Direct analysis in real time mass spectrometry of potential by-products from homemade nitrate ester explosive synthesis

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ABSTRACT

This work demonstrates the coupling of direct analysis in real time (DART) ionization with time-of-flight mass spectrometry (MS) in an off-axis configuration for the trace detection and analysis of potential partially nitrated and dimerized by-products of homemade nitrate ester explosive synthesis. Five compounds relating to the synthesis of nitroglycerin (NG) and pentaerythritol tetranitrate (PETN) were examined. Deprotonated ions and adducts with molecular oxygen, nitrite, and nitrate were observed in the mass spectral responses of these compounds. A global optimum temperature of 350 °C for the by-products investigated here enabled single nanogram to sub nanogram trace detection. Matrix effects were examined through a series of mixtures containing one or more compounds (sugar alcohol precursors, by-products, and/or explosives) across a range of mass loadings. The explosives MS responses experienced competitive ionization in the presence of all by-products. The magnitude of this influence corresponded to both the degree of by-product nitration and the relative mass loading of the by-product to the explosive. This work provides a characterization of potential by-products from homemade nitrate ester synthesis, including matrix effects and potential challenges that might arise from the trace detection of homemade explosives (HMEs) containing impurities. Detection and understanding of HME impurities and complex mixtures may provide valuable information for the screening and sourcing of homemade nitrate ester explosives.

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1. Introduction

Rapid explosives detection with minimal sample preparation remains an area of interest to forensic science, homeland security, and military agencies. The class and state of explosives investigated varies widely across these fields and may include military-grade secondary explosives, homemade explosives (HMEs) such as nitrate esters and peroxides, primary fuel-oxidizer explosives, improvised explosive device (IED) components, synthesis precursors, and detonated decomposition products. There is an extensive literature base involving the detection of military-grade nitrated organic explosives, *e.g.* RDX or TNT, including common binders and plasticizers [1]. As non-state terrorism has evolved, there is an increased need to explore the detection of HMEs, including their precursors, synthesis by-products, impurities, and decomposition products. The detection of these compounds and their mixtures may enhance chemical libraries or provide valuable information into the route of synthesis and source materials. Because of the potential additional information

provided, it is crucial to not only detect these compounds but also understand how they behave in mixtures with the explosives.

One of the major classes of HMEs, nitrate ester explosives, represents a broad category of organic explosives, both military-grade and homemade, including compounds such as nitroglycerin (NG), pentaerythritol tetranitrate (PETN), and erythritol tetranitrate (ETN). Nitrate esters are synthesized through nitration of a sugar alcohol (polyol) precursor, as simplified in Fig. 1. This synthesis reaction may result in several potential by-products, namely partially nitrated and polymeric nitrated species. While a number of nitrate ester explosives exist, this work focuses on the nitration of glycerol (leading to NG) and pentaerythritol (leading to PETN) and their potential synthesis impurities. Both explosives have been synthesized militarily and illicitly, and are studied extensively [1–3]. A number of studies, mainly using liquid chromatography mass spectrometry (LC/MS), have identified impurities from NG and PETN synthesis, including partially nitrated and dimer species [4–7]. Partially nitrated species, such as 1,3-dinitroglycerin (DNG), can occur from incomplete nitration of the sugar alcohol due to lack of available free nitrate ions, abrupt cessation of the reaction, or other improper synthesis conditions [2,8]. Partially nitrated species can also form via hydrolysis of a fully nitrated nitrate ester [2]. Likewise, improper termination of
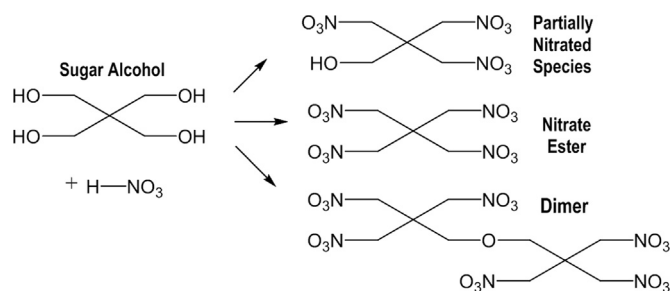
Fig. 1. Reaction pathway and potential by-products that occur during the synthesis and decomposition of nitrate ester explosives. In this example, pentaerythritol, pentaerythritol tetranitrate, and related compounds are shown.

the reaction process can cause the formation of dimer, trimer, and other polymeric species. Dimer species can also be formed from impurities in the starting sugar alcohol, such as the presence of diglycerol [9,10]. In addition to by-products formed during the reaction, a number of decomposition products, also partially nitrated species, may be created [4,6,7,9]. The relative amount of these impurities and degradation products are dependent on the route of synthesis and/or length of decomposition. Relative levels of DNG in groundwater samples containing NG were 50% to 100% that of NG [4]. Similarly, the presence of PETriN in degradation samples ranged from 20% to 100% that of PETN, while neat samples contained only approximately 0.1% [7].

This work highlights the characterization of potential by-products and decomposition products of NG and PETN using direct analysis in real time (DART) mass spectrometry (MS). DART-MS is an increasingly used ambient ionization (AI)-MS technique in forensic science laboratories [11], requiring minimal or no sample preparation, and has previously demonstrated detection of nitrate ester explosives [12–14] and their sugar alcohol precursors [15]. Extensive details of DART ionization pathways and analysis can be found in the literature [11,13,16]. The characterization presented here focused on identifying the mass spectral response of potential by-products and decomposition products. The compounds investigated included: 1-mononitroglycerin (1-MNG), 2-mononitroglycerin (2-MNG), 1,3-dinitroglycerin (DNG), pentaerythritol trinitrate (PETriN), and dipentaerythritol hexanitrate (diPEHN). In addition to the DART-MS characterization of these compounds, analysis of mixtures with their corresponding explosive (NG or PETN) and/or precursors (glycerol or pentaerythritol) was conducted. All compounds were readily detected in negative ionization mode as adducts with anions such as molecular oxygen, nitrite, and nitrate detectable in the low nanogram to sub nanogram range. The detection of explosives from mixtures with by-products demonstrated increasing ionization competition as by-product nitration increased. The large volatility difference between monomers and dimers produced significantly less competitive ionization with the explosive signal. Competitive ionization for the mixtures examined increased as the mass ratio of by-product to explosive increased.

2. Materials and methods

Liquid chromatography-mass spectrometry (LC-MS) Chromasolv® grade acetonitrile was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used for sample dilution.[1]

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[1] Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by National Institute of Standards and Technology, nor does it imply that such products are necessarily the best available for the purpose.

1-mononitroglycerin (1-MNG), 2-mononitroglycerin (2-MNG), and 1,3-dinitroglycerin (DNG) were purchased from Cerilliant (Round Rock, TX, USA) while pentaerythritol trinitrate (PETriN), and dipentaerythritol hexanitrate (diPEHN) were purchased from AccuStandard (New Haven, CT, USA) at a concentration of 1 mg/mL or 0.1 mg/mL, in either methanol or acetonitrile, and further diluted in acetonitrile to desired concentrations. Nitric acid (Sigma-Aldrich) diluted in acetonitrile was used as an additional precursor in mixture analysis. Glycerol (gly) and pentaerythritol (PE) were purchased in pure form from Sigma Aldrich and dissolved/diluted in acetonitrile. Nitroglycerin (NG) and pentaerythritol tetranitrate (PETN) were purchased as 1 mg/mL standards from AccuStandard (New Haven, CT, USA) and diluted in acetonitrile. Samples were deposited by directly pipetting 1 μL – 2 μL aliquots of the desired compounds onto polytetrafluoroethylene (PTFE, Teflon) wells, coated on glass slides (Tekdon Inc., Mayakka City, FL, USA). Polyethylene glycol 600 (PEG 600) (Sigma-Aldrich) diluted in acetonitrile was used as the MS tuning compound.

For this work a Vapur® interface (IonSense, Saugus, MA, USA) was used, coupling the DART ionization source (IonSense) sampling region and the time-of-flight mass spectrometer (JEOL AccuTOF JMS-T100LP, JEOL USA, Peabody, MA, USA). The Vapur® allowed for off-axis sampling [15] (45° with respect to the sample surface) by pulling the aerosolized/vaporized sample towards the mass spectrometer inlet at a rate of approximately 3.8 L/min. Off-axis analysis, completed by pulling the gas flow into the mass spectrometer instead of allowing direct transmission of the DART gas into the mass spectrometer permitted larger samples and sample areas to be analyzed. Off-axis analysis resulted in a decrease in atmospheric noise, potentially increasing sensitivity. In the off-axis system used, the substrate was mounted vertically on a manual 3-axis stage and positioned less than 1 mm away from the ceramic tip on the Vapur® inlet. The DART source was then turned to 45°, relative to the MS inlet, for analysis. Base mass spectrometer parameters included a 350 °C DART gas stream temperature, 100 °C orifice temperature, $\pm$ 20 V orifice 1 voltage, $\pm$ 5 V ring and orifice 2 voltages, $\pm$ 2000 V detector voltage, $\pm$ 400 V peaks voltage and a mass scan range of 40 m/z to 800 m/z. Unless otherwise noted, 100 ng aliquots of the compounds were deposited onto PTFE coated glass slides and interrogated for 45 s to 60 s at 0.5 s/scan for analyses.

3. Results and discussion

3.1. Mass spectral characteristics and sensitivities

Five compounds of interest (1-MNG, 2-MNG, DNG, PETriN, and diPEHN) were analyzed directly off PTFE coated glass slides, using DART-MS, to obtain characteristic mass spectra in both negative and positive ionization modes. Peaks of interest were identified and mass assignments were made based upon accurate mass measurements ($\pm$ 0.005 Da mass accuracy), which are highlighted in Table 1. No identifiable peaks attributed to the compounds of interest were detected at the 100 ng level in positive ionization mode; therefore, the remainder of this discussion focuses on negative ionization mode. The response of these compounds was dependent upon the first orifice voltage, which controls declustering and the extent of fragmentation/adduct formation.

At relatively low orifice voltage (− 10 V), these compounds readily formed adducts with a number of ionic species generated through DART ionization pathways [17], including molecular oxygen $[M+O_2]^-$, nitrite $[M+NO_2]^-$, and nitrate $[M+NO_3]^-$. Dimers of the compounds with these adducts ($[2M+O_2]^-$, $[2M+NO_2]^-$, and $[2M+NO_3]^-$) were also observed (Figs. 2 and 3 and Table 1). In all instances, "M" denotes an intact molecule of the