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Dear Sir,

Screening of organic nitrate explosives: selective ion/molecule reactions for the diagnostic ion NO_2^+

Highly efficient explosive screening has become a major analytical challenge and, owing to its outstanding speed, selectivity and sensitivity, mass spectrometry (MS) is placed at the center of attention in this field.[1] An efficient explosive detection system should be able to discriminate simultaneously a broad range of explosives at trace levels in mixtures with many background compounds normally present at much higher concentrations. The analytical technique employed must therefore provide diagnostic molecular signatures for each explosive to enable detection that is immune to false positives. MS efforts have been concentrated, therefore, on finding the most appropriate ionization technique or selective derivatization method for each single explosive, often using ion/molecule reactions.[2-5]

Because the great majority of explosive screenings are expected (and actually found) to be negative, an explosive-by-explosive multivariate screening approach should greatly benefit from preliminary broad-range screening with much enhanced high-throughput capabilities. When using MS first an 'in/out' screening could be performed for a set of diagnostic ions of each major class of explosives. Fortunately, major explosives belong to just a few classes; actually, the majority of them are organic nitrates such as TNT (trinitrotoluene), DNT (dinitrotoluene), TNB (trinitrobenzene), DNB (dinitrobenzene), NG (nitroglycerine), EGDN (ethyleneglycol dinitrate), PETN (pentaerythritol tetranitrate), RDX (hexahydro-1,3,5-trinitro-1,3,5 triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine), nitroguanidine and tetryl. It is most interesting that in MS explosive detection most organic nitrates dissociate extensively upon electron ionization (EI), forming the nitronium ion NO_2^+ of m/z 46 either at high or at sufficiently high abundances, as Fig. 1 illustrates for RDX.

NO_2^+ could serve, therefore, as a selective diagnostic ion for the MS screening of organic nitrates. This ion is also attractive since other isobaric ions of m/z 46 are rare, which should therefore minimize interferences. For broad-range screenings, false positives should, however, be reduced to a nearly null level, so NO_2^+ detection based

only on m/z measurement could compromise reliability. Here, we describe an efficient and structure-diagnostic ion/molecule reaction applicable to highly selective NO_2^+ detection.

On the basis of the structural analogy of $O=N^+=O$ with acylium ions $R-C^+=O$, and their similar amphoteric natures[6] we, using a pentaquadrupole mass spectrometer,[7] tested for mass-selected NO_2^+ a series of ion/molecule reactions[8] that occur promptly for acylium ions. Among these reactions, we found that NO_2^+ reacts efficiently by the gas-phase Meerwein reaction,[9,10] by acetalization with diols and analogues[11,12] and, most efficiently, by transacetalization[13,14] with cyclic acetals (Scheme 1).

Figure 2 shows, as a typical example, the product ion mass spectra for reactions of mass-selected NO_2^+ with 2,2-dimethyl 1,3-dioxolane performed under close to 1-eV multiple collision conditions. Note that the ion reacts promptly by transacetalization to form the product ion of m/z 90 in a highly thermodynamically favored process (Fig. 3). Formal CH_3^- abstraction that proceeds likely by electron abstraction followed by fast dissociation of the nascent ionized molecule of 2,2-dimethyl 1,3-dioxolane by CH_3 radical loss to form the ion of m/z 87 is also a major reaction. NO_2^+ also reacts analogously with two other volatile cyclic acetals, 2-methyl and 2,2-pentamethyl 1,3-dioxolane (spectra not shown).

Figure 4 shows the sequential product ion mass spectra for the mass-selected product ion of m/z 90. Upon CID, the transacetalization product of m/z 90 re-forms to only a limited extent the reactant ion of m/z 46, dissociating instead mainly to NO^+ of m/z 30. We rationalize such a favored process by sequential loss of two formaldehyde molecules (Scheme 2).

In conclusion, a broad-range method for trace screening of organic nitrate explosives is proposed on the basis of the highly selective MS detection of the diagnostic ion NO_2^+ performed first by mass analysis and subsequently, after m/z 46 detection, by structure-diagnostic ion/molecule reactions of the mass-selected ion with cyclic acetals. With 2,2-dimethyl 1,3-dioxolane, the gaseous NO_2^+ ion reacts efficiently by transacetalization to form a characteristic and unprecedented product ion of m/z 90. Enhanced selectivity can be achieved by dissociating the ion of m/z 90; upon CID, it forms mainly NO^+ of m/z 30.

It appears to us that detection of the diagnostic NO_2^+ ion could be most efficiently performed using EI in miniaturized ion
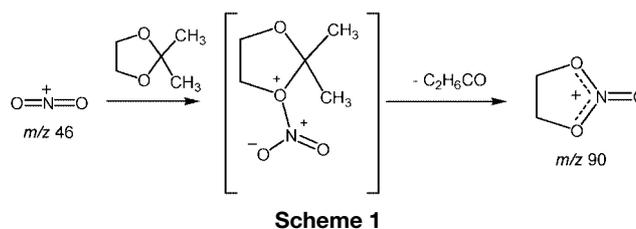
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Scheme 1
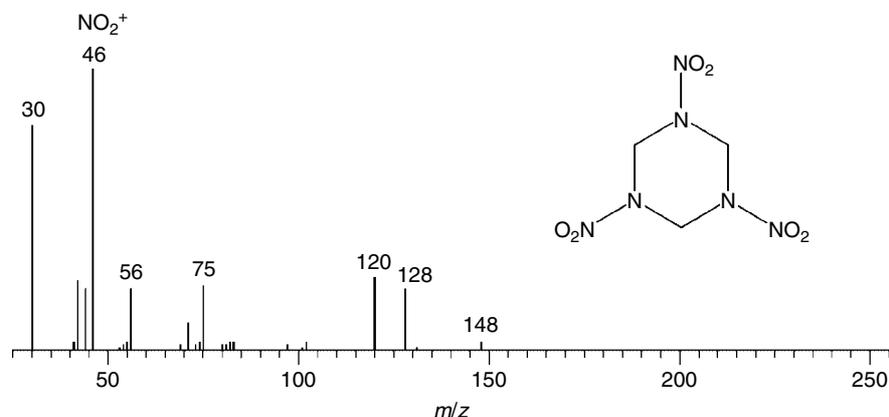
Figure 1. 70-eV EI mass spectra of RDX showing extensive dissociation of the molecular ion of m/z 220 (not detected) and formation of NO_2^+ as the most abundant fragment ion. Source: NIST library of mass spectral data.
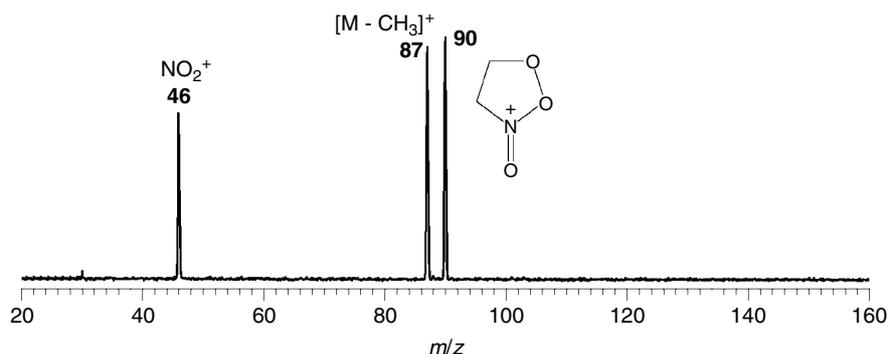
Figure 2. Product ion mass spectrum for reactions of NO_2^+ with 2,2-dimethyl-1,3-dioxolane.
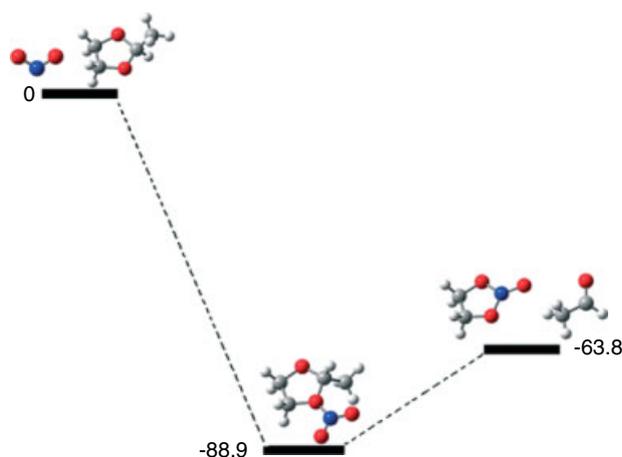
Figure 3. Potential energy diagram for transacetalization of NO_2^+ with 2-methyl-1,3-dioxolane. Calculations were performed using Spartan at the B3LYP-6-31G(d,p) level. Energies are in Kcal mol^{-1}.
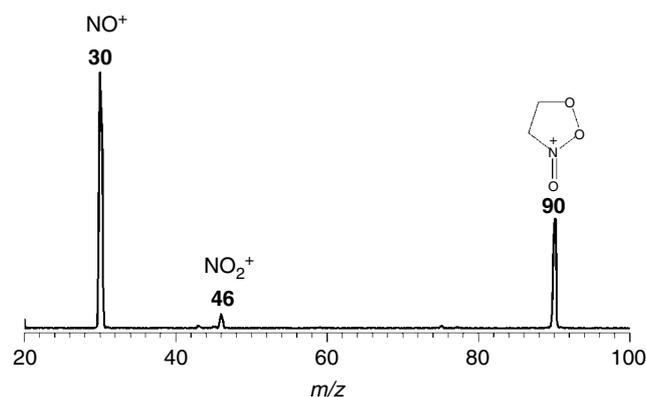
Figure 4. Sequential product ion mass spectrum for CID of the NO_2^+ transacetalization product ion of m/z 90.
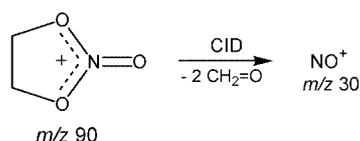
Scheme 2

traps.[15] Owing to minimal pumping requirements, EI has been easily implemented in most miniaturized equipments for on-site field inspection. Using ion-trapping devices, ions of m/z 46 could be trapped for relatively long times for highest sensitivity followed by ion/molecule reactions that are easily performed with volatile neutrals in such devices. Although the limits of detection (LOD) depends on many parameters and varies considerably according to the type of explosive, matrix and sampling, we estimate that LOD as low as part-per-trillion could be attained. Also, in ion traps, the double-reaction monitoring approach m/z 46 $\rightarrow$ m/z 90 $\rightarrow$ m/z 30 could be easily implemented for highly selective broad-range MS screening of organic nitrate explosives.

Yours,

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