
Nitramine Anion Fragmentation: A Mass Spectrometric and Ab Initio Study

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The fragment ion formation characteristics of the radical anions generated from hexahydro-1,3,5-trinitrotriazine (RDX) and its three nitroso metabolites were studied using GC/MS with negative chemical ionization (NCI) to understand the fragmentation mechanisms responsible for the formation of the most abundant ions observed in their NCI mass spectra. Ab initio and density functional theory calculations were used to calculate relative free energies for different fragment ion structures suggested by the m/z values of the most abundant ions observed in the NCI mass spectra. The NCI mass spectra of the four nitramines are dominated by ions formed by the cleavage of nitrogen–nitrogen and carbon–nitrogen bonds in the atrazine ring. The most abundant anions in the NCI mass spectra of these nitramines have the general formulas $C_2H_4N_3O$ (m/z 86) and $C_2H_4N_3O_2$ (m/z 102). The analyses of isotope-labeled standards indicate that these two ions are formed by neutral losses that include two exocyclic nitrogens and one atrazine ring nitrogen. Our calculations and observations of the nitramine mass spectra suggest that the m/z 86 and m/z 102 ions are formed from either the $(M-NO)^-$ or $(M-NO_2)^-$ fragment anions by a single fragmentation reaction producing neutral losses of CH_2N_2O or $CH_2N_2O_2$ rather than a set of sequential reactions involving neutral losses of HNO_2 or HNO and HCN . (J Am Soc Mass Spectrom 2007, 18, 835–841) © 2007 American Society for Mass Spectrometry

Hexahydro-1,3,5-trinitrotriazine (RDX, Royal Demolition Explosive) is an explosive widely used for commercial and military purposes since World War II. Contamination of groundwater and soil has resulted from large-scale production and accidental release of RDX into the environment over the years [1, 2]. RDX is toxic to a variety of organisms in terrestrial [3, 4] and aquatic environments [5] and is believed to be carcinogenic in humans [6], although the mechanism of metabolism that might be responsible for the initiation of carcinogenesis remains unknown. As a result, a great deal of effort has been focused on

developing methods for the analysis of RDX and its metabolites in different environmental matrices.

Studies of the microbe-induced metabolism of RDX may provide some insight into its adverse health effects in humans. The biodegradation of RDX has been studied under a number of different conditions in the hopes of identifying cost-effective methods of remediating explosives-contaminated sites [7–13]. One of the major anaerobic metabolism pathways involves the sequential reduction of the exocyclic nitro to nitroso groups [7, 8] to form three distinct metabolites that contain up to three nitrogen–nitrosoneitrogen bonds: hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX). Reduction of RDX to MNX was suggested as a potential first step in the formation of ring-cleavage products under anaerobic microbial conditions [14], whereas microbiological degradation under aerobic conditions was suggested to proceed through an initial denitration step [13]. Compounds containing nitrogen–nitrosoneitrogen bonds have been previously identified as carcinogens [15], suggesting that the formation of one of these

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three RDX metabolites may be a putative step in the initiation of cancer. The toxicity of MNX to Sprague–Dawley rats was recently shown to be similar in magnitude and adverse effects to that of RDX [16]. Studies with deer mice suggest potential reproductive effects arising from TNX exposure through drinking water [17]. The goal of this study is to identify the structures of fragment ions that may be used to identify and quantify these three metabolites with gas chromatography/mass spectrometry (GC/MS) negative chemical ionization (NCI) analyses.

Analytical methods for RDX and other explosives can be grouped into two categories. One group of methods is used for identification of explosives in complex matrices for forensic purposes. Several mass spectrometry techniques based on atmospheric pressure chemical ionization [18–21] and electrospray ionization [22–24] have been developed to identify RDX and other explosives in post-detonation residues. A number of different sensors have also been developed to screen the atmosphere for explosives [25].

The second set of analytical methods is designed to assess environmental contamination brought about by the discharge of explosives into the environment. High-performance liquid chromatography (HPLC) with UV detection according to the Environmental Protection Agency Method 8330 [26] is widely used for environmental analysis of explosives, but many laboratories are now using GC coupled with electron capture detection (ECD) as described in Method 8095 [27] for increased sensitivity, given the large electron affinities of many explosives [28–30]. Analytical methods based on GC/MS with NCI offer sensitivity similar to that based on GC/ECD but yield more structural information. GC/MS and NCI have previously been used to analyze RDX [31, 32], but no mechanistic studies of the ion formation processes for this compound have been carried out to date.

RDX is quantified with GC/MS-NCI by monitoring the fragment ions of m/z 102 and m/z 129. The empirical formulas of these anions have been identified as $C_2H_4N_3O_2^-$ and $C_3H_5N_4O_2^-$, respectively, but their structures are not known [33]. The goals of this study are to determine the fragmentation pathways and fragment ion structures derived from NCI of RDX and its nitroso metabolites. Ab initio quantum chemical calculations were carried out to identify the most probable structures of the most abundant fragment ion species suggested by the NCI mass spectra of RDX, its nitroso metabolites, and different isotopically labeled compounds. Previous computational studies at the ab initio level were successful in predicting the structures of the decomposition products formed during the detonation of (neutral) RDX [34–38], but did not address fragmentation pathways for the anions observed in the NCI mass spectra of RDX or its nitroso metabolites.

Experimental

Compounds

MNX, $^{15}N_3$ -MNX, DNX, TNX, and $^{15}N_3$ -RDX were obtained from Dr. Ron Spanggard (SRI International, Menlo Park, CA USA). RDX was purchased from Sigma Chemical (St. Louis, MO, USA) and $^{13}C_3$ -RDX was acquired from Cambridge Isotope Laboratories (Andover, MA, USA). All compounds were used without further purification. Structures of these compounds are shown in Figures 1 and 2.

Instrumentation

A ThermoFinnigan TraceGC/MS (San Jose, CA, USA) equipped with negative chemical ionization source was used for all analyses. The instrument was equipped with a Rtx-5MS column, 15 m \times 0.25 mm (Restek Corp., Bellefonte, PA, USA). Picomolar quantities of analyte were analyzed in the splitless mode. The GC was heated from 40 to 250 °C at a rate of 30 °C/min. The injector temperature was 150 °C; the source temperature was 200 °C. The flow rate of methane CI gas was optimized to 1.5 mL/min using the manufacturer's software. The electron energy was 70 eV.

Computational Methods

The relative free energies of the product ions formed by the decomposition of the RDX and TNX radical anions in the gas phase were calculated at the MP2/AUG-cc-pVDZ//B3LYP/6-31G(d) level of ab initio quantum mechanical theory. At this level, the energy is determined by the second-order perturbation theory (MP2) using the correlation-consistent polarized valence double-zeta basis set that is augmented by diffuse functions [39]. This energy is evaluated for geometries determined using Becke's three-parameter hybrid exchange functional (B3) that is combined with the correlation functional of Lee, Yang, and Parr (LYP) [40, 41]. These functionals operate on electron density, which is expanded using the 6-31G(d) polarized split-valence basis set.

The rotational and vibrational contributions to the enthalpy and entropy were evaluated at 298 K using rigid-rotor and harmonic-oscillator approximations, and vibrational energy levels calculated at the Hartree-Fock (HF) level using the 6-31G(d) basis set. Calculations for open-shell systems were carried out using unrestricted MP2, B3LYP, and HF Hamiltonians. Relative free energies for isomers of the TNX radical anion decomposition products of m/z 86 and m/z 113 were determined by using the Gaussian-3 (G3) procedure of Curtiss and coworkers [42]. This procedure extrapolates series of high-level ab initio calculations to the full-CI/complete basis set accuracy. All quantum chemical calculations were carried out using the Gaussian 03 program [43].

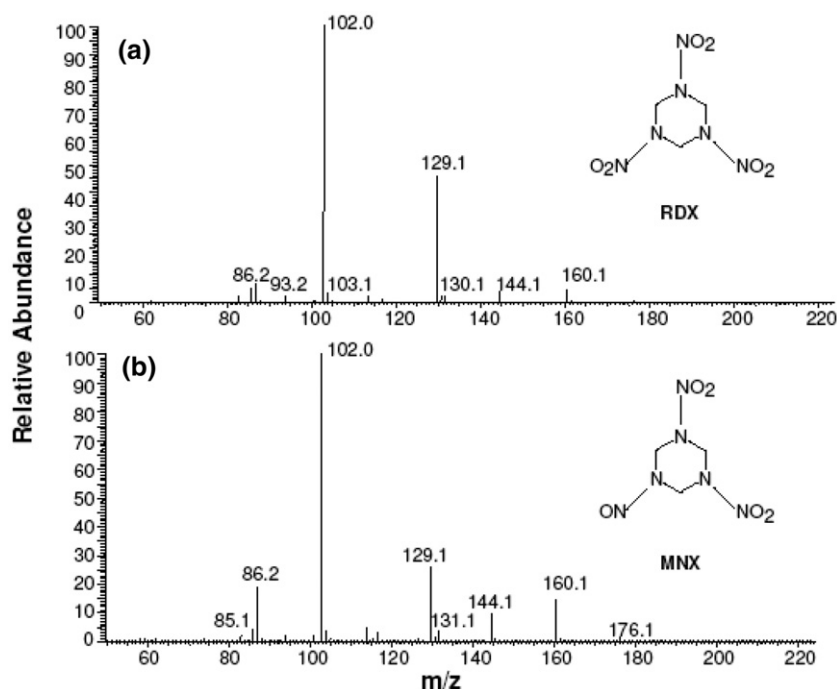


Figure 1. Full-scan NCI mass spectra of (a) hexahydro-1,3,5-trinitrotriazine (RDX) and (b) hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX).

Results and Discussion

Fragmentation of Nitramine Anions

Full-scan NCI mass spectra of the four nitramines in this study are presented in Figures 1 and 2. Abundant fragment ions are formed by the homolytic cleavage of

the exocyclic NO_x groups. Further decomposition steps involve cleavage of C—N bonds in the triazine ring.

Fragment ions formed by the cleavage of a single exocyclic nitrogen–nitrogen bond, $(\text{M}-\text{NO}_x)^-$, become more abundant as the number of NO groups attached to the atrazine ring increases. The NCI mass spectrum of

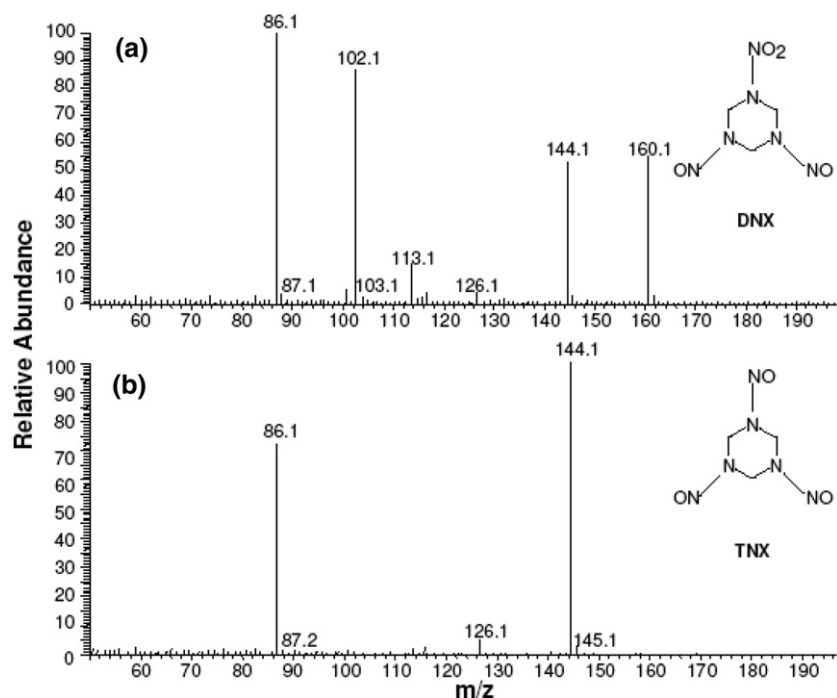


Figure 2. Full-scan NCI mass spectra of (a) hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX) and (b) hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX).

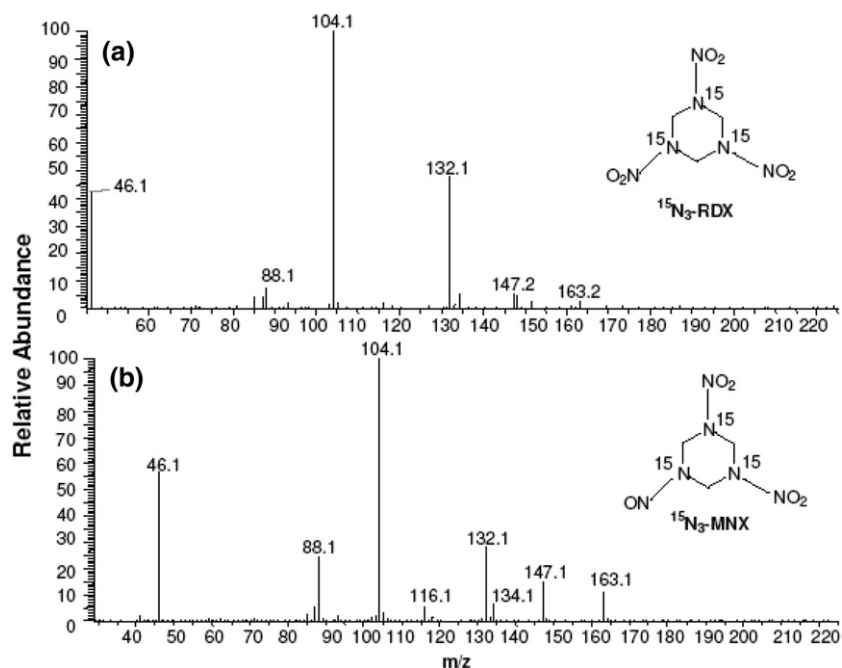


Figure 3. Full-scan NCI mass spectra of (a) ring-labeled $^{15}\text{N}_3$ -hexahydro-1,3,5-trinitrotriazine (RDX) and (b) ring-labeled $^{15}\text{N}_3$ -hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX).

RDX (Figure 1A) shows little or no measurable amounts of an $(\text{M}-\text{NO}_2)^-$ ion (m/z 176), whereas MNX, which has one nitroso group, yields an $(\text{M}-\text{NO}_2)^-$ of m/z 160 with 20% relative abundance. DNX, a compound with two nitroso groups and one nitro group, yields $(\text{M}-\text{NO})^-$ and $(\text{M}-\text{NO}_2)^-$ ions at roughly 60% relative abundance (m/z 160 and m/z 144, respectively, in Figure 2A). The base peak in the Figure 2B NCI spectrum of TNX, a compound that has three nitroso groups, is the $(\text{M}-\text{NO})^-$ ion of m/z 144.

The presence of the m/z 102 ion in the mass spectra of RDX and MNX (Figure 1A and B) suggests that it may be formed by a loss of HCN from the m/z 129 ion, $\text{C}_3\text{H}_5\text{N}_4\text{O}_2^-$, that contains a single NO_2 group. Neither fragment ion is observed in the NCI mass spectrum of TNX, which has no appended nitro groups, suggesting that at least one NO_2 group is lost when the m/z 102 ion is formed. The m/z 129 ion may result from loss of HNO_2 and NO_2 from RDX or HNO_2 and NO from MNX. The m/z 86 ion is observed in all four spectra, but in greater abundance in the spectra of DNX and TNX (Figure 2A and B) than in the spectra of RDX and MNX (Figure 1A and B). The mass of this ion suggests that it contains one less oxygen atom than the m/z 102 that is prevalent in the NCI spectra of RDX and MNX.

The goals of this study are to determine the fragmentation pathways that promote the formation of the most abundant ions (summarized above) in the NCI mass spectra of RDX and its N-nitroso products that may serve as targets for single-ion monitoring analyses. The mechanisms of formation for these fragment anions were investigated by calculating the free energies of formation of the structures consistent with the empiri-

cal formulas of these ions suggested by their m/z values. NCI analyses of C-13 and N-15 ring-labeled nitramines were carried out to clarify these fragmentation pathways as well.

The presence of the ion of m/z 132 in the NCI mass spectra of ring-labeled standards, $^{15}\text{N}_3$ -MNX and $^{15}\text{N}_3$ -RDX (Figure 3), suggests that none of the atrazine ring nitrogens is involved in the HNO or HNO_2 neutral losses that lead to the formation of m/z 129 observed in the Figure 1 mass spectra. The two most abundant ions observed in the NCI mass spectra of the isotopically labeled species shown in Figure 3 discussed here are the m/z 104 and m/z 132 anions. The relative abundances and m/z values of these ions suggest their empirical formulas are the same as the ions of m/z 102 ($\text{C}_3\text{H}_4\text{N}_3\text{O}_2^-$) and m/z 129 ($\text{C}_3\text{H}_5\text{N}_4\text{O}_2^-$) in the mass spectra of the unlabeled RDX and MNX (Figure 1). The presence of the ion of m/z 104 in the NCI mass spectra of the ring-labeled species suggests that one of the ring nitrogens is incorporated in the neutral loss that leads to the formation of the ion of m/z 102 observed in the NCI mass spectra of RDX and MNX.

The NCI mass spectrum of the ring-labeled $^{13}\text{C}_3$ -RDX (not shown) is nearly identical to that of the $^{15}\text{N}_3$ -labeled RDX, consistent with the supposition that one atrazine ring nitrogen is lost in the formation of the m/z 102 ion. The mass spectra of DNX and TNX (Figure 2) suggest that analogous fragmentation pathways based on consecutive losses of HNO and HCN may not be prevalent for these compounds, given the low relative abundance of the m/z 113 anion that might serve as a precursor (by loss of HCN) to the m/z 86 anion. To gain a better understanding of these fragmentation path-

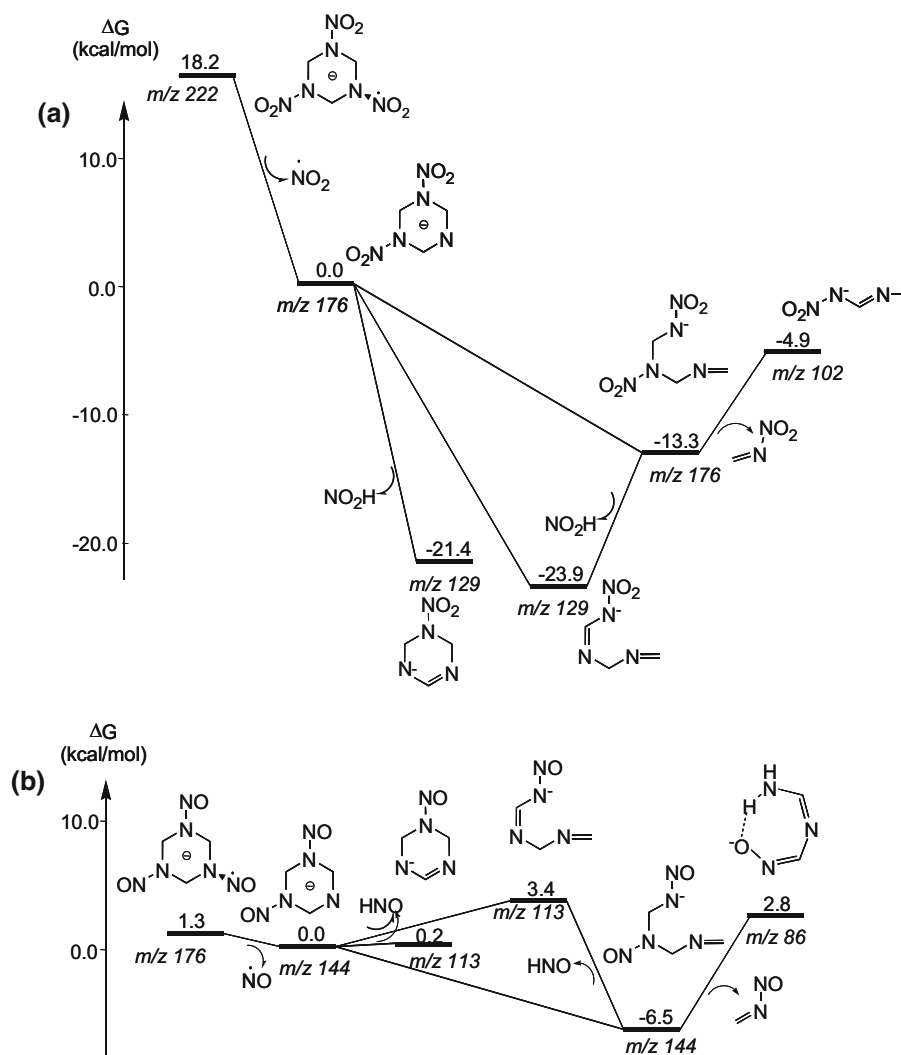


Figure 4. Relative free energies for fragment anion structures formed from (a) RDX and (b) TNX during NCI of nitramines.

ways, the free energies of formation were calculated for several structures consistent with each of m/z values of the ions observed in the NCI mass spectra.

Free Energy Calculations

Free energies of several different structures derived from an empirical formula specified by a particular m/z value were calculated for the major ions observed in the NCI mass spectra of these nitramines. The relative free energies were calculated using the structures of the $M\text{---}NO_x$ fragment anions of RDX (m/z 176) and TNX (m/z 144) presented in Figure 4 as reference points ($\Delta G = 0$). The free energies of 11 different isomers representing the m/z 86 ion (observed in the spectra of the three nitramines with nitroso groups in Figures 1 and 2) were calculated and are presented in Figure 5 as an example. The ion structures with the lowest relative free energies consistent with the m/z values of the most abundant ions observed in the Figures 1 and 2 NCI

mass spectra are shown in Figure 4. Calculations suggest that cleavage of the $N\text{---}NO_2$ bond is favored over the $N\text{---}NO$ bond by 16.9 kcal/mol. These results are consistent with observed relative abundances of $(M\text{---}NO_2)^-$ and $(M\text{---}NO)^-$ fragment anions in the NCI mass spectra of MNX and DNx (Figures 1B and 2A) and are also consistent with the greater calculated equilibrium bond length of the $N\text{---}NO_2$ bond relative to the $N\text{---}NO$ bond. The $N\text{---}NO$ bond is shorter in the radical anion because the Mulliken electron spin density is shared between the two nitrogen atoms, whereas the electron spin density is found almost exclusively on the atrazine ring nitrogen in the $N\text{---}NO_2$ bond. Our calculations suggest that once the nitrogen–nitrogen bond is broken, the negative charge will be centered on the atrazine ring nitrogen forming a closed-shell anion.

The relative abundance of the $(M\text{---}NO_2)^-$ anion is observed to increase as the number of exocyclic NO groups attached to the atrazine ring increases, suggesting that the $(M\text{---}NO_2)^-$ anions become more stable as the

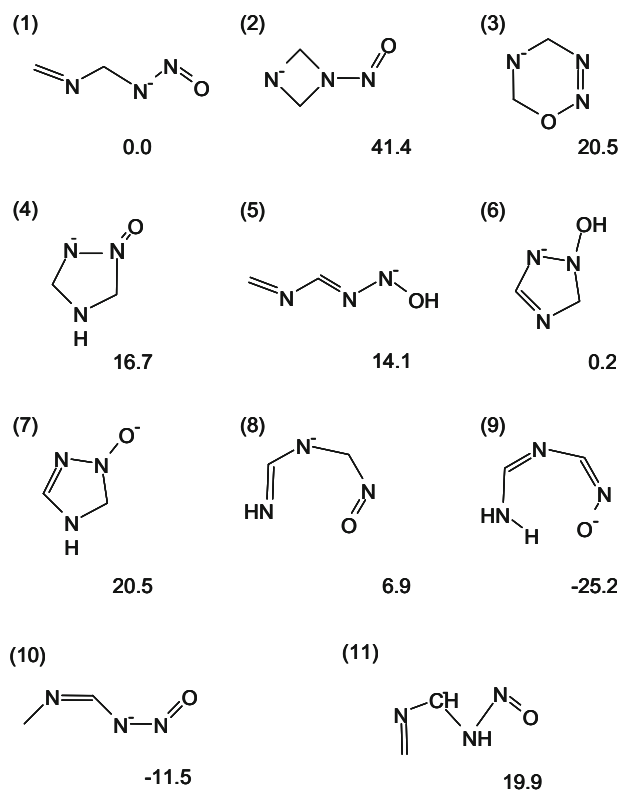


Figure 5. Relative free energies (kcal/mol) for different structures consistent with the empirical formula ($C_2H_4N_3O$) of the m/z 86 ion.

number of exocyclic NO groups on the atrazine ring increases. This is consistent with the relative free energies associated with the structures given in Figure 4. The loss of HONO from the ($M-NO_x$) fragment anions is favored over the loss of HNO by as much as 27.3 kcal/mol. This is consistent with the observed relative abundances of the m/z 176, m/z 160, and m/z 144 ions seen in the mass spectra of MNX and DNX in Figures 1 and 2.

The relative free energies of the most stable structures in Figure 4 and the lack of any significant abundance of m/z 113 ion in the NCI mass spectra of TNX and other nitroso-containing compounds suggest that the fragment anions with the empirical formulas $C_3H_5N_4O_x$ (m/z 113 and m/z 129) and $C_2H_4N_3O_x$ (m/z 86 and m/z 102) are formed by competing losses of HNO_x and $CH_2N_2O_x$, respectively, from the ($M-NO_x$) anion rather than by consecutive losses of HNO_x and HCN. The proposed mechanism of fragmentation is summarized in Figure 6. The relative free energies of the $C_3H_5N_4O_2$ (m/z 129) ions in Figure 4 are at least 16.5 kcal/mol less than the $C_2H_4N_3O_2$ ion (m/z 102). Also, the activation energy associated with the HCN loss pathway (e.g., m/z 129 \rightarrow m/z 102 in Figure 1) is at least 15 kcal/mol larger than the activation energy required for the loss of $CH_2N_2O_x$ from the ($M-NO_x$) anion. These computational results are consistent with the NCI mass spectra of TNX where only two major fragment ions are observed: the ($M-NO$) anion of m/z 144 and the $C_2H_4N_3O$ anion of m/z 86 (Figure 4).

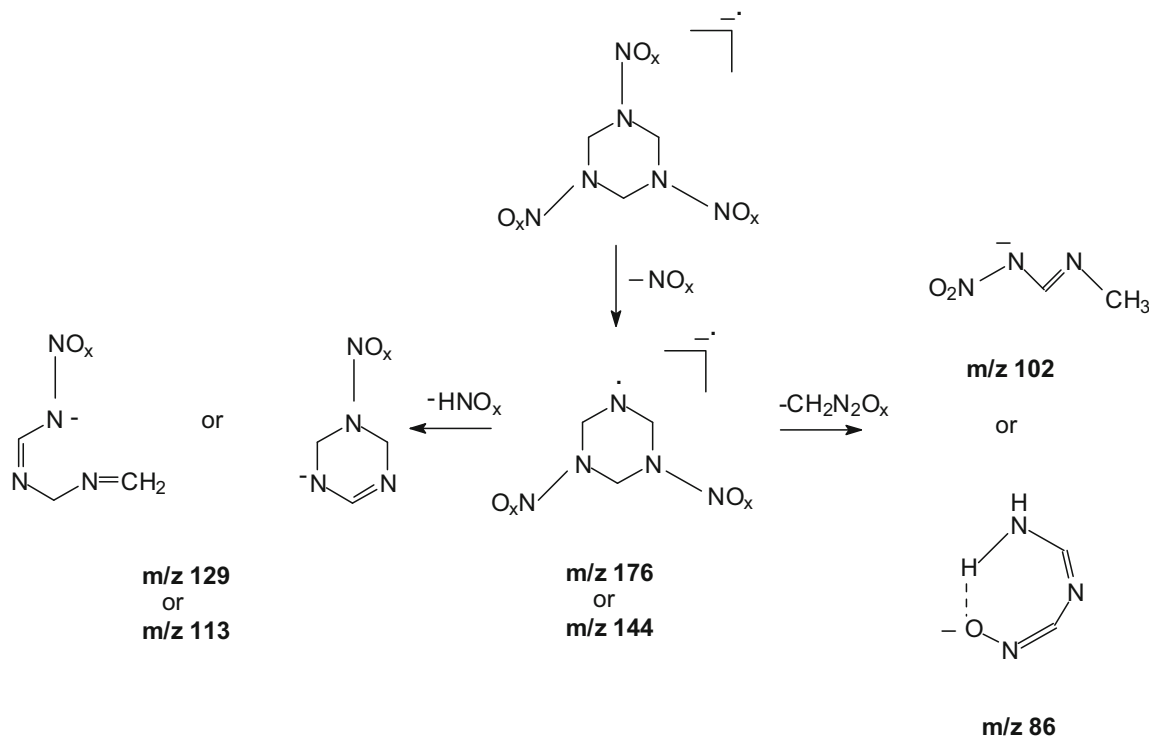


Figure 6. Proposed mechanism of fragmentation of RDX and its nitroso metabolites (MNX, DNX, and TNX) after negative chemical ionization.

Conclusion

The NCI mass spectra of RDX and its three nitroso metabolites were studied to elucidate the fragmentation mechanisms associated with the most abundant ions observed. Free energies of formation for several structures consistent with the m/z values of the anions observed in the mass spectra were calculated to gain insight into the mechanism of fragmentation. The lowest energy structures and the overall appearance of the mass spectra suggest a fragmentation mechanism where $C_2H_4N_3O_x$ anions are formed from the $(M-NO_x)$ fragment anions by neutral loss of $CH_2N_2O_x$ rather than by sequential losses of HNO_x and HCN .

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