant	4-Nitrobenzonitrile		Isobutyramide	

^a Purified air (5–25 ppm water and 50–100 ppm carbon dioxide) was used for both the sample and drift gases.

at a temperature of 205 $^{\circ}\text{C}$. For negative ion detection, hexachloroethane is used as the reagent chemical, 4-nitrobenzonitrile is used as the internal calibrant, and the IMS housing temperature is maintained at 115 $^{\circ}\text{C}$. For positive ion detection, isobutyramide is used as both the reagent chemical and internal standard while the IMS housing temperature is maintained at 225 $^{\circ}\text{C}$. Thermocouples are placed at multiple locations on the IMS housing and regularly monitored to ensure uniform temperature across the drift region. House air purified with a purge gas generator (Parker Balston Model 75) is used as the carrier and drift gases for both negative and positive polarity operation. The purified air is measured to have a water content of 1–10 ppm and a carbon dioxide content of 50–100 ppm using a moisture and carbon dioxide sensor.

The method used to interface the IMS system to the API 2000 is described elsewhere [1,14,15]. Briefly, the Faraday plate in the IMS system is replaced with a custom Faraday plate which contains a centered hole for passing a portion of the ion beam into the mass spectrometer. The custom Faraday plate along with the unmodified portion of the IMS system is positioned immediately before the orifice in the atmospheric pressure interface of the API 2000 using a custom interface flange.

The API 2000 is composed of a differentially pumped interface and a triple quadrupole mass analyzer [12]. The differentially pumped interface, namely the skimmer electrode, is altered to include ion gating capabilities as well as to permit the electric field strengths and pressures in the interface to be adjusted. Specifically, the alternations involved electrically isolating the skimmer from the chamber of the mass spectrometer such that the electrode can be biased relative to ground as well as changing the opening in the skimmer such that the hole size in the electrode can be either 400 μm or 1100 μm . A 400 μm skimmer opening is used when a pressure of 1 mTorr is desired in the second stage of the differentially pumped interface while a 1100 μm skimmer opening is used when a pressure of 8 mTorr is desired.

2.2. Data acquisition

The benchtop IMS instrument can only be used to obtain mobility spectra whereas the IMS/MS/MS instrument can be used to obtain mobility spectra, mass and tandem mass spectra in the continuous ion flow mode, mass spectra in the selected mobility monitoring mode, and mass-selected mobility spectra (see Table S2 in supplementary material) [1,4,14,16,17]. To acquire a mobility spectrum, the ion gate in the IMS system is pulsed open to pass a packet of ions into the drift region and the ion intensity at the Faraday plate is registered relative to the drift time between the ion gate and the Faraday plate. In the continuous ion flow mode, the ion gates in the IMS system and the API 2000 are continuously held in the open position while the mass analyzer is operated in the scan only or product ion scan mode to acquire mass or tandem mass spectra. The selected mobility monitoring mode is used to acquire mass spectra for the individual peaks in a mobility spectrum. In the selected mobility monitoring mode, the ion gate in the IMS system is pulsed open while the ion gate in the API 2000 is opened after a specified time delay. The time delay is selected to permit only the ions with a desired mobility range to pass into the API 2000. This mobility filtered population is analyzed by operating the mass analyzer in the scan only mode to obtain a mass spectrum. To acquire a mass-selected mobility spectrum, the ion gate in the IMS system is pulsed open while the ion gate in the API 2000 is held in the open position and the mass analyzer is operated to pass only the ions with a specified m/z (i.e. the mass analyzer is operated in the single ion monitoring mode). The ion intensity at the electron multiplier in the API 2000 is registered relative to the drift time between the ion gate in the IMS system and the electron multiplier in the mass spectrometer to produce a mobility spectrum for the ions with the specified m/z only.

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