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Hexanitrohexaazaisowurtzitane Ion Dissociation Mechanisms Based on Mass-Analyzed Ion Kinetic Energy Spectrum

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The ion dissociation pathways of hexanitrohexaazaisowurtzitane (HNIW) are studied in this paper. A mass spectrometer with mass-analyzed ion kinetic energy spectrum is used for studying ions produced by electron impacts on HNIW. Dissociation processes from various precursor ions to product ions are proposed. Fifteen fragments including the largest m/z 392 and the smallest m/z 67 and m/z 54 are discussed. Dissociation of HNIW precursor ions with NO_2 was found to produce product ions with removal of NO_2 or NO molecules through β-inducement or α-inducement effects. HNIW framework precursor ions produce ions at (m-27)/z through losing HCN and ions at (m-1)/z through losing H atoms. Possible structures of HNIW-NO_2 ions and framework ions are suggested.

Introduction

HEXANITROHEXAAZAISOWURTZITANE (HNIW) is a high-energetic compound. Replacement of cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX) with HNIW is expected to significantly increase the energy of propellants. Figure 1 shows that the molecular structure of HNIW consists of a basic, isowurtzitane cage with one nitro group attached to each of the bridging nitrogen atoms. It exists in four different polymorphic structures, termed α, β, γ, and ε at ambient conditions. Among them, ε-HNIW is preferable for applications in solid propellants and mixing explosives.[1–3]

A number of important studies have been made of the decomposition mechanisms of HNIW.[4–11] Patil and Brill[4,5] suggested that the N—NO_2 bond is the first to break, followed by the carbon C(1)—C(7) bridge bond. Qasim et al.[6] reported that the cleavage of the C(1)—C(7) bond is the principle mechanism in the biodegradation of HNIW. According to Patil and Brill,[4,5] under fast heating (2000 K/s) the thermolysis of HNIW at 250 to 400°C as studied by Fourier transform infrared ray showed that homolysis of the N—NO_2 bond with activation energy E_a of 160 kJ/mol is the dominant decomposition mechanisms. The major gaseous products are NO_2, and NO with smaller amounts of HCN, CO, N_2O, and CO_2. Above 285°C, the elemental composition of the residue from the thermal decomposition of HNIW averages to about $C_4H_4N_4O_2$. It contains C=O, C=N, and NH bonds. Pesce-Rodriguez et al.[7] observed that there are similarities and differences among the decomposition products of HNIW, RDX, and HMX. At 500 and 1000°C, their thermolysis produces nearly the same amounts of CO and NO, but the amounts of the products CO_2 and N_2O from HNIW are twice and half that produced by RDX or HMX, respectively. Oxley et al.[8] suggested that the triggering mechanism is N—NO_2 homolysis in the decomposition of nitramines.

According to thermogravimetric-analysis experiments,[9] the thermal decomposition of HNIW has a two-step mechanism, and the initial step is partly controlled by particle size. Fine particles of HNIW, however, do not show such two-step decomposition at low heating rates. A low-temperature shoulder was observed in the exothermic differential scan calorimeter peak of HNIW, indicating two superimposed decomposition steps.[9] A first-order autocatalytic decomposition model was suggested for the solid-phase decomposition of HNIW, and the noncatalytic and autocatalytic activation energy at 160 to 280°C are 172 and 185 kJ/mol, respectively.

Pace[10] studied electron-paramagnetic-resonance (EPR) spectra of photochemical NO_2 formation in HMX, RDX, and HNIW. It was found that under UV irradiation HNIW produce one order of magnitude more NO_2 radicals than either RDX or HMX. The NO_2 formed can be stably trapped in the HNIW crystal even at room temperature. Ryzhkov and McBride[11] also researched low-temperature photolysis of the α and β crystals of HNIW with ^{15}N-labeled nitro groups by EPR. For the α-polymorph of HNIW, the cavity NO from the nitro group attached to the six-membered ring is twice that on the five-membered ring, and the cavity NO_2 slightly prefers to be from the nitro group attached to the five-membered ring.

The electron-impacting (EI) mass spectrometry of HNIW was reported by Robert and Doyle[12] and Pesce-Rodriguez et al.[7] Chemical formulas of most of the ions from HNIW in the spectra were given in the literature.[12]

In EI mass spectrometry, species at the heating probe vaporize and then enter the ion source. In the ion source the species are impacted by high-energy electrons and become charged. The positively charged species in the source are inducted into the analyzer by an anode. In the analyzer, ions of different mass can be selected singly with a changeable magnetic field. Finally, an EI mass spectrum can be recorded. The conventional EI mass spectrum of a compound can, however, contain ions that are formed by thermal decomposition followed by ionization and rearrangement and give no information concerning their formation.

Mass-analyzed ion kinetic energy spectrometry (MIKES) is a kind of mass spectrometry/mass spectrometry (MS/MS) analytical technique for metastable ions. It can be used to isolate a particular metastable ion and observe its fragmentation. A metastable ion can be selected by specific magnetic field. The metastable ion in the free field of the mass spectrometer undergoes unimolecular decomposition, in which its product ions and stable molecules are produced. The product ions can be isolated under a changeable electrostatic field. The stable molecules can be inferred from the process from the precursor ions to product ions. Therefore, a MIKES study of the metastable molecular ion, as well as of the product ions, of a compound will provide information on the fragmentation pathways of that compound.

In this paper, dissociation processes of various kinds of precursor ions from electron impacts on HNIW are analyzed with MIKES, and chemical pathways from precursor ions to product ions are revealed by inference.

Experiments

An ε-HNIW sample of 99% purity was synthesized by the Energetic Laboratory at the Beijing Institute of Technology. The mass

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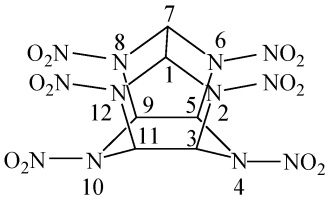
spectrometer (ZAB-HS, Micromass, Manchester, United Kingdom) for this study is a double-focusing instrument coupled with an 11-250 data system. The resolution was set to 1000 $M/\Delta M$ in EI mass spectra. The temperature of the EI ion source was 200°C. Samples were introduced into the mass spectrometer by direct probe. The temperature was set at 300°C. The heating rate was 30°C/min. In the heating process, when temperature of the probe rose to 250°C, the ion flow intensity recorded was very weak. In fact, the temperature of the probe was first set at 250°C, but the EI mass spectrum signals recorded at that temperature were also very weak. Therefore, the EI mass spectra in this paper were obtained at a probe temperature of 300°C. The ionizing energy was 70 eV with a trap current of 200 μA and an emission current of 1.2 mA. The accelerating potential was 8 kV. MIKES of selected ions were obtained by changing electrostatic field and were recorded using the 11-250 data system. The mass range scanned in the MIKES was from m/z 20 to value of m/z of precursor ion.

Fig. 1 Structure of HNIW.



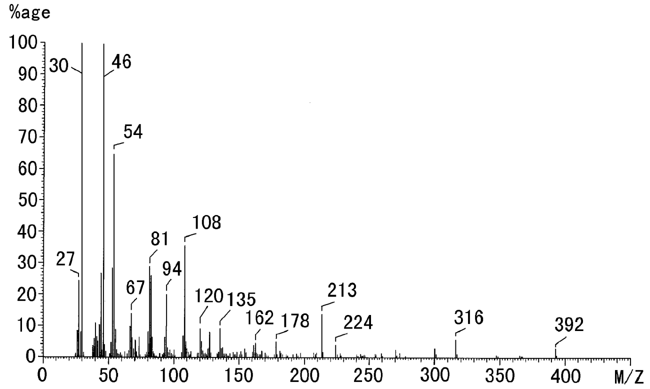


Fig. 2 Electron impacting mass spectra of HNIW at 300°C.

Results

Figure 2 shows EI mass spectra of HNIW obtained by the authors. The resulting EI spectrum might contain degradation products of HNIW because HNIW can undergo fast thermal decomposition at 250°C at the atmospheric pressure. The largest ions at m/z 392 can result from thermal degradation of HNIW and dissociation of HNIW under electron impacting.

Chemical ionization (CI) and collision-induced dissociation mass spectra of HNIW were described in a previous paper by the authors.[13] The largest ion in the CI mass spectra is the molecular ion at m/z 439 of HNIW; it was abundant. This means that HNIW molecules were desorbed intact from the heated probe.

The dissociation product ions of the precursor ions are listed in Table 1. This study focused on the mechanisms of dissociation from precursor ions to product ions.

Table 1 shows that the precursor HNIW-NO_2 ions produce product ions at (m-46)/z, (m-30)/z or (m-76)/z in most cases. This implies that cleavage reactions of the precursor HNIW ions are carried through loss of NO_2, NO, or $NO_2 + NO$. The cleavage reactions under electron impacting and possible structures of the precursor HNIW-NO_2 ions are listed in Table 2.

Ions at m/z 392

The ions at m/z 392 are produced by the loss of one NO_2 group from the HNIW molecule. The precursor ions (m/z 392

Table 1 Selected precursor HNIW-NO_2 ions and their product ions

Precursor ions (m/z)/(%)	Product ions (m/z)/(%)			
392 (100)	346 (10)	316 (83)	300 (<0.4)	46 (<0.4)
346 (100)	316 (3.3)	300 (6.4)	270 (0.6)	——
316 (100)	270 (1)	224 (0.4)	——	——
300 (100)	273 (0.5)	270 (0.8)	254 (0.5)	207 (0.9)
270 (100)		240 (0.5)	224 (1.6)	
224 (100)		178 (3)		
213 (100)		167 (1.4)		

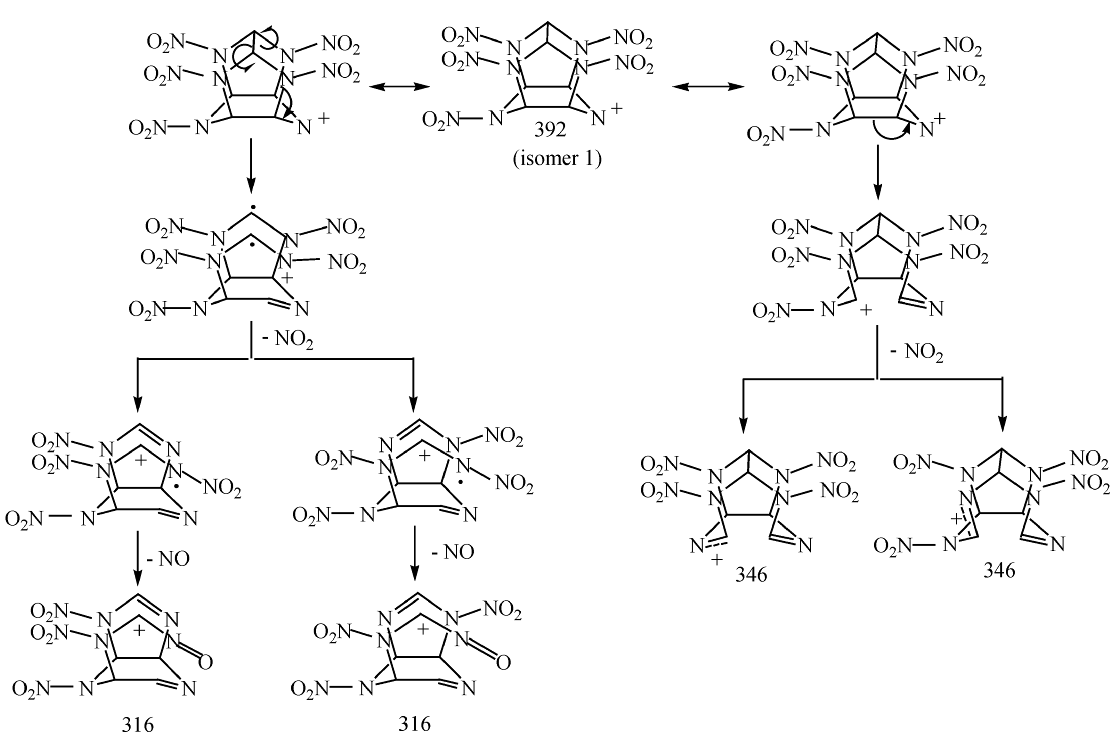
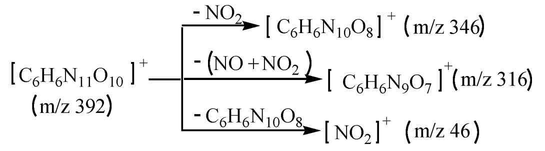
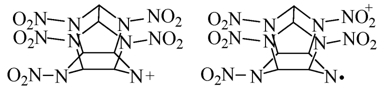
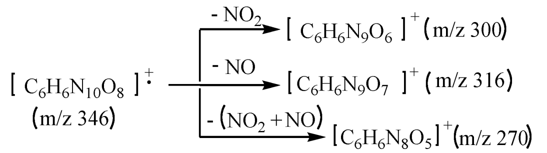
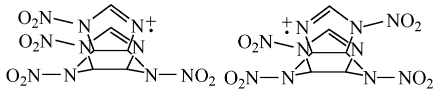
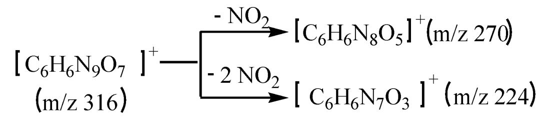
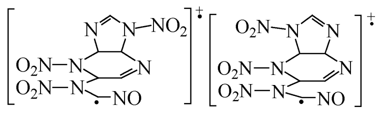
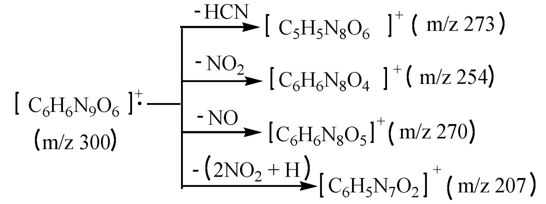
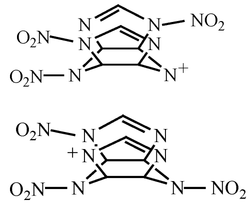
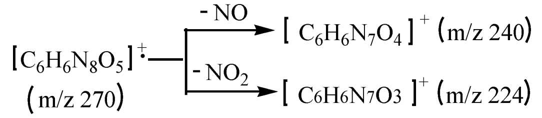
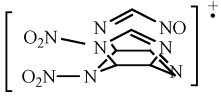
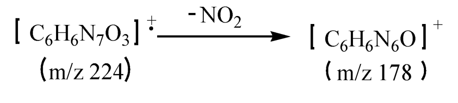
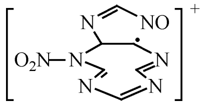
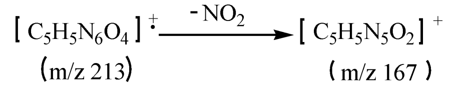
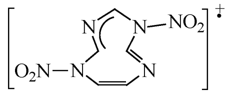


Fig. 3 Scheme 1.

Table 2 Dissociation reactions and possible structures of the precursor HNIW-NO2 ions in MIKE spectra

Precursor ions	Dissociation reactions of the precursor ions to product ions	Possible structures of the precursor ions
m/z 392	 $[C_6H_6N_{11}O_{10}]^+$ (m/z 392) $\xrightarrow{-NO_2}$ $[C_6H_6N_{10}O_8]^+$ (m/z 346) $\xrightarrow{-(NO+NO_2)}$ $[C_6H_6N_9O_7]^+$ (m/z 316) $\xrightarrow{-C_6H_6N_{10}O_8}$ $[NO_2]^+$ (m/z 46)	
m/z 346	 $[C_6H_6N_{10}O_8]^{+\cdot}$ (m/z 346) $\xrightarrow{-NO_2}$ $[C_6H_6N_9O_6]^+$ (m/z 300) $\xrightarrow{-NO}$ $[C_6H_6N_9O_7]^+$ (m/z 316) $\xrightarrow{-(NO_2+NO)}$ $[C_6H_6N_8O_5]^+$ (m/z 270)	
m/z 316	 $[C_6H_6N_9O_7]^+$ (m/z 316) $\xrightarrow{-NO_2}$ $[C_6H_6N_8O_5]^+$ (m/z 270) $\xrightarrow{-2\,NO_2}$ $[C_6H_6N_7O_3]^+$ (m/z 224)	
m/z 300	 $[C_6H_6N_9O_6]^{+\cdot}$ (m/z 300) $\xrightarrow{-HCN}$ $[C_5H_5N_8O_6]^+$ (m/z 273) $\xrightarrow{-NO_2}$ $[C_6H_6N_8O_4]^+$ (m/z 254) $\xrightarrow{-NO}$ $[C_6H_6N_8O_5]^+$ (m/z 270) $\xrightarrow{-(2NO_2+H)}$ $[C_6H_5N_7O_2]^+$ (m/z 207)	
m/z 270	 $[C_6H_6N_8O_5]^{+\cdot}$ (m/z 270) $\xrightarrow{-NO}$ $[C_6H_6N_7O_4]^+$ (m/z 240) $\xrightarrow{-NO_2}$ $[C_6H_6N_7O_3]^+$ (m/z 224)	
m/z 224	 $[C_6H_6N_7O_3]^{+\cdot}$ (m/z 224) $\xrightarrow{-NO_2}$ $[C_6H_6N_6O]^+$ (m/z 178)	
m/z 213	 $[C_5H_5N_6O_4]^{+\cdot}$ (m/z 213) $\xrightarrow{-NO_2}$ $[C_5H_5N_5O_2]^+$ (m/z 167)	

$[C_6H_6N_{11}O_{10}]^+$) produce main three product ions at m/z 346 $[C_6H_6N_{10}O_8]^+$, m/z 316 $[C_6H_6N_9O_7]^+$ and m/z 46 $[NO_2]^+$. The reaction of m/z 392 $[C_6H_6N_{11}O_{10}]^+ \to$ m/z 316 $[C_6H_6N_9O_7]^+$ has been described in the literature.[12] The formation of m/z 300 $[C_6H_6N_9O_6]^+$ from m/z 392 $[C_6H_6N_{11}O_{10}]^+$ losing two nitro groups also occurred, but the peak intensity of m/z 300 $[C_6H_6N_9O_6]^+$ was very weak (<0.5%). The reaction of m/z 392 $[C_6H_6N_{11}O_{10}]^+ \to$ m/z 46 $[NO_2]^+$ also took place, but the peak of m/z 46 is also very weak. For the ions at m/z 392 there exist many possible isomers. Different isomers probably have different dissociation pathways such as isomer 1 at m/z 392 as shown in scheme 1 (Fig. 3).

If the ion at m/z 392 $[C_6H_6N_{11}O_{10}]^+$ forms by removal of an electron of the N(4) atom, either the C(3)—N(2) bond or the C(3)—C(11) bond can proceed with *i*-cleavage. In that case, the two competing dissociation reactions of $[m/z\ 346]^+ \leftarrow [m/z\ 392]^+ \to [m/z\ 346]^+ \to [m/z\ 316]^+$ can proceed from the m/z 392 isomer 1 as shown in scheme 1. In the literature[12] it has been pointed out that the reaction of $[m/z\ 392]^+ \to [m/z\ 346]^+ \to [m/z\ 316]^+$ occurs according to the intermediate observed in the MS studies on HNIW.

In the dissociation pathway of $[m/z\ 392]^+ \to [m/z\ 316]^+$, *i*-cleavage of the C(3)—N(2) bond results in N(2) bearing positive charge. The C(1)—C(7) bond cleaves in a homolytic fashion under inducement of the positive charge at N(2). A nitro group at N(6) or N(8) is lost by inducement of the single electron of the C(7) atom in the β position relative to the nitro group (β-inducement effect); furthermore, a C(7)=N(6) or C(7)=N(8) double bond is formed. The nitro group at the N(2) atom is influenced by the electron at the N(2) atom in the α position relative to the nitro group and a NO molecule is removed (α-inducement effect).

In the dissociation pathway of $[m/z\ 392]^+ \to [m/z\ 346]^+$, *i*-cleavage of the C(3)—C(11) bond results in the C(11) atom bearing a positive charge. A nitro group at N(10) or N(12) is lost under the effect of β-inducement of the positive charge of the C(11) atom located at the β position relative to the nitro group.

Among the isomers at m/z 392, there can exist an isomer whose a nitro group is ionized. Formation of NO_2^+ can result from the removal of the ionized nitro group from the isomer (see Table 2).

Ions at m/z 346

In the EI mass spectra of HNIW, the peak of the ion at m/z 347 is weak, but abundance of the ion at m/z 346 is much lower than that of the ion at m/z 347. The ion at m/z 346 is a positive HNIW ion that has lost two nitro groups. The appearance of more ions at m/z 347 than m/z 346 means that many ions at m/z 346 acquire hydrogen in the ion source.

The ions at m/z 346 probably have several kinds of isomers. The precursor ions (m/z 346) can produce several product ions (m/z 316, m/z 300, and m/z 270) in the MIKES. The dissociation pathways

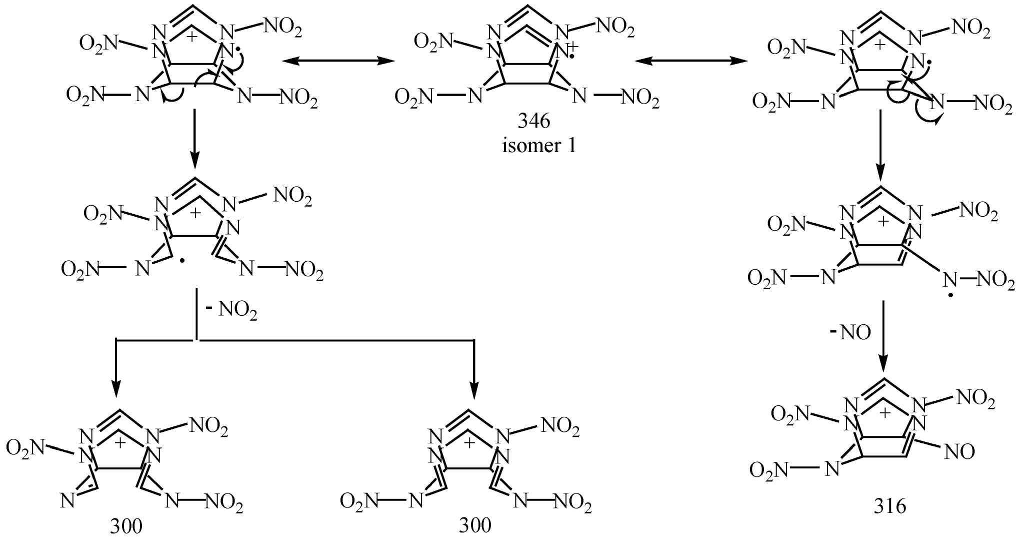


Fig. 4 Scheme 2.

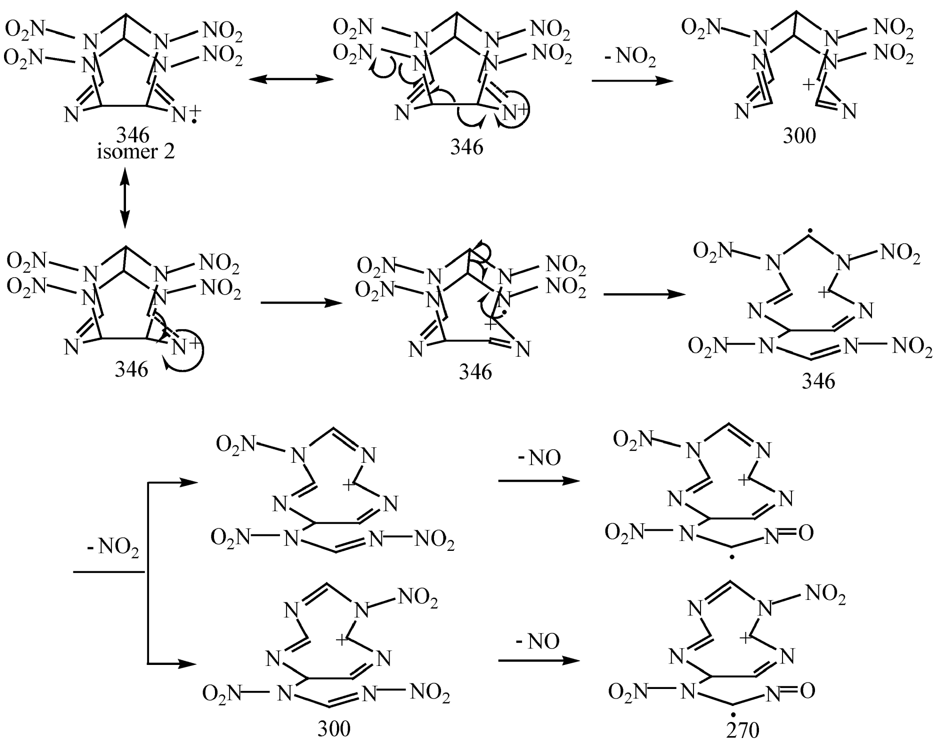
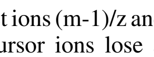


Fig. 5 Scheme 3.

of one isomer of precursor ions at m/z 346 are shown in scheme 2 (Fig. 4).

Scheme 2 indicates competing reaction pathways. In one pathway, the α-cleavage of the C(3)—N(4) bond results in N(4) bearing a single electron. Under the influence of the single electron of N(4) at the α position, an NO molecule is lost, and an ion at m/z 316 is formed. In another pathway, the α-cleavage of the C(3)—C(11) bond makes the C(11) atom bear a single electron. The nitro group at N(10) or N(12) is induced by the single electron of C(11) at the β position is lost, which results in formation of the C(11)=N(10) or C(11)=N(12) bond.

Scheme 3 (Fig. 5) shows that isomer 2 at m/z 346 probably yields two product ions ([m/z 270]$^+$ and [m/z 300]$^+$). If it proceeds with the α-cleavage reaction of the C(3)—C(11) bond, the NO$_2$ group attached to N(12) will be removed, and the ion at m/z 300 will be yielded owing to the β-inducement effect from the C(11) radical. If it proceeds with the α-cleavage reaction of the N(2)—C(3) bond, the C(1)—C(7) bond will cleave because of the influence of the N(2) radical; an intermediate radical ion at m/z 300 is further produced with the loss of the nitro group attached to N(8) under the β-inducement effect from the C(7) radical. Finally, the nitro group attached to N (2) can lose NO and form ions at m/z 270 by an intermediate structure



through cleavages of the N(2)—N and N—O bonds.

HNIW Framework Ions

The framework ions studied here include m/z 162, m/z 135, m/z 121, m/z 108, m/z 94, m/z 81, m/z 67, and m/z 54. The dissociation products of the precursor ions are listed in Table 3.

In the dissociation of the HNIW framework ions, most of the precursor ions produce product ions (m-1)/z and (m-27)/z (see Table 3). This means that the precursor ions lose an H atom or an HCN molecule. Dissociation reactions of the precursor ions to product ions are listed in Table 4.

Ions at m/z 162

Ions at m/z 162, the biggest framework ions, can produce two kinds of product ions: $[m/z\ 161]^+$ and $[m/z\ 135]^+$. The process of the precursor ion $[m/z\ 162]^+ \rightarrow [m/z\ 135]^+$ (losing an HCN molecule) shows that the ion at m/z 162 is of ring structure because an ion with a chain structure probably loses other fragments. One of the possible structures of the ion is shown as in Table 4. As shown in scheme 4 (Fig. 6), the isomer ion at m/z 162 removes an HCN molecule through α-cleavage and i-cleavage reactions followed by the cyclization between the two radical atoms.

Table 3 Selected HNIW framework ions and their product ions

Precursor ions (m/z)/(%)	Product ions (m/z)/(%)
162 (100)	161 (0.7) 135 (0.8)
135 (100)	134 (0.8) 108 (2)
121 (100)	120 (<0.4) 94 (2.1)
108 (100)	81 (2)
94 (100)	93 (0.4) 67 (0.4)
81 (100)	80 (0.6) 79 (0.9) 54 (0.5)
67 (100)	66 (0.8) 65 (0.7) 41 (<0.4) 40 (0.4)
54 (100)	53 (1.8) 39 (0.4) 28 (0.4)

Ions at m/z 135

The ion at m/z 135 proceeds to α-cleavage and i-cleavage reactions successively, resulting in the removal of HCN and formation of an ion at m/z 108 of an eight-membered ring. The cyclization occurs between the N and C atoms of a single electron at two ends of the acyclic radical ion as seen in scheme 5 (Fig. 7).

Like the ion at m/z 162, the HNIW framework ions at m/z 135, 121, 108, 94, 81 only undergo loss of one HCN molecule in MIKES.

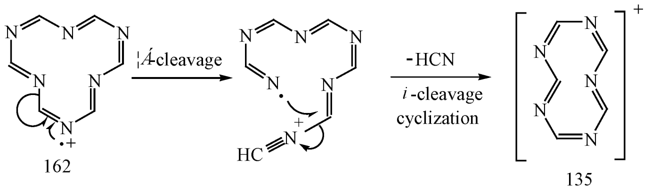
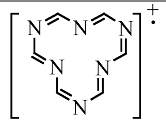
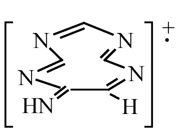
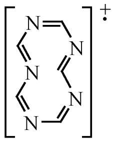
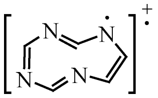
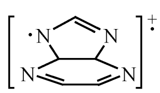
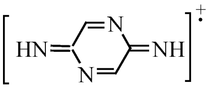
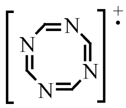
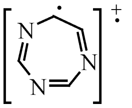
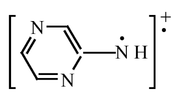
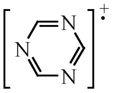
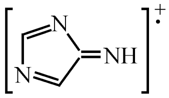
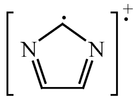
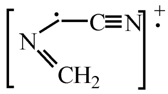
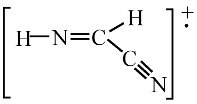
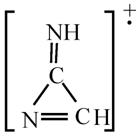


Fig. 6 Scheme 4.

Table 4 Dissociation reactions and possible structures of the precursor framework ions to product ions

Precursor ions (m/z)	Dissociation reactions of the precursor ions to product ions	Possible structures of the precursor ions
162	$[C_6H_6N_6]^{+\cdot}$ (m/z 162) $\xrightarrow{-H}$ $[C_6H_5N_6]^+$ (m/z 161) $\xrightarrow{-HCN}$ $[C_5H_5N_5]^+$ (m/z 135)	 a
135	$[C_5H_5N_5]^{+\cdot}$ (m/z 135) $\xrightarrow{-H}$ $[C_5H_4N_5]^+$ (m/z 134) $\xrightarrow{-HCN}$ $[C_4H_4N_4]^+$ (m/z 108)	 b  c
121	$[C_5H_5N_4]^{+\cdot}$ (m/z 121) $\xrightarrow{-H}$ $[C_5H_4N_4]^+$ (m/z 120) $\xrightarrow{-HCN}$ $[C_4H_4N_3]^+$ (m/z 94)	 d  e
108	$[C_4H_4N_4]^{+\cdot}$ (m/z 108) $\xrightarrow{-HCN}$ $[C_3H_3N_3]^+$ (m/z 81)	 f  g
94	$[C_4H_4N_3]^{+\cdot}$ (m/z 94) $\xrightarrow{-H}$ $[C_4H_3N_3]^+$ (m/z 93) $\xrightarrow{-HCN}$ $[C_3H_3N_2]^+$ (m/z 67)	 h  i
81	$[C_3H_3N_3]^{+\cdot}$ (m/z 81) $\xrightarrow{-H}$ $[C_3H_2N_3]^+$ (m/z 80) $\xrightarrow{-2H}$ $[C_3HN_3]^+$ (m/z 79) $\xrightarrow{-HCN}$ $[C_2H_2N_2]^+$ (m/z 54)	 j  k
67	$[C_3H_3N_2]^{+\cdot}$ (m/z 67) $\xrightarrow{-H}$ $[C_3H_2N_2]^+$ (m/z 66) $\xrightarrow{-2H}$ $[C_3HN_2]^+$ (m/z 65) $\xrightarrow{-CN}$ $[C_2H_3N]^+$ (m/z 41) $\xrightarrow{-HCN}$ $[C_2H_2N]^+$ (m/z 40)	 l  m
54	$[C_2H_2N_2]^{+\cdot}$ (m/z 54) $\xrightarrow{-H}$ $[C_2HN_2]^+$ (m/z 53) $\xrightarrow{-NH}$ $[C_2HN]^+$ (m/z 39) $\xrightarrow{-CN}$ $[CH_2N]^+$ (m/z 28)	 n  o

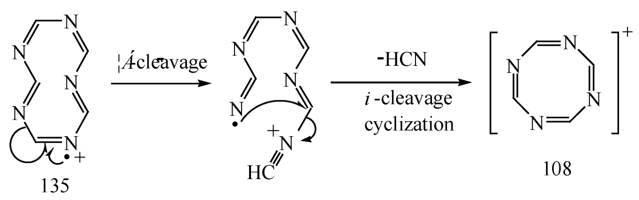


Fig. 7 Scheme 5.

They are considered to have cyclic structures. If they are chain structures, they certainly contain both —CN and =CH$_2$ groups, but their MIKE spectra do not show a loss of CN or CH$_2$ or other fragments larger than HCN molecule. Suggested structures of these framework ions are depicted as in Table 4, based on the structural characteristics of the HNIW framework.

Abundance of the ions at m/z 135 and m/z 121 are not high in the EI spectra. This can be attributed to their unstable structures. If the ion at m/z 135 exists in both structures b and c as shown in Table 4, the structures are certainly nonplanar structures with low conjugative effect because of the spatial effect of the C—H bond pointing to the inside of the structures. For the ion m/z 121, its possible structure d also is nonplanar.

The m/z 108 ions are the most abundant among the ions greater than m/z 54. This should be chiefly attributed to its planar, conjugative structure f. The ions at m/z 94, m/z 81, and m/z 67 should have similar structures. Thus they are observed to be very abundant.

The ion at m/z 67 loses a radical ·CN to form an ion at m/z 41 and loses an HCN molecule to form an ion at m/z 40, respectively. This shows that two isomers probably exist in the ion at m/z 67. The former contains a CN group, that is, it is of a chain structure (m). The later can be of a cyclic structure (l).

The ion at m/z 54 can lose a radical ·CN or ·NH and forms ions at m/z 28 or at m/z 39, respectively. This shows that it has at least two isomers. One contains a CN group (n) and another contains an NH group (o).

A given m/z ion generally has several possible isomers. Different precursor ion isomers can produce different product ions. In the authors' analysis, the dissociation mechanisms suggested are for a specific precursor ion isomer to a specific product ion. In fact, similar mechanisms also possibly occur for other isomers.

Discussion

In the present analysis, it is shown that dissociation of HNIW-NO$_2$ precursor ions produces product ions with the removal of an NO$_2$ or NO molecule. For HNIW-NO$_2$ ions, the cleavage of C—N* makes the N* atom in C—N*—NO$_2$ bear a positive charge or radical electron; The effect of α-inducement of the N* atom (C—N*—NO$_2$) to the nitro-group results in loss of NO from the ion. The cleavage of the C—C* bond usually makes the C* atom in C—C*—N—NO$_2$ bear a positive charge or radical electron; The effect of β-inducement of the C* atom to the nitrogroup attached via the N atom to the C* atom (C—C*—N—NO$_2$) finally leads to the loss of NO$_2$ from the ion.

For framework ions, the precursor ions larger than m/z 67 lose only an HCN molecule and an H atom to produce the product ions (m-27)/z and (m-1)/z. This means that these HNIW framework precursor ions are of cyclic structure. Linear structure framework ions should be able to produce other product ions. The ion at m/z 67 can lose a ·CN radical and an HCN molecule, and the ion at m/z 54 can lose a ·CN radical and a ·NH radical. For the m/z 67 and m/z 54 ions, linear isomers should exist.

Even though thermal decomposition is much more complicated than the ion dissociation discussed here, as a simplified treatment, chemical reactions removing HCN, NO$_2$, and NO from HNIW might be considered to be an initial step of the thermal decomposition of HNIW. Products of C and N cyclic structure can be formed based on the framework of HNIW after most of NO$_2$ groups have been removed.

Conclusions

Based on the study on El and MIKES mass spectra for HNIW, ion dissociation mechanisms of HNIW ions were set up. Dominate dissociation mechanism of the HNIW ions with NO$_2$ group is the removal of NO$_2$, or NO, or NO$_2$ + NO molecules. For the large HNIW framework ion without NO$_2$ group, dominate dissociation mechanism is the removal of H atom or HCN molecule. The large HNIW framework ions were considered to be of cyclic structure.

Acknowledgments

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