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# Characterization of TATP gas phase product ion chemistry via isotope labeling experiments using ion mobility spectrometry interfaced with a triple quadrupole mass spectrometer

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## ABSTRACT

Identification of the fragment ion species associated with the ion reaction mechanism of triacetone triperoxide (TATP), a homemade peroxide-based explosive, is presented. Ion mobility spectrometry (IMS) has proven to be a key analytical technique in the detection of trace explosive material. Unfortunately, IMS alone does not provide chemical identification of the ions detected; therefore, it is unknown what ion species are actually formed and separated by the IMS. In IMS, ions are primarily characterized by their drift time, which is dependent on the ion's mass and molecular cross-section; thus, IMS as a standalone technique does not provide structural signatures, which is in sharp contrast to the chemical and molecular information that is generally obtained from other customary analytical techniques, such as NMR, Raman and IR spectroscopy and mass spectrometry. To help study the ion chemistry that gives rise to the peaks observed in IMS, the hardware of two different commercial IMS instruments has been directly coupled to triple quadrupole (QQQ) mass spectrometers, in order to ascertain each ion's corresponding mass/charge ( $m/z$ ) ratios with different dopants at two temperatures. Isotope labeling was then used to help identify and confirm the molecular identity of the explosive fragment and adduct ions of TATP. The  $m/z$  values and isotope labeling experiments were used to help propose probable molecular formulas for the ion fragments. In this report, the fragment and adduct ions  $m/z$  58 and 240 of TATP have been confirmed to be  $[\text{C}_3\text{H}_6\text{NH}\cdot\text{H}]^+$  and  $[\text{TATP}\cdot\text{NH}_4]^+$ , respectively; while the fragment ions  $m/z$  73 and 89 of TATP are identified as having the molecular formulas  $[\text{C}_4\text{H}_9\text{NH}_2]^+$  and  $[\text{C}_4\text{H}_9\text{O}_2]^+$ , respectively. It is anticipated that the work in this area will not only help to facilitate improvements in mobility-based detection (IMS and MS), but also aid in the development and optimization of MS-based detection algorithms for TATP.

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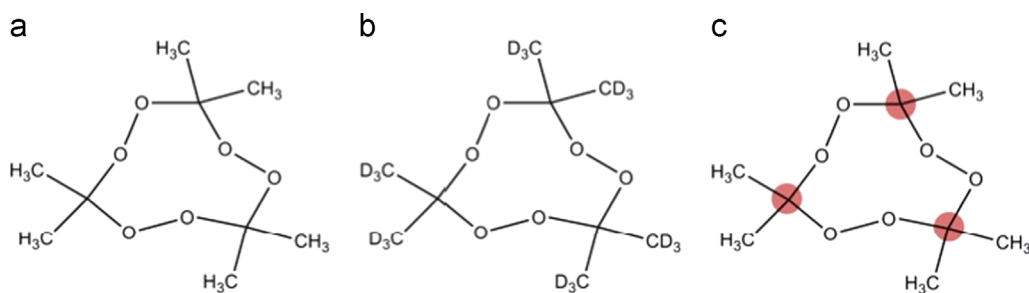
## 1. Introduction

The organic peroxide, triacetone triperoxide (TATP), Fig. 1a, is a common component of improvised explosive devices (IEDs) used by terrorists [1]. For this reason, there is a great demand for designing or determining methods that can be used to improve the capability and efficiency of detecting TATP, and other compounds in the class of organic peroxides [2,3]. The first reported synthesis of TATP was by Wolffenstein in 1895, and its energetic

properties were initially attributed to the ether used in the re-crystallization process and not to the TATP itself [4]. In 1959, a more efficient acid-catalyzed synthetic method for activating the ketone (acetone) was described by Milas [5], with variations of this method recently being used by Oxley et al. [6] and Dubnikova et al. [7]. TATP exhibits explosive power similar to that of 2,4,6-trinitrotoluene (TNT), and is very sensitive to flame, heat, impact and friction [7–10]. The explosive properties of TATP have been well characterized [7,11] and it has been established that TATP can be detected using analytical methods such as mass spectrometry [3,12]. However, while the signatures used for field detection successfully identify the presence of TATP, a thorough knowledge of the molecular chemistry or product ion formula that is associated

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**Fig. 1.** Chemical structures of (a) TATP, (b) deuterated TATP ( $d_{18}$ -TATP), and (c)  $^{13}\text{C}$ -TATP, with the labeled ring carbons highlighted (red dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with the detection signatures is lacking. Previous studies have been performed in attempts to increase this knowledge; however, results reported to date reveal that there still exists a knowledge gap regarding the chemical or formula identification of the ion chemistry of TATP under atmospheric pressure ionization conditions.

A key and proven analytical method for the field detection of TATP and other contraband is ion mobility spectrometry (IMS), with tens-of-thousands of IMS-based instruments being used by both military and civilian security [13–15]. In many commercial off the shelf (COTS) IMS explosive trace detectors (ETDs), samples of explosive particulates are thermally vaporized, and then ionized by atmospheric pressure chemical ionization (APCI) processes, followed by ion separation based on positive or negative charge, mass, size and geometry. IMS systems identify ions produced in its reaction region (product ions) by their drift time (i.e. mobility value or specific peak positions in the mobility spectrum) as compared to established algorithmic libraries based on empirical data, with the aid of recognition algorithms facilitating TATP detection. When used as a standalone method, IMS does not provide the specificity, resolving power, or molecular signature capability to identify an ion's molecular chemistry or formula.

Most conventional explosives, such as TNT, pentaerythritol tetranitrate (PETN), trinitroglycerin (NG) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), have similar ion chemistry in that they contain active nitro or nitrate functional groups with high electron affinity, giving rise to strong responses in the IMS-negative ion detection mode. The subsequent product ions that are generated for PETN, RDX and NG have been identified to be adducts of the conventional explosive with chloride ( $\text{Cl}^-$ ), nitro ( $\text{NO}_2^-$ ), or nitrate ( $\text{NO}_3^-$ ) ions, while TNT forms  $\text{M}^-$ , by way of electron loss, when ionized with nitrogen as the only supporting atmosphere or ( $\text{M}-\text{H})^-$ , by way of proton abstraction, in the presence of ions such as  $\text{O}_2^-$  or  $\text{Cl}^-$  [16]. The chloride ions are added to the ETDs as a reagent chemical, most commonly as dichloromethane or hexachloroethane, while the formation and presence of the nitro and nitrate adduct groups are attributed to the decomposition of the explosive parent molecules, with the presence of oxygen coming from air. These adduct ions, in turn, act to stabilize other explosive fragments or parent ions, where applicable, aiding in their detection.

TATP displays very different ion chemistries than conventional military explosives. TATP has been shown to generate product ion response peaks in the IMS-negative ion detection mode that have been assigned to mass/charge ( $m/z$ ) ratios of 143 and 145, of proposed formulas  $\text{C}_3\text{H}_8\text{O}_4 \cdot ^{35}\text{Cl}^-$  and  $\text{C}_3\text{H}_8\text{O}_4 \cdot ^{37}\text{Cl}^-$ , respectively. [17] Unfortunately, this peak response has been shown to be sample dependent, and therefore is unreliable for the detection of pure TATP in the negative ion mode [18].

In contrast, in the IMS-positive ion detection mode, in the presence of isobutyramide (IBA) or ammonia ( $\text{NH}_3$ ) dopants, TATP gives strong product ion peak responses; however, a thorough

knowledge of the molecular chemistry or product ion formula that is associated with the IMS peaks of TATP is lacking. A variety of ionization and sample introduction methods and mass spectrometry techniques (i.e., IMS, MS and IMS/MS) have been previously conducted to help address this knowledge gap. These studies have identified product ion  $m/z$  ratios for TATP and correlated signatures in TATP detection in attempts to identify the ion chemistry [9,12,18–24]. Specifically, at lower temperatures (i.e. at lower thermal desorption, inlet, and drift temperatures), below  $\sim 140^\circ\text{C}$ , with the ammonia dopant, the  $m/z$  240 peak is prominent and has been identified as having the molecular formula  $\text{TATP} \cdot \text{NH}_4^+$ , with a reduced mobility ( $K_0$ ) of  $1.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [9,18–24]. While at higher temperatures, above  $\sim 150^\circ\text{C}$ , either  $m/z$  89 ( $K_0 = 2.18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [18] or  $m/z$  91 ( $K_0 = 2.00 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [19] tend to dominate; however, only Widmer et al. reported seeing both  $m/z$  89 and 91 peaks in the same experiment [22]. It has been postulated that the  $m/z$  91 peak has the molecular formula  $\text{C}_3\text{H}_6\text{O}_3 \cdot \text{H}^+$  [19,20,25], while the formula of the  $m/z$  89 peak has yet to be proposed [18,22,23]. Only Marr and Groves [18] reported observing  $m/z$  73 ( $K_0 = 2.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), however no possible molecular formula was proposed. Shen et al [20], employing the ammonia dopant in their reaction conditions, were the first to attribute the observed  $m/z$  58 ( $K_0 = 2.32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [18,19] peak to an unknown species and not to the previously assumed molecular formula of acetone  $(\text{CH}_3)_2\text{C}=\text{O}$ , as originally proposed by Marr and Groves [18]. More recently, Ewing et al. [19] has demonstrated that the  $m/z$  58 species is actually due to protonated 2-propanimine, with a molecular formula of  $(\text{CH}_3)_2\text{C}=\text{NH} \cdot \text{H}^+$ . The literature reveals that there still exists a paucity of information regarding the chemical or formula identification of the “product ions” of TATP under atmospheric pressure ionization conditions.

To facilitate the chemical identification of the product ions that give rise to IMS peaks in COTS ETDs, the hardware from two COTS IMS-based units has been coupled to triple-quadrupole (QQQ) mass spectrometers (MS). In this recently developed configuration [26], the product ions that are produced in the reaction region of the IMS are passed through an interface region and are detected using either the Faraday plate of the IMS or the mass spectrometer electron multiplier, wherein the product ion intensity is registered as a function of the drift time. By adjusting the operational mode of the mass analyzer, a mobility spectrum and a corresponding mass spectrum (i.e.  $m/z$  ratios) can be obtained for the product ions. The full details of the interfacing methodology of these IMS-MS based instruments and the proof of their operational effectiveness in the characterization of TNT, PETN and RDX have been described in previous publications [26,27]. These systems have been employed in this study, along with the chemical additive reagents IBA and ammonia, utilizing the positive ion detection mode, to obtain mobility spectra and corresponding  $m/z$  ratios for each product ion of TATP produced. Following mass determinations, isotope labeling experiments were conducted and the isotopic shift results were used to verify the product ions from TATP in

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