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Gas-phase reactions for selective detection of the explosives TNT and RDX

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Highly selective gas-phase reactions with ethyl vinyl ether (EVE) of major electron (EI) and chemical ionization (CI) fragment ions of the explosives TNT and RDX have been uncovered. The fragment ion of *m/z* 210 from TNT undergoes $[4^+ + 2]$ cycloaddition with EVE to form an oxo-iminium ion of *m/z* 282, which dissociates by acetaldehyde loss after a [1,5-H] shift to form a quinolynium ion of *m/z* 238. The fragment ion of *m/z* 149 from RDX reacts with EVE by a formal vinylation reaction, that is, the elusive cyclic adduct loses ethanol to yield a nitro-iminium ion of *m/z* 175, which reacts further with EVE to form a second cyclic product ion of *m/z* 247. Calculations and MS/MS experiments support the proposed structures. These highly characteristic reactions of diagnostic EI and CI fragment ions improve selectivity for TNT and RDX detection.

Explosives detection is a topic of increasing interest.[1] For such an important task, several analytical methods have been developed, including gas chromatography either with electron capture or nitrogen phosphorus detectors, mass spectrometry[2] (MS) and high performance liquid chromatography with ultraviolet or MS detection.[3] Improved performance, including greater selectivity (to minimize false positives) and sensitivity, remains highly desirable and tandem mass spectrometry[4] is an obvious candidate. While collision-induced dissociation is very selective, highly complex matrices call for additional selectivity. This might be provided by ion/molecule reactions of mass-selected ions with appropriate neutral reagents. Previous experiments on trinitrotoluene (TNT) suggest that such gas-phase reactions can provide an excellent MS method for rapid, sensitive, and highly selective chemical analysis.[5]

Gas phase cycloadditions are highly selective for compound class and geometry, and are therefore prime candidates for diagnostic reactions. We have systematically studied a variety of such reactions by tandem MS.[6] For instance, *N*-alkylpiperidienes form *N*-alkyl-2-azabutadienyl cations upon 70 eV electron ionization (EI) and these ions undergo structurally diagnostic $[4^+ + 2]$ cycloadditions with vinyl ethers followed by prompt alcohol loss.[6d] Herein we report that highly selective cycloaddition or cyclization reactions (Scheme 1) occur for the TNT fragment ion of *m/z* 210 (**1**) and the hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) fragment ion of *m/z* 149 (**2**) with ethyl vinyl ether (EVE). Proposed product ion structures are corroborated *via* MS/MS experiments and AM1 calculations. The EVE cycloaddition of **1**, an iminium ion, is similar to that of *N*-alkyl-2-azabutadienyl cations,[6a,b] whereas the EVE cyclization reaction of **2** (a formal vinylation reaction) is unprecedented.

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Interestingly, we found **1** and **2** also to be formed as the major product ions *via* chemical ionization (CI) of TNT and RDX with 1,2-dichloroethane through H_2O and CH_2NNO_2 loss, respectively.[7] This increases the sensitivity of the analysis making **1** and **2** excellent candidates for both EI and CI diagnostic ions in TNT and RDX detection. Ions **1** and **2** were individually mass-selected and reacted with EVE and Fig. 1 shows the resulting mass spectra. The ion of *m/z* 282 (Fig. 1a) is likely the expected regioselective $[4^+ + 2]$ EVE cycloadduct[6c] of **1**, which loses acetaldehyde after a [1,5-H] shift to form the second product ion of *m/z* 238. For **2**, the intact $[4^+ + 2]$ EVE adduct of *m/z* 221 is not observed likely owing to prompt ethanol loss that forms the ion of *m/z* 175 (Fig. 1b). Then, cyclization of *m/z* 175 with a second EVE molecule forms *m/z* 247. Competitive reactions in both cases form protonated EVE of *m/z* 73 and ethylated EVE of *m/z* 101,[6b] whereas CID of **1** forms *m/z* 193, *m/z* 164, and that of **2** forms *m/z* 85 and *m/z* 75 (not shown).

Potential energy surface diagrams for the proposed reactions of **1** and **2** with EVE as elaborated from semi-empirical AM1 calculations[8] show that both reactions are highly exothermic (Fig. 2). Because they are abundant in 70 eV EI and CI spectra, **1** and **2** are important target ions for TNT and RDX, respectively; hence, their characteristic reactions with EVE herein described function as a highly diagnostic method for TNT and RDX detection.

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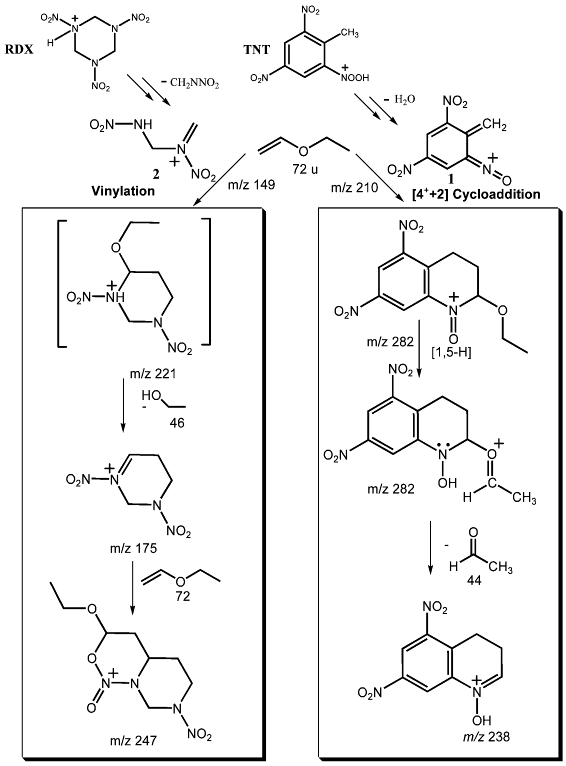

Scheme 1 Reaction mechanisms of vinylation for the ion **2** of *m/z* 149 and $[4^+ + 2]$ cycloaddition for the ion **1** of *m/z* 210.

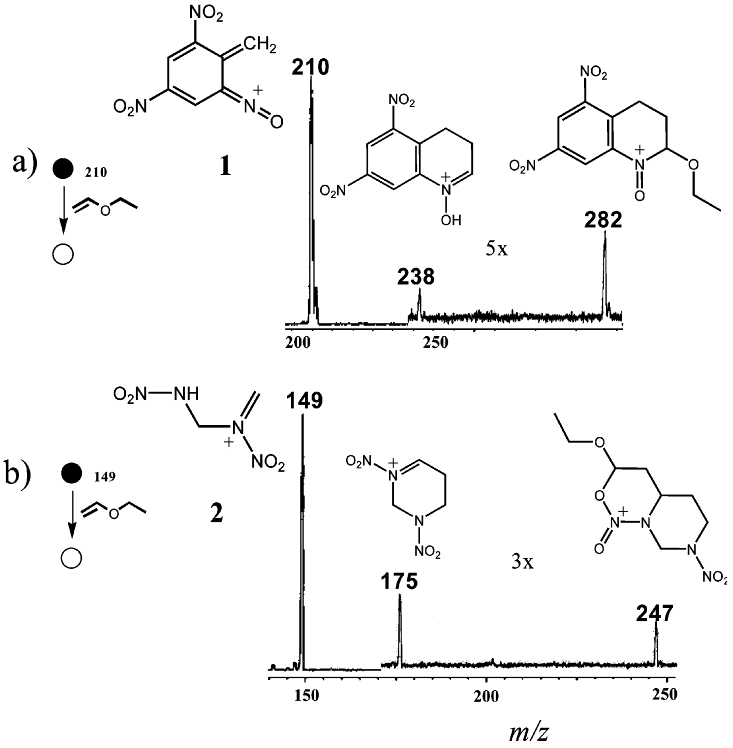

Fig. 1 Product ion mass spectra showing the ion/molecule reactions of EVE with a) ion **1** of *m/z* 210 and b) ion **2** of *m/z* 149.

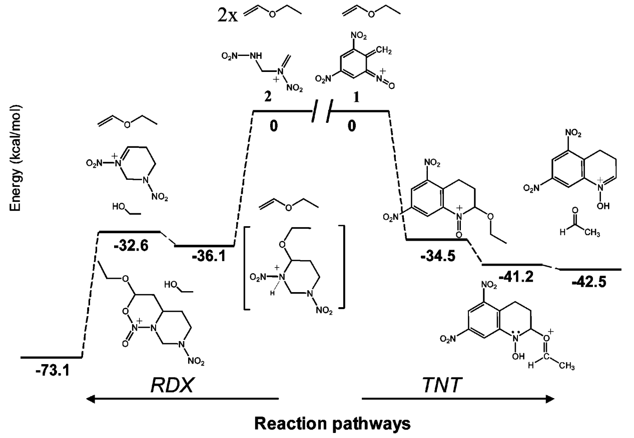

Fig. 2 Potential energy surface diagram for [4^+ + 2] cycloaddition and subsequent aldehyde loss from **1** and EVE (right pathway) and cyclization with fast ethanol loss and a second EVE addition from **2** and EVE (left pathway). The energies of the full geometry optimized species in kcal mol^{-1} are: **1** ion (258.38), EVE (−31.33), adduct1 (**1** − EVE) (192.59), adduct2 (**1** − EVE − acetaldehyde) (185.81), product (quinolynium) (226.07), acetaldehyde (−41.56), **2** ion (265.39), adduct3 (**2** − EVE) (197.38), adduct4 (**2** − EVE − ethanol) (264.12), adduct5 [(**2** − EVE − ethanol) − EVE] (192.33) and ethanol (−62.66).

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