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The Analysis of Explosives by Tandem Mass Spectrometry

REFERENCE: McLuckey, S. A., Glish, G. L., and Carter, J. A., **"The Analysis of Explosives by Tandem Mass Spectrometry,"** *Journal of Forensic Sciences*, JFSCA, Vol. 30, No. 3, July 1985, pp. 773-788.

ABSTRACT: Data obtained via tandem mass spectrometry are reported for ions derived from several explosives and related compounds. Electron impact ionization, isobutane chemical ionization, and negative chemical ionization methods were used to form ions from each of the compounds studied. These compounds include *o*-, *m*-, and *p*-nitrotoluene; *m*-dinitrobenzene; 2,4-dinitrotoluene; 2,4,6-trinitrotoluene; 2,4-dinitrophenol; picric acid; 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX); 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane (HMX); nitroglycerin; pentaerythritol tetranitrate (PETN); and ethylene glycol dinitrate (EGDN). For a given ionization method each class of compounds (that is, nitrobenzenes, heterocyclic nitramines, and nitrate esters) shows common decompositions. This promises to facilitate rapid screening for particular types of explosives by the neutral loss scanning procedure. Of the three ionization methods employed, electron impact ionization is least suitable for analysis of explosives by tandem mass spectrometry. Positive and negative chemical ionization methods, in contrast, tend to generate the types of ions most useful for analysis by tandem mass spectrometry.

KEYWORDS: forensic science, explosives, spectroscopic analysis

The detection and identification of explosives are important tasks in many forensic science laboratories. These tasks are particularly challenging when the explosive materials are present in trace quantities in such matrices as, for example, post-explosion debris, biological fluids, and the atmosphere. In these cases, the analytical method must be both extremely sensitive and highly specific. Single-stage mass spectrometry (MS) employing one or more of several ionization techniques is often the method of choice since it is highly sensitive and can be very specific. However, when dealing with a complex mixture containing relatively small amounts of the compound(s) of interest, some type of separation before MS is usually necessary. Typically, the separation consists of solvent abstraction(s) followed by gas or liquid chromatography. Despite the usefulness of these types of separation procedures, gas or liquid chromatography may be too time-consuming or may be inappropriate for a particular sample.

Tandem mass spectrometry, or mass spectrometry/mass spectrometry (MS/MS), provides an alternative approach to these problems. Tandem MS refers to the use of two stages of mass spectrometry in which the first stage serves as a separator for the second. Recently

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Research sponsored by the U.S. Department of Energy, Office of Safeguards and Security, under Contract DE AC05-840R21400 with Martin Marietta Energy Systems, Inc. Received for publication 5 Oct. 1984; revised manuscript received 9 Nov. 1984; accepted for publication 16 Nov. 1984.

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this technique has been shown to be very useful for complex mixture analysis in a wide variety of applications [1,2]. The technique is rapid and is particularly advantageous for targeted compound analysis. The latter feature results from the capability to select at will and in any order the mass/charge ratios of the ions to be studied and from the capability to scan the two mass spectrometers in concert in various ways to allow for functional group screening [3,4]. These features make tandem MS a powerful tool for many forensic science applications.

Since the mid 1970s MS/MS has evolved rapidly, and a rather wide variety of instrumental configurations have been developed. For most of these instruments the usual procedure is to set the first mass spectrometer to pass ions of a particular mass/charge ratio and scan the second mass spectrometer to detect ions that result from fragmentation in the region between the analyzers. To increase the fraction of ions which fragment in this region, a gas is usually admitted between the analyzers to excite or activate collisionally the ions. The resulting fragmentation is referred to as collisionally activated decomposition (CAD). This reaction can be symbolized as:

$$m_1^+ \xrightarrow{N} m_2^+ + m_3$$

where m_1^+ is the precursor or parent ion, N is a neutral collision gas atom or molecule, m_2^+ represents a fragment or daughter ion, and m_3 is a neutral fragment. An attractive feature of MS/MS for mixture analysis is the flexibility in scanning modes. The procedure described above is frequently referred to as a daughter ion scan where all m_2^+ from m_1^+ are detected. Two other useful scan modes for functional group screening are the so-called parent and neutral loss scans. In the former, the spectrometer detects all m_1^+ which give a particular m_2^+, while in the latter case all fragmentations which result in a specified m_3 are detected.

The extensive literature on the mass spectrometry of explosives (reviewed recently by Yinon [5]) reflects the applicability of MS in this area, as well as the interest in these compounds. However, because of the relatively recent development of MS/MS, only a few reports have appeared that describe MS/MS data from explosives [6,7]. This paper reports the MS/MS spectra derived from daughter ion scans of ions formed from a number of explosives and related compounds via electron impact ionization (EI), isobutane chemical ionization (CI), and negative chemical ionization (NCI). The compounds investigated fall into one of three classes of explosives: nitroaromatics, nitrate esters, and heterocyclic nitramines.

Experimental Procedure

All data were acquired using a VG Gas Analysis ZAB mass spectrometer converted for organic compound analysis. The instrument is fitted with a VG EI/CI ion source and a syringe needle collision cell [8] situated above the intermediate focal point. Accelerating voltages of 5-7 kV were used with the polarity depending upon the desired ion charge. Mass spectra were obtained by scanning the magnetic field while fixing the source and electrostatic analyzer plate voltages at the proper values to pass fully accelerated ions. Daughter ion spectra were obtained by fixing the source voltage and magnetic field to pass a particular momentum/charge ratio and scanning the electric sector. This procedure results in a kinetic energy/charge spectrum (which is linearly proportional to a mass/charge spectrum in this case) of the ions that fragment after exiting the magnetic field and before entering the electric field. When collision gas is admitted into this region to increase fragmentation, the resulting daughter ion spectrum is referred to herein as a CAD spectrum to distinguish it from a spectrum obtained from ions which fragment spontaneously in this region, that is, metastable ions. Where CAD spectra were acquired, nitrogen collision gas was admitted so that the parent ion beam current was diminished by 25 to 50%. All samples were introduced via a direct insertion probe.

For electron impact studies, an ionizing electron energy of 70 eV was employed with a measured trap current of 100 to 200 μA. The repeller voltage was typically 0 V with respect to the ion block. When samples were admitted the source pressure as indicated by an ion gauge situated over the source diffusion pump increased by less than 1.3×10^{-5} Pa (1×10^{-7} torr). In the absence of sample the indicated pressure is $\sim 6.6 \times 10^{-6}$ Pa ($\sim 5 \times 10^{-8}$ torr).

For positive ion chemical ionization, the adjustable EI/CI slit was positioned for CI, and isobutane was admitted to an indicated pressure of 10.4×10^{-3} to 2.6×10^{-2} Pa (8×10^{-5} to 2×10^{-4} torr) on the source ion gauge. These pressures correspond to pressures within the ion volume of 20 to 26 Pa (0.15 to 0.20 torr) as indicated by the 43/57 ion ratio in the mass spectrum [*9*]. An ionizing electron energy of 70 eV was used with typically a 0-V difference between the ion repeller and the source block.

For analysis of negative ions, the polarities of the ion source and electric sector plates were reversed, as was the direction of the magnetic field. As for positive ions, the potential of the front of the multiplier was held at −1.5 kV. Fragment ions are therefore discriminated against more severely in the negative ion MS/MS experiments than in the positive ion MS/MS studies. For negative ion chemical ionization, isobutane was used as a moderator gas at 20 to 26 Pa (0.15 to 0.20 torr). Under these conditions several ionization mechanisms are operative [*10*], including resonance electron capture, dissociative electron capture, proton transfer, and adduct formation. In no case was the source heated other than by the filament. The source block temperature is estimated to be ~200°C.

Samples of 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane (HMX), pentaerythritol tetranitrate (PETN), dynamite, and 2,4-dinitrotoluene (DNT) were provided by Sandia National Laboratory. All other samples were obtained from commercial sources and were used as supplied.

Results and Discussion

A number of explosives and related compounds have been investigated. The description of the results is divided according to compound class beginning with nitroaromatic compounds, followed by nitrate esters, and ending with heterocyclic nitramines. Within each compound class the results are further divided into electron impact, positive chemical ionization, and negative ion chemical ionization data. The emphasis throughout is primarily on the MS/MS spectra, but pertinent mass spectral data are also presented or described.

Nitroaromatics

Positive ion and negative ion MS/MS data have been collected for *o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT), *m*-dinitrobenzene (DNB), DNT, 2,4-dinitrophenol (DNP), TNT, and 2,4,6-trinitrophenol (picric acid).

Electron Ionization—The electron ionization mass spectra of aromatic nitro compounds are discussed at length in the review by Yinon [5]. All of the nitroaromatic compounds studied here exhibit an intense molecular cation under electron impact conditions. Other major ions in the upper mass region include those resulting from losses of $NO\cdot$ and $NO_2\cdot$ from the molecular ion. In cases where a methyl group is ortho to a nitro group, a major loss of OH is observed largely a result of the "ortho effect" [*11*].

Table 1 lists the abundances of the major ions observed in the CAD spectra of the molecular cations of these nitro-aromatic compounds and Table 2 gives the corresponding information for the metastable ion spectra. The tables are listed in terms of mass losses from the molecular ion in order to make evident common fragmentations.

Figure 1 shows the CAD spectrum of ionized TNT. This spectrum is typical of all of the CAD spectra acquired from the nitroaromatic molecular ions in that they exhibit less exten-

TABLE 1—*CAD spectra of nitroaromatic molecular ions.*[a]

Mass Loss, AMU	*o*-NT	*m*-NT	*p*-NT	DNB	DNT	TNT	DNP	Picric Acid
16 (-O·)		121(5)		152(8)			168(12)	213(8)
17 (-OH·)	120(100)	120(7)			165(100)	210(100)	167(10)	
30 (-NO·)	107(5)	107(64)	107(64)	138(7)	152(5)		154(100)	199(100)
34 (-2OH·)						193(5)		
46 (-NO_2·)	91(6)	91(100)	91(100)	122(100)	136(5)		138(7)	183(5)
47 (-HNO_2)	90(5)	90(16)	90(24)			180(67)		
58								171(18)
63					119(5)			
72		65(7)	65(22)					
76,77				91, 92(34)		150, 151(7)	107, 108(19)	152, 153(15)
93				75(55)				136(18)

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are indicated.

TABLE 2—*Metastable ion spectra of nitroaromatic molecular ions.*[a]

Mass Loss, AMU	*o*-NT	*m*-NT	*p*-NT	DNB	DNT	TNT	DNP	Picric Acid
17 (-OH·)	120(100)	120(18)			165(100)	210(100)		
30 (-NO·)		107(100)	107(100)	138(100)			154(100)	199(100)
46 (-NO_2·)		91(54)						

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are indicated.

sive fragmentation than the corresponding EI mass spectrum. This is probably due mostly to the generally lower internal energies deposited in kilo electron volt energy collisional activation than in 70-eV EI [12,13]. The spectra exhibit other similarities. For example, where the methyl group of a nitrotoluene is ortho to a nitro group, OH · loss is the predominant decomposition route. When two nitro groups are ortho to a methyl group, as is the case with TNT, two hydroxyl radicals are lost. All molecular ions except that of TNT lose NO · to some extent. Ions with an electron donating group para to a nitro group such as DNP and picric acid show an intense NO · loss peak which is dish-topped, indicating a large release of kinetic energy associated with the decomposition. This previously observed phenomenon has been discussed elsewhere [14]. For ionized TNT and DNT, NO · loss does not compete effectively with OH · loss. The mechanisms for both fragmentations involve rearrangement, with the former being apparently much slower. Loss of NO_2· is also observed for all of the ions, and other frequently observed losses are those of HNO_2 and O.

Positive Chemical Ionization—The methane CI mass spectra of most of these compounds have been reported [15,16]. The isobutane CI mass spectra do not differ substantially. In each case, the most abundant peak in the mass spectrum is due to the protonated molecule (MH^+), and very little fragmentation is observed.

Table 3 summarizes the CAD spectra, and Table 4 summarizes the metastable ion spectra of the series of protonated nitroaromatic compounds, listing the abundances of those ions

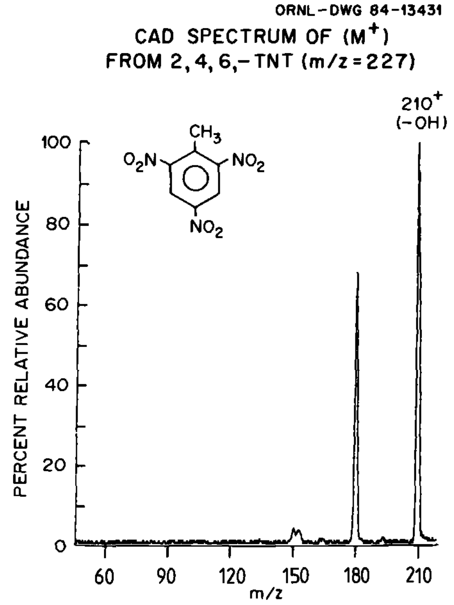

FIG. 1—*CAD spectrum of the molecular ion of 2,4,6-TNT (precursor ion peak not shown).*

TABLE 3—*CAD spectra of nitroaromatic MH^+ ions.*[a]

Mass Loss, AMU	*o*-NT	*m*-NT	*p*-NT	DNB	DNT	TNT	DNP	Picric Acid
15 (-$CH_3\cdot$)		123(5)	123(5)					
17 (-$OH\cdot$)	121(46)	121(34)	121(52)	152(100)	166(100)	211(98)	168(100)	213(100)
30 (-$NO\cdot$)	108(26)	108(38)	108(13)					
34 (-$2OH\cdot$)					149(43)	194(100)		
46 (-$NO_2\cdot$)	92(42)	92(80)	92(34)		137(17)	182(33)	139(10)	184(22)
47 (-$HNO_2\cdot$)	91(100)	91(100)	91(100)	122(91)	136(28)	181(25)	138(11)	183(7)
63						165(20)		
64					119(13)	164(30)	121(8)	166(12)
76					107(11)	152(7)		
77				92(21)	106(14)	151(7)		
94				75(18)	89(67)	134(29)	91(24)	136(13)
139						89(48)		91(41)
Others:	89(24)	89(28)	89(28)			89(48)		
	76(10)	76(6)	76(6)		76(11)	76(10)		76(16)
	65(25)	65(23)	65(14)					
	63(14)	63(10)	63(8)		63(21)	63(17)		63(21)
	50(10)	50(6)	50(5)			50(5)		

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are indicated.

TABLE 4—*Metastable ion spectra of nitroaromatic MH^+ ions.*[a]

Mass Loss, AMU	o-NT	m-NT	p-NT	DNB	DNT	TNT	DNP	Picric Acid
17 (-OH·)	121(100)	121(10)	121(62)	152(100)	166(100)	211(100)	168(100)	213(100)
30 (-NO·)		108(38)	108(32)					
34 (-2OH·)					149(11)	194(19)		
46 ($-NO_2\cdot$)	92(52)	92(100)	92(100)		137(5)	182(16)		184(10)
47 ($-HNO_2$)				122(32)	136(18)	181(28)		
64					119(24)	164(15)		
76					107(22)			

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are indicated.

which are >5% of the most intense fragment ion. Since fragment ion peaks are often quite broad in MS/MS spectra when an electric sector is the second analyzer, adjacent masses often overlap so that peak intensities are sometimes difficult to assign. This is mostly a problem for low mass fragments where energy spreads tend to be large and clusters of fragments which are separated by 1-AMU intervals are frequently observed. The table in these cases shows only the abundance of the most intense peak of the cluster. For example, Fig. 2 shows the CAD spectrum of protonated TNT. Note an intense fragment ion peak centered at *m/z* 89 corresponding to $C_7H_5^+$. Although the mass resolution is insufficient to rule out the presence of smaller peaks at, for example, *m/z* 90 or 88, only *m/z* 89 is listed in the tables.

For all of the protonated molecules, OH· loss gives an abundant peak in the CAD spectrum. Yinon et al [*16*] have demonstrated that protonation of a nitro group and subsequent

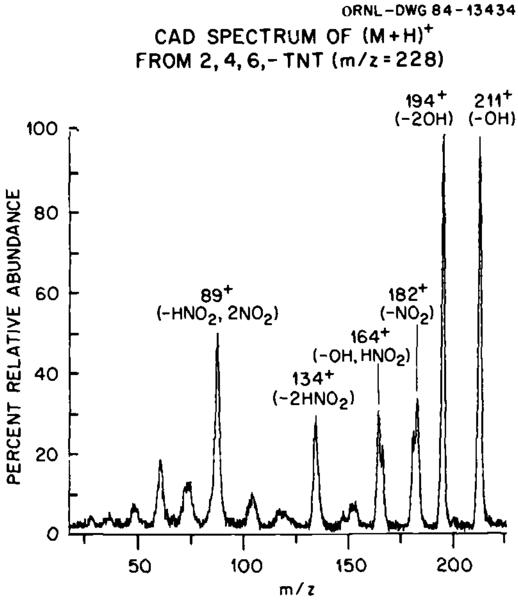

FIG. 2—*CAD spectrum of protonated 2,4,6-TNT formed via chemical ionization using isobutane as the reagent gas.*

loss of that proton in the OH · group is the predominant mechanism in those compounds in which an ortho effect is absent. When an ortho effect is possible, both mechanisms can contribute and the loss of two hydroxyl groups is observed. The protonated nitrotoluenes and protonated nitrophenols show an abundant $NO_2\cdot$ loss and, to varying degrees, the loss of HNO_2. Interestingly, none of the dinitro ions shows a significant loss of NO ·, whereas this is an important decomposition route for the protonated mononitrotoluenes. The CAD spectra also show common features in the low mass region where fragment ions appear which are characteristic of the ring.

Negative Chemical Ionization—The negative chemical ionization (NCI) mass spectra of the nitroaromatics are very sensitive to ion source conditions as is typical of isobutane NCI in general [*17*]. The mass spectra tend to vary substantially with ion source pressure, temperature, and probe temperature. Since several ionization mechanisms can contribute significantly to a mass spectrum, changing the source conditions can markedly affect their relative contributions. For the conditions used here, all of the nitroaromatic compounds gave an intense molecular anion. For the nitrotoluenes and DNT, the molecular anion was the base peak. For TNT, DNP, and picric acid the base peak corresponded to $(M\text{-}OH\cdot)^-$ and along with the molecular anion intense peaks corresponding to $(M\text{-}NO\cdot)^-$ and $(M\text{-}HNO_2)^-$ were observed. DNB yielded a molecular anion with an intensity 85% of that of the $(M\text{-}NO\cdot)^-$ base peak and also gave an abundant $(M\text{-}2NO\cdot)^-$ peak. Under some conditions an intense $(M\text{-}H)^-$ ion could be formed from DNT, TNT, DNP, and picric acid. These conditions, however, proved to be less reproducible than those which gave predominantly molecular anions. Presumably $(M\text{-}H\cdot)^-$ ions could have been more readily produced had a reagent gas mixture such as N_2O/isobutane, which gives an abundant proton abstractor (that is, OH^-), been used.

Table 5 summarizes the CAD spectra of the molecular anions. It is noteworthy that the CAD spectra of the di- and trinitro-substituted species do not differ significantly from the corresponding metastable ion spectra. That is, more extensive fragmentation is not observed in the spectra when collision gas is added, nor do the fragment ion currents increase. In fact they decrease slightly. This is not the case, however, with the mononitrotoluene anions for which little or no fragment ion current caused by metastable ion decompositions could be detected. All of the spectra show OH· loss, NO· loss, and HNO_2 loss to be important decomposition reactions. (HNO_2 and NO_2 losses are grouped together in Table 5 because they are not easily resolved in the spectra.) In addition to these reactions, the mononitrotoluenes also lose $CH_3\cdot$ to varying degrees and show the NO_2^- fragment ion.

Table 6 summarizes the MS/MS spectra of the $(M\text{-}H)^-$ ions where M = DNT, TNT, DNP, or picric acid. The nitrophenol spectra show dramatic differences in decomposition when compared with the corresponding molecular anion spectra. For example, OH · loss is absent but O loss is observed. The base peak is loss of $NO_2\cdot$ while NO · loss is also extensive and is observed with a large kinetic energy release. The $(M\text{-}H)^-$ spectra of DNT and TNT, on the other hand, show the same losses as do the molecular anion spectra, but in slightly different proportions. Hydroxyl radical loss is again the base peak but NO·, $NO_2\cdot$, and HNO_2 losses increase in relative abundance. This might be expected considering that fewer protons are available for the ortho effect mechanism leading to OH · loss.

Nitrate Esters

A comparatively limited set of MS/MS data could be obtained for the nitrate esters nitroglycerin (NG), ethylene glycol dinitrate (EGDN), and pentaerythritol tetranitrate (PETN), caused mainly by the propensity of these compounds to fragment extensively, giving predominantly low mass fragment ions.

Electron Ionization—No intense structurally informative ions were observed in the upper mass region of the electron impact mass spectra of any of the nitrate esters. In each case the

TABLE 5—*MS/MS spectra of nitroaromatic molecular anions.*[a]

Mass Loss, AMU		*o*-NT[b]	*m*-NT[b]	*p*-NT[b]	DNB		DNT		TNT		DNP		Picric Acid	
		CAD	CAD	CAD	CAD	m*	CAD	m*	CAD	m*	CAD	m*	CAD	m*
15	(-$CH_3\cdot$)	122(18)	122(87)	122(100)										
17	(-$OH\cdot$)	120(45)	120(25)	120(23)			165(100)	165(100)	210(100)	210(100)	167(100)	167(100)	212(100)	212(100)
30	(-$NO\cdot$)	107(100)	107(100)	107(92)	138(100)	138(100)	152(45)	152(45)	197(15)	197(15)	154(38)	154(38)	199(8)	199(8)
46,47		91, 90(19)	91, 90(16)	91, 90(10)			136, 135(8)	136, 135(8)	181, 180(5)	181, 180(5)	138, 137(5)	138, 137(5)	183, 182(9)	183, 182(9)
91		46(6)	46(9)	46(9)										

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are listed.

[b] No appreciable signals as a result of decompositions of metastable ions were observed.

TABLE 6—*MS/MS spectra of nitroaromatic* $(M\text{-}H)^-$ *ions.*[a,b]

Mass Loss, AMU	DNT	TNT	DNP	Picric Acid
	m*	m*	m*	m*
16 (-O·)			167(26)	212(35)
17 (-OH·)	164(100)	209(100)		
30 (-NO·)	151(56)	196(27)	153(83)	198(73)
46 ($-NO_2\cdot$)			137(100)	182(100)
47 ($-HNO_2$)	134(16)	179(7)		
60 (-2NO·)		166(5)	123(12)	
76 ($-NO; NO_2\cdot$)			107(19)	152(7)

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are reported.

[b] The CAD spectra were identical to the spectra of the metastable ions.

base peak was the NO_2^+ ion, with smaller intensities of NO^+ and $CH_2ONO_2^+$. No MS/MS spectra were recorded using this ionization mode.

Positive Chemical Ionization—The chemical ionization mass spectra of these compounds have been described for a number of reagent gases [*18*]. NO_2^+ was the base peak in the isobutane CI mass spectra recorded in this work for all three nitrate esters, with a peak at *m/z* 76 ($CH_2ONO_2^+$) a few percent in intensity of the base peak. Small signals for the MH^+ ions of NG and EGDN were observed ($<0.1\%$), and CAD spectra were recorded.

These spectra show only one identifiable fragment ion peak, which corresponds to NO_2^+. Because of the relatively poor signal/noise of these spectra identification of other fragments $<10\%$ of the NO_2^+ signal is not possible. The mass spectrum of PETN shows a MH^+ of $\sim 1\%$ abundance relative to NO_2^+. Figure 3 shows the CAD spectrum of this ion. NO_2^+ gives by far the largest fragment ion signal with lesser peaks at *m/z* 76 and 30. Peaks slightly smaller than the MH^+ peak were also observed in the upper mass portion of the mass spectrum corresponding to $(M + NO)^+$, $(M + NO_2)^+$, and $(MH^+ - NO_2)$.

Negative Chemical Ionization—NCI data were acquired for PETN and NG. In both cases the base peak in the mass spectrum is observed at *m/z* 62, corresponding to the ONO_2^- anion with a peak for NO_2^- at a slightly smaller intensity. For both compounds by far the most abundant peak in the high mass region corresponds to the $(M + NO_3)^-$ adduct ion. Three major fragment ions appear in the CAD spectrum of $(NG + NO_3)^-$: NO_3^- (100%), $(NO_3)_2^-$ (70%), and a peak at *m/z* 180 (30%) probably resulting from losses of both NO_3 and HNO_2 (or HNO_3 and NO_2) from the adduct ion. The $(PETN + NO_3)^-$ CAD spectrum (Fig. 4) also shows NO_3^- and $(NO_3)_2^-$ fragments, but the most abundant fragment ions are detected at *m/z* 362 and 315 corresponding to O and HNO_3 losses, respectively. The process by which HNO_3 loss occurs takes place with a rather large kinetic energy release as reflected by the deeply dished peak.

Heterocyclic Nitramines—RDX, HMX

Two common heterocyclic nitramine explosives, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane (HMX), have been investigated.

Electron Ionization—As previously reported [*19,20*], the 70-eV electron impact mass spectra of these compounds show extensive fragmentation with small signals arising from the molecular ions. In contrast to the results of Yinon et al [*6*] obtained in a similar CAD study, no $(M + NO)^+$ or $(M + NO_2)^+$ adducts were observed in the mass spectra. Despite their

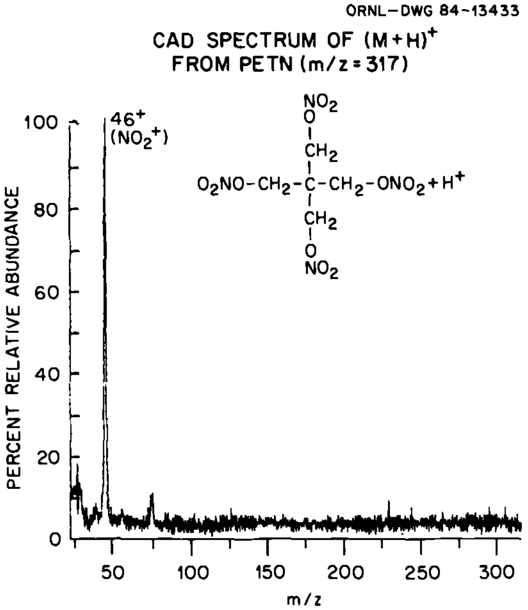

FIG. 3—*CAD spectrum of protonated PETN formed via chemical ionization using isobutane as the reagent gas.*

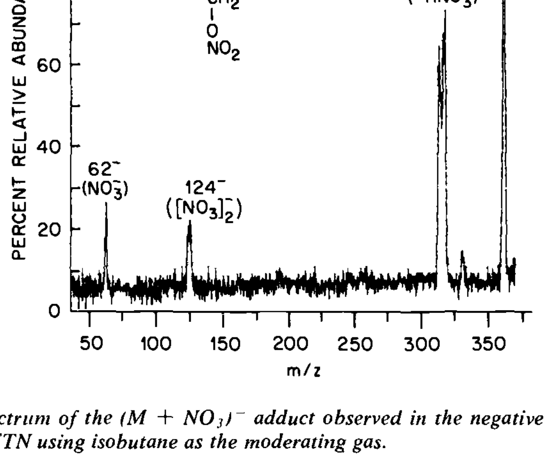

FIG. 4—*CAD spectrum of the* $(M + NO_3)^-$ *adduct observed in the negative chemical ionization mass spectrum of PETN using isobutane as the moderating gas.*

relatively low abundances, CAD spectra of the RDX and HMX molecular ions were acquired. Only one peak is observed in the CAD spectrum of ionized HMX corresponding to loss of a CH_2NNO_2 group to give an ion at *m/z* 222. The base peak in the CAD spectrum of ionized RDX (Fig. 5) also results from CH_2NNO_2 loss, but in this case a number of other fragments are also produced.

Positive Chemical Ionization—Prominent high mass ions in the isobutane CI mass spectra of RDX and HMX include MH^+, $(M + NO)^+$, $(M + NO_2)^+$, and MH^+-CH_2NNO_2. The CAD spectra of these ions show the same fragment ions reported in the previous CAD study [*6*]. Many of these fragment ions, however, are of very low abundance. For example, Fig. 6 shows the CAD spectrum of protonated RDX. All of the fragment ions reported earlier except $(M\text{-}NO_2\cdot)^+$ are present, but only the fragment ions at *m/z* 75, 105, and 106 are greater than 5% of the base peak at *m/z* 149, which corresponds to MH^+-CH_2NNO_2. In fact, for all of the aforementioned adduct ions, loss of CH_2NNO_2 is the most abundant process except for the $(M + NO)^+$ adducts, which lose predominantly $NO\cdot$. Successive losses of CH_2NNO_2 are also common for these ions. This is evident in Table 7, which summarizes the CAD spectra of the adduct ions of HMX, listing only those fragment ions with intensities 5% or greater than that of the base peak.

Negative Chemical Ionization—Isobutane NCI mass spectra have been reported for these compounds [*21*]. The mass spectra obtained in this study, however, are significantly different from those reported earlier and are therefore reproduced in Figs. 7 and 8. The major differences are the relative absence of significant ion current at *m/z* 93 presumably due to $(NO_2HNO_2)^-$, reduced NO_2^- signal, much larger ion current observed at *m/z* 102, and consequently a relatively large $M + 102^-$ adduct. Tables 8 and 9 summarize the CAD spectra of the major ions observed in the mass spectra. Both $(M + 102)^-$ adducts lose 16, 47, and 56 mass units, with the latter being the predominant loss. Both $(M + NO_2)^-$ adducts tend to lose HNO_2 to give the $(M\text{-}H)^-$ anion. The most abundant fragment ion in both spectra is observed at *m/z* 221, corresponding to HNO_2 loss from $(RDX + NO_2)^-$ and to,

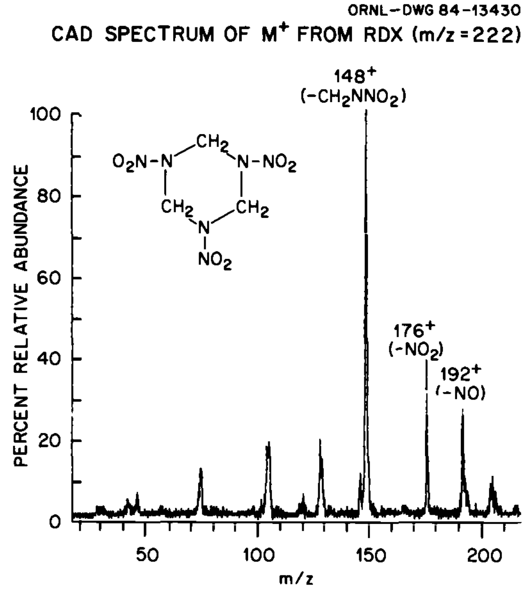

FIG. 5—*CAD spectrum of the molecular ion of RDX.*

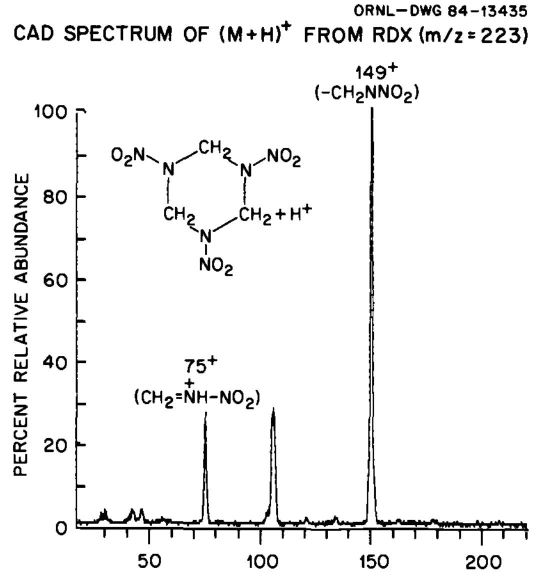

FIG. 6—*CAD spectrum of protonated RDX formed via chemical ionization using isobutane as the reagent gas.*

presumably, HNO_2 and CH_2NNO_2 loss from $(HMX + NO_2)^-$. In contrast to the positive ion CI data for these compounds which show the loss of a single CH_2NNO_2 group from the parent ion to be most probable, the loss of 74 AMU is only seen to be of major abundance for the $(HMX\text{-}H)^-$ anion and the $(M\text{-}NO_2)^-$ anion which shows exclusively CH_2NNO_2 loss.

Conclusions

Electron ionization is clearly, as anticipated, the least suitable ionization method used in this study for MS/MS analysis of explosives. The relatively extensive degree of fragmentation observed depletes the ion current due to molecular and other high mass ions and complicates mass spectra of mixtures. The isobutane positive and negative chemical ionization mass spectra tend to be much simpler and generally exhibit much greater molecular or adduct ion signals. Negative chemical ionization is, perhaps, the most sensitive ionization method for many explosives due to their high electron affinities [5], but positive CI using a "soft" reagent gas in conjunction with MS/MS is probably suitable for many applications. The similarities observed within each compound class for each ionization method make feasible scanning methods to screen rapidly mixtures for the targeted class. For example, all protonated nitrotoluenes lose $OH\cdot$ and $NO_2\cdot$ so neutral loss scans that detect losses of 17 and 46 AMU could be used to identify quickly possible nitroaromatic components in a sample. The substituted nitroaromatic molecular anions studied here all lose $OH\cdot$ and $NO\cdot$ indicating that scanning for loss of 17 and 30 AMU is useful for screening for these compounds in the negative ion mode. Once ions that show these losses have been identified, the precursor ion masses can indicate if a component is likely to be one of the common explosives. If necessary, further specificity can be obtained by acquiring a complete daughter ion MS/MS spectrum.

TABLE 7—*CAD spectra of positive adduct ions of HMX.*[a]

Mass Loss, AMU		$(HMX + H)^+$	$(HMX + NO)^+$	$(HMX + NO_2)^+$	$(HMX + CH_2NNO_2)^+$	$(HMX + C_3H_7)^+$
30	$(-NO\cdot)$		296(100)			
42	$(-C_3H_6)$					297(20)
74	$(-CH_2NNO_2)$	223(100)	252(38)	268(100)	296(100)	265(100)
104			222(5)			
106		191(9)				
116						223(7)
148	$(-CH_2NNO_2)_2$	149(10)	178(7)		222(7)	191(5)
222	$(-CH_2NNO_2)_3$	75(5)			148(5)	117(5)

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the ion. Only peaks of abundance 5% or greater are indicated.

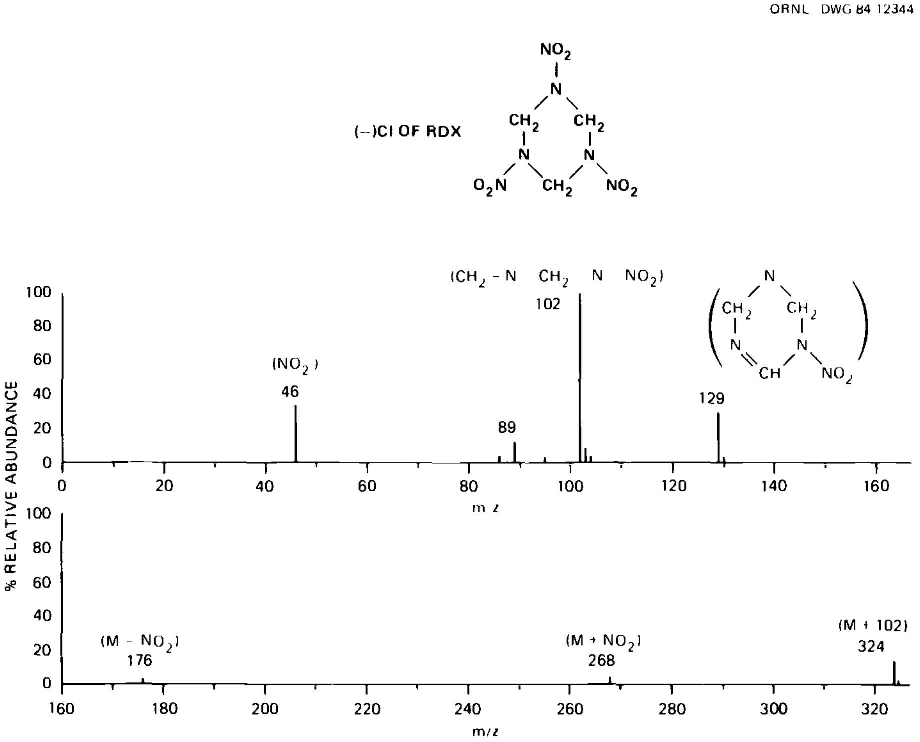

FIG. 7—*Isobutane negative chemical ionization mass spectrum of RDX at a source pressure of 20 Pa (0.15 torr).*

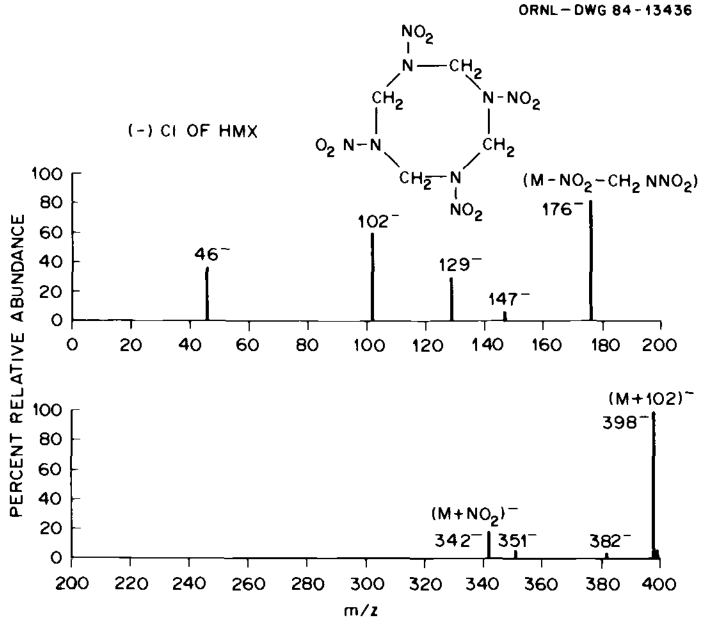

FIG. 8—*Isobutane negative chemical ionization mass spectrum of HMX at a source pressure of 20 Pa (0.15 torr).*

TABLE 8—*CAD spectra of the major ions in the NCIMS of RDX.*[a]

102^-		129^-		176^- $(RDX - NO_2)^-$		268^- $(RDX + NO_2)^-$		324^- $(RDX + 102)^-$	
m/z	(%RA)	*m/z*	(%RA)	*m/z*	(%RA)	*m/z*	(%RA)	*m/z*	(%RA)
86	(31)	86	(50)	102	(100)	252	(29)	308	(7)
74	(95)	84	(50)			221	(100)	278	(11)
60	(34)	82	(100)			176	(22)	268	(100)
54	(12)	46	(21)			129,130	(41)	250	(5)
46	(100)					102	(61)	221	(9)
						93	(46)	102	(45)
						46	(7)		

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the fragment ion.

TABLE 9—*CAD spectra of the major ions in the NCIMS of HMX.*[a,b]

295^- (HMX − H)$^-$		342^- (HMX + NO_2)$^-$		398^- (HMX + 102)$^-$	
m/z	(%RA)	*m/z*	(%RA)	*m/z*	(%RA)
254	(58)	295	(47)	382	(13)
249	(12)	268	(12)	351	(31)
238	(42)	221	(100)	342	(100)
221	(100)	193,194	(21)	322	(8)
147	(11)	176	(14)		
		147	(15)		

[a] Fragment ion abundances are expressed as a percentage of the abundance of the largest fragment peak and are listed parenthetically alongside the *m/z* value of the fragment ion.

[b] Intense ions at *m/z* 176, 129, and 102 were also observed and each yielded a CAD spectrum virtually identical to the corresponding spectrum listed in Table 8.

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