Mass Spectral Fragmentation Pathways in 1,3,3-Trinitroazetidine

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The electron impact (EI) fragmentation pathways of 1,3,3-trinitroazetidine (TNAZ) along with some ^{15}N and ^{2}H analogs were studied. Collision-induced dissociation was also used to investigate important peaks in the EI spectra. Isotopically labeled compounds allowed the determination of most of the major fragmentation peaks. It was found that the major pathway involves the loss of NO_2 or HNO_2 from the dinitroalkyl group followed by a loss of NO_2 or NO from the nitramine group. The peak at m/z 46, $[NO_2]^+$, the base peak, resulted primarily from N—N bond scission while the peak at m/z 30, $[NO]^+$, was equally likely to come from any NO_2 bond. The fragmentation pathway of TNAZ showed similarities with other nitramine and nitrocarbon explosives. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Since World War II there have been explosives [i.e. 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetazacyclooctane (HMX)] available that are more powerful than 2,4,6-trinitrotoluene (TNT), but TNT remains in military use because it is unique among common explosive fills in being melt castable. In recent years, several new explosives have been synthesized which are more powerful than most currently used military explosives.[1] Among these, 1,3,3-trinitroazetidine (TNAZ) holds promise, being both highly energetic and steam castable (melting point 101 °C), and therefore is being considered as a substitute for TNT.[2,3] The evaluation of TNAZ for use as a military explosive requires stability studies which include detailed characterization of intermediates and products associated with thermal decomposition.[4] Elucidation of fragmentation pathways from electron impact (EI) mass spectrometry may provide insights into thermal decomposition mechanisms of energetic materials.

The EI fragmentation pathways of TNAZ and isotopically labeled analogs, shown in Fig. 1, were determined using a Finnigan-MAT TSQ-700 tandem mass spectrometer. In addition to EI, chemical ionization (CI) spectra were also obtained. The $[M + 1]^+$ fragment observed in CI spectra confirmed the EI assignment. Collision-induced dissociation (CID) spectra for critical fragmentation ions of TNAZ and its labeled analogs yielded information on the origins of fragments and helped to determine molecular formulas. Some plausible structures for the fragments are presented. Verifications of structures were made with the help of the isotopically labeled analogs. The TNAZ-d_4 and $[^{13}C]$TNAZ analogs were used to determine formulas and chemical structures of smaller fragments.

EXPERIMENTAL

A Varian Model 3400 gas chromatograph (GC) equipped with a capillary column (J&W DB-5MS, 30 m × 0.25 mm i.d.) was used to introduce TNAZ into a

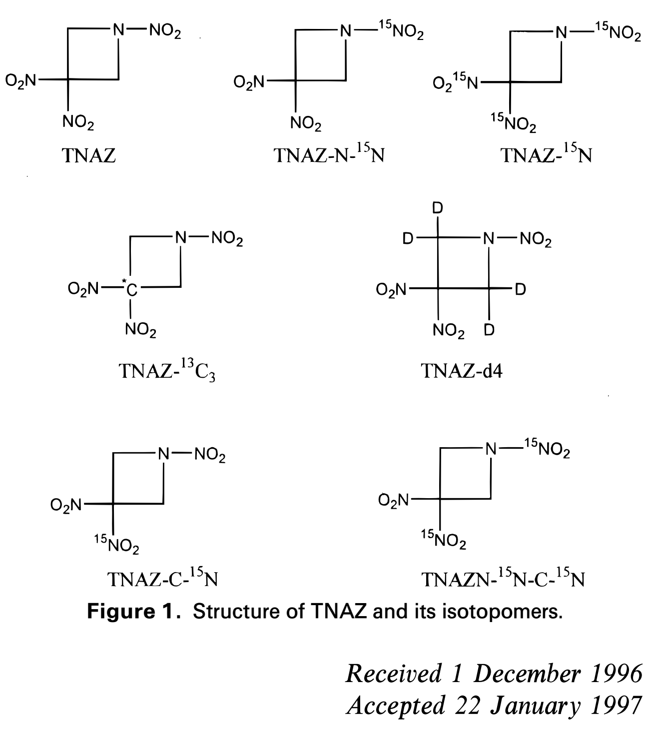
TNAZ
TNAZ-N-^{15}N
TNAZ-^{15}N
TNAZ-$^{13}C_3$
TNAZ-d4
TNAZ-C-^{15}N
TNAZN-^{15}N-C-^{15}N

Figure 1. Structure of TNAZ and its isotopomers.

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Finnigan-MAT TSQ-700 tandem mass spectrometer. The injector temperature was 200 °C and the transfer line temperature was 220 °C. The oven temperature was held at 80 °C for 1 min and then ramped at 7.5 °C min^{-1} to 210 °C. Injection volumes were 1 μl of 0.02% TNAZ in acetone. EI and CI ionizations were carried out at 70 eV with emission currents of 400 μA. The ion source was operated at 150 °C. For CI, methane was used as the reagent gas. CID was carried out at collision energy of 15 eV, with 0.5–1 mTorr (1 Torr = 133.3 Pa) of argon as the collision gas. All spectra shown in this paper were obtained using a GC inlet. A solids probe was also used to obtain mass spectra of the TNAZ compounds. These spectra matched those obtained using the GC inlet. The use of the GC inlet was preferred because less sample was required. When the solids probe was used, much of the sample was lost due to sublimation before the probe reached the ion volume.

RESULTS AND DISCUSSION

Figure 2 shows the EI mass spectra of TNAZ and its six isotopomers. The base peak for TNAZ is at *m/z* 46, $[NO_2]^+$, with almost no molecular ion observed. Fragmentation ions of TNAZ and isotopically labeled analogs produced by EI are listed in Table 1 along with their relative abundances. Although the molecular ion and the $[M + 1]^+$ ion were extremely small, obtaining CID spectra of them was still possible. For the $[M + 1]^+$ ion using a 1% TNAZ solution to obtain good CID spectra was necessary. Table 2 lists the CID ions from TNAZ fragments and their abundances relative to the largest CID peak. From these tables a fragmentation map for TNAZ was constructed (Scheme 1). The initial step is a loss of either NO_2 or HNO_2 to form the *m/z* 146 and 145 ions (Fig. 3). Loss of NO_2 or HNO_2 is often reported in mass spectrometric studies of explosives[5–7] and is consistent with proposed decomposition pathways of TNAZ.[4,8,9] While the heaviest fragments seen for TNAZ were of *m/z* 146/145, for [N-^{15}N] TNAZ the heaviest fragments were of *m/z* 147/146 (Table 1). This indicates that the nitro group was still attached to the azetidine nitrogen and cleavage of $C{-}NO_2$ is the first step in the EI fragmentation of TNAZ. Further loss of $NO_2{}^+/NO_2$ or NO from the *m/z* 146 fragment is the result of $N{-}NO_2$ bond cleavage. This is evidenced by the fact that the *m/z* 146 fragment of TNAZ and the *m/z* 147 fragment of [N-^{15}N] TNAZ both form fragments of *m/z* 100 and 116 (Table 1, Fig. 3).

The spectra for TNAZ, [N-^{15}N]TNAZ and [C-^{15}N]TNAZ shows that most of the *m/z* 46/47 $[NO_2]^+$ fragment is from the $N{-}NO_2$ nitro group (Fig. 2). This result is consistent with the CID spectrum, which shows that TNAZ fragments below *m/z* 145 exhibit no $NO_2{}^+$ (*m/z* 46) fragments (Table 2). Since little $NO_2{}^+$ appeared to originate from the $C{-}NO_2$ bonds, we assumed that these are more likely to be due to fragments of *m/z* 146 or 147 with accompanying neutral loss of NO_2 or HNO_2, respectively. While the

Table 1. Fragmentation ions in the mass spectra (EI) of TNAZ isotopomers

TNAZ	TNAZ-d_4	[N-^{15}N]TNAZ	[^{15}N]TNAZ	[^{13}C]TNAZ	[C-^{15}N]TNAZ	[N-^{15}N, C-^{15}N]TNAZ
26 (6.5)	28 (4.9)	26 (8.4)	26 (6.6)	27 (14.2)	26 (6.8)	26 (6.9)
27 (16.7)		27 (21.5)	27 (16.6)	28 (17.3)	27 (16.9)	27 (17.3)
28 (17.3)	30 (47.9)	28 (22.5)	28 (17.2)	29 (8.8)	28 (17.8)	28 (18.3)
29 (1.0)		29 (1.3)	29 (1.2)		29 (1.1)	29 (1.2)
30 (20.5)		30 (20.1)		30 (20.6)	30 (14.4)	30 (8.4)
		31 (6.8)	31 (20.4)		31 (7.3)	31 (13.6)
39 (2.7)		39 (3.6)	39 (2.7)	40 (3.2)	39 (2.8)	39 (2.9)
40 (2.6)	42 (4.2)	40 (3.4)	40 (1.9)	41 (4.3)	40 (2.3)	40 (2.4)
41 (15.2)	44 (10.3)	41 (19.8)	41 (16.2)	42 (16.8)	41 (16.2)	41 (16.7)
42 (4.6)		42 (6.0)	42 (4.8)	43 (1.3)	42 (4.8)	42 (5.0)
46 (100)	46 (100)	46 (23.5)		46 (100)	46 (100)	46 (6.4)
47 (1.3)	47 (1.6)	47 (100)	47 (100)	47 (3.1)	47 (3.9)	46 (100)
		49 (3.0)				
		51 (1.2)		52 (1.2)	52 (8.3)	52 (8.5)
52 (8.0)	54 (5.8)	52 (10.5)	52 (7.9)	53 (8.6)	53 (5.6)	53 (5.8)
53 (5.4)	56 (3.4)	53 (7.0)	53 (5.4)	54 (5.3)	54 (2.2)	54 (2.3)
54 (2.1)	58 (3.7)	54 (2.7)	54 (2.0)	55 (2.1)	56 (1.1)	56 (1.2)
56 (2.0)		56 (2.5)	57 (2.1)	57 (2.2)	57 (1.2)	57 (1.3)
68 (2.2)	70 (2.0)	68 (2.7)	68 (2.6)	69 (2.2)	68 (2.5)	68 (2.6)
99 (6.7)	102 (5.4)	99 (8.3)	100 (6.7)	100 (7.2)	99 (3.8)	99 (3.8)
100 (1.9)	104 (1.0)	100 (2.3)	101 (1.8)	101 (1.9)	100 (4.2)	100 (4.4)
					101 (1.0)	101 (1.1)
116 (1.4)	120 (1.0)	116 (1.7)	117 (1.4)	117 (1.4)	116 (1.0)	116 (1.0)
145 (12.1)	148 (8.6)	146 (15.9)	147 (11.9)	146 (12.7)	145 (6.5)	146 (7.1)
146 (9.1)	150 (15.1)	147 (9.7)	148 (8.4)	147 (9.1)	146 (10.4)	147 (10.6)
					147 (4.9)	148 (4.7)

[a] Only those with relative abundance >1.0% considered. Numbers in parentheses are relative abundances (%).

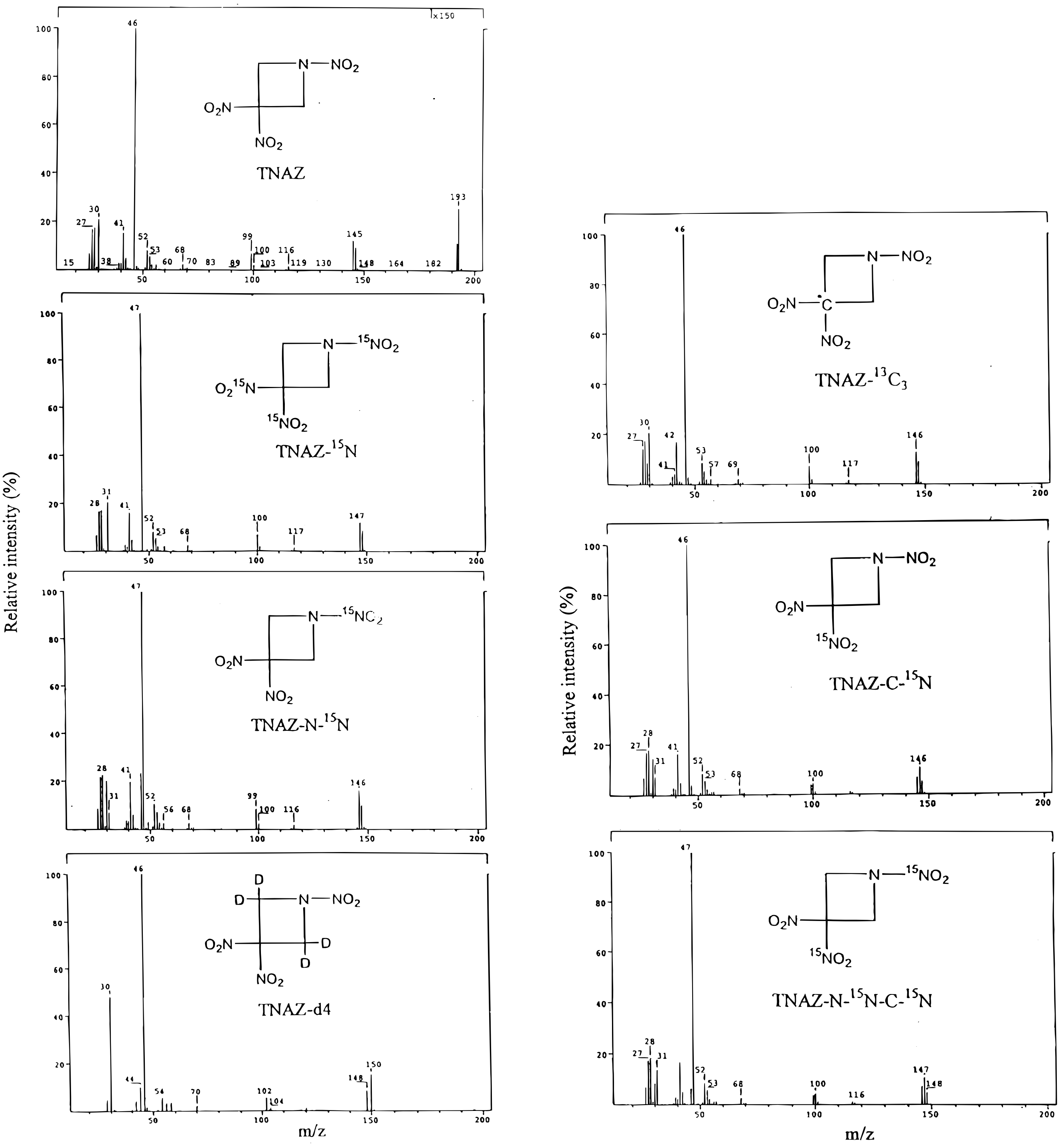
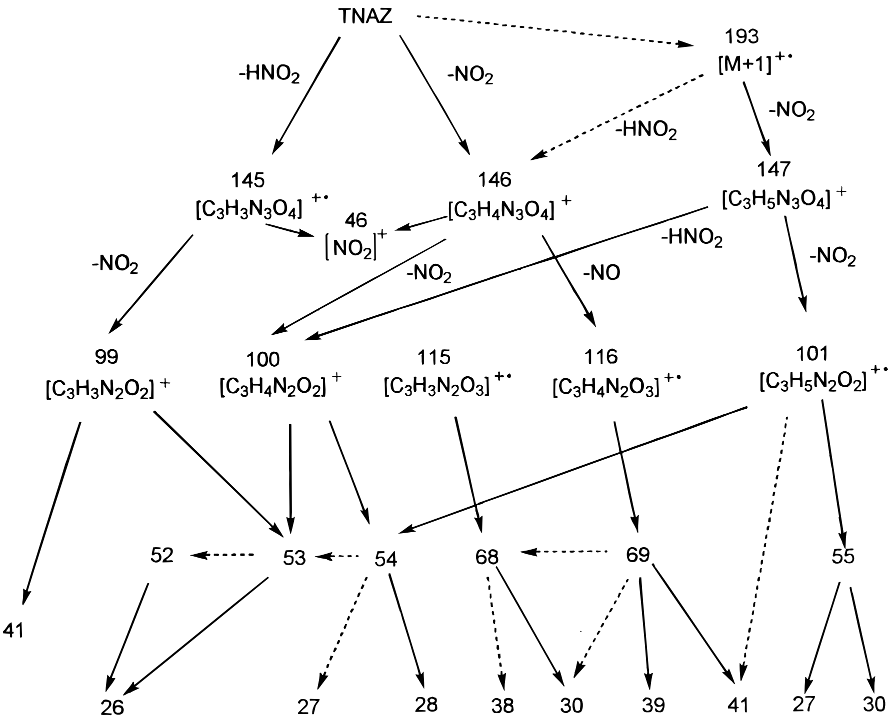


Figure 2. Mass spectra of TNAZ and its isotopomers. (A) TNAZ; (B) [^{15}N]TNAZ; (C) [N-^{15}N]TNAZ; (D) TNAZ-d_4; (E) [$^{13}C_3$]TNAZ; (F) [C-^{15}N]TNAZ; (G) [N-^{15}N, C-^{15}N]TNAZ.

fragment of *m/z* 46 mostly arises from NO_2^+ from N—NO_2 bond scission, the fragment of *m/z* 30, $[NO]^+$, is equally likely to originate from any of the nitro groups, as evidenced by both *m/z* 30 and 31 in the fragmentation of [N-^{15}N]TNAZ.

Chemical formulas were assigned to each of the major peaks and some of the minor peaks that appeared to play an important role in the TNAZ decomposition pathways (Fig. 3, Scheme 1). Some lower m/z peaks could not be assigned unequivocally; these include m/z 41 (C_2H_3N or C_2HO), *m/z* 28 (CH_2N^+ or CO^+) and 27 (HCN^+ or $C_2H_3^+$). A small abundance of *m/z* 193 $[M + H]^+$ was observed in the 0.02% TNAZ solution; this peak became larger as the sample concentration increased to 1% TNAZ. CID spectra for EI of *m/z* 193 were the same as the CID spectra for CI of *m/z* 193 (Fig. 4), confirming our assignment of *m/z* 193 as $[M + H]^+$.[10] With the aid of CID spectra of the TNAZ isotopomers, structural assignments were made for many of the peaks in the TNAZ fragmentation scheme



Scheme 1. CID fragmentation map of TNAZ.

(Figs 5 and 6). Although open-chain species can be formulated to meet the observed fragmentation, we speculate that many of these compounds retain the azetidine ring structure. Other mass spectral studies have reported fragments containing azetidine ring structures,[11,12] and both theoretical calculations and mass spectral studies have identified such structures in the thermal decomposition pathway of TNAZ.[4,9] The fragment of *m/z* 69 has been assigned two different structures, based on its mode of fragmentation. It is interesting that one possible structure for the peak at *m/z* 53 is that of acrylonitrile, $[C_3H_3N]^+$. CID spectra for the peaks at

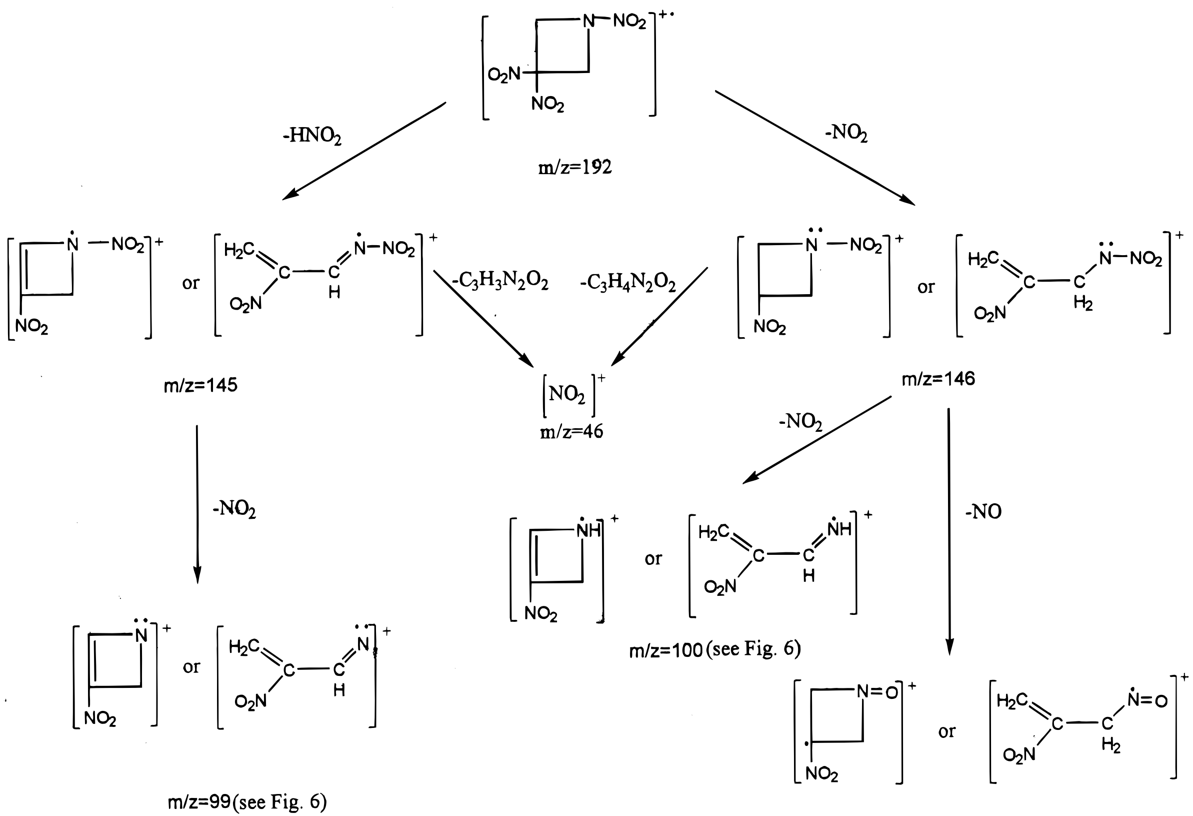


Figure 3. TNAZ fragmentation: heavy fragments.

Table 2. CID of EI fragments of TNAZ

Fragment ion	+1	+0	+1−NO_2	−NO_2	−HNO_2	−NO_2−NO	−HNO_2−NO	−2NO_2	−HNO_2−NO_2	−2NO_2−OH	−HNO_2−NO_2−NO	−2HNO_2−NO
P	193	192	147	146	145	116	115	100	99	83	69	68
P−OH								83 (1)				
P−NO				116 (2)					69 (1)	53 (22)	39 (16)	38 (1)
P−NO_2	147 (17)	146 (17)	101 (16)	100 (4)	99 (38)			54 (2)	53 (3)			
P−HNO_2	146 (1)		100 (28)			69 (98)	68 (88)	53 (35)				
P−NO_2−NO		116 (4)										
P−HNO_2−NO				69 (1)		39 (23)						
P−2NO_2	101 (15)	100 (28)			53 (1)							
P−HNO_2−NO_2	100 (39)	99 (18)		53 (1)								
P−2NO_2−NO	71 (2)											
P−HNO_2−NO_2−NO		69 (3)	55 (7)									
						68 (1)						
	59 (2)											
CH_2CNO										56 (10)		
C_3H_4NH	55 (8)											
C_3H_4N			54 (3)									
C_3H_3N	53 (4)	53 (1)	53 (3)									
HNO_2			47 (6)									
NO_2	46 (16)	46 (100)	46 (78)	46 (100)	46 (39)							
								44 (4)				
								43 (1)				
C_2H_4N				42 (2)				42 (5)				
C_2H_3N/C_2HO		41 (25)	41 (9)	41 (2)	41 (30)	41 (1)		41 (2)	41 (26)		41 (3)	
NO	30 (10)	30 (2)			30 (11)		30 (8)	30 (3)	30 (4)			30 (10)
CH_2N/CO								28 (5)				
C_2H_2								26 (3)				

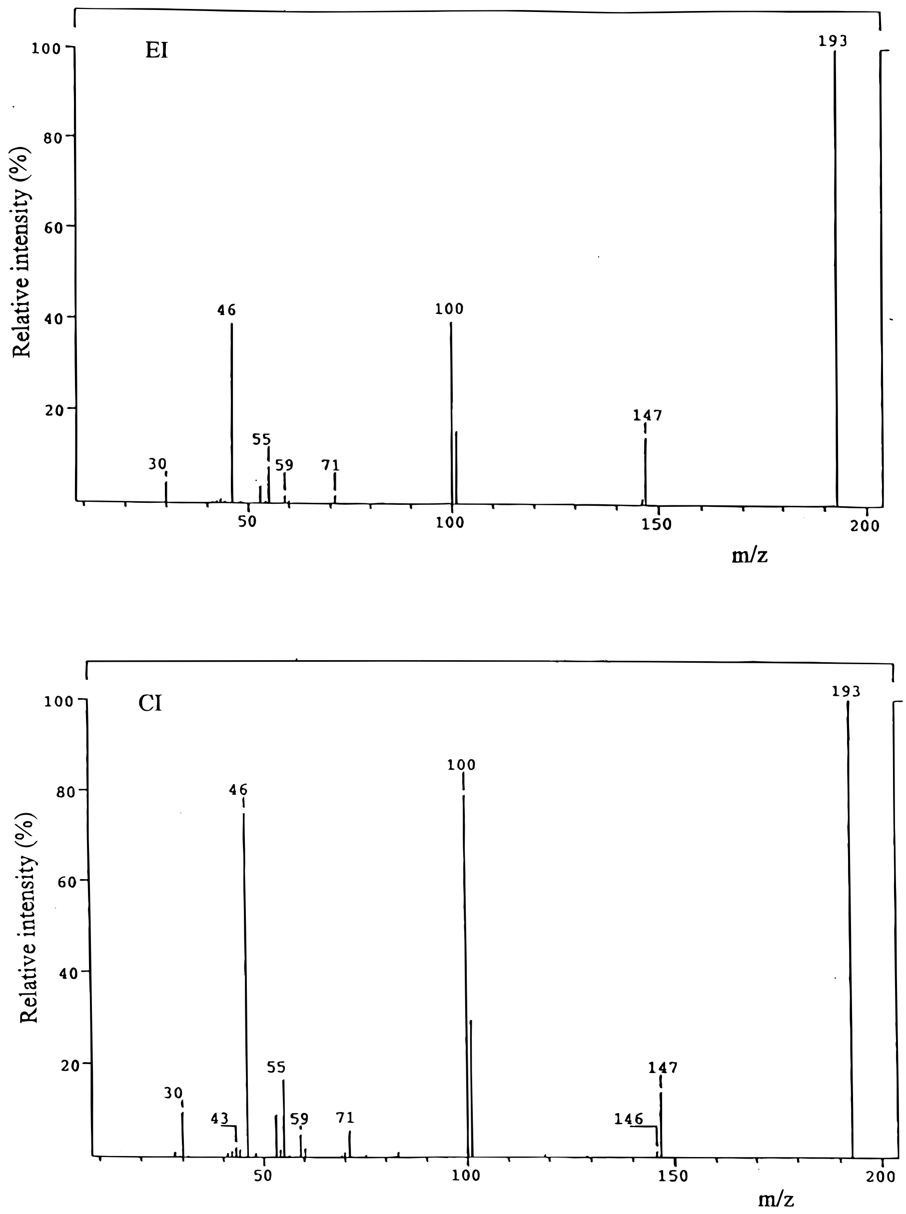


Figure 4. CID mass spectra of TNAZ ion of *m/z* 193 from EI and CI.

m/z 53 and 52 in acrylonitrile were similar to those for the peaks at *m/z* 53 and 52 in TNAZ; however, this does not rule out other possible structures for those peaks in the TNAZ spectra.

The fragmentation spectra of TNAZ are similar to those of the nitramine explosives RDX and HMX in that the base peak is at *m/z* 46 and that there are no molecular ions in the EI mass spectra.[5] The large *m/z* 46 peak would be expected because of the possibility of $N—NO_2$ bond scission. TNAZ does not show CH_2NNO_2 or CH_2NNO elimination like RDX or HMX;[13] considering the difference in their structures, it would not be expected to do so. The neutral loss of NO_2 and HNO_2 from the TNAZ $C—NO_2$ bond is similar to that seen in other cyclic nitro compounds.[14] However, there was no evidence of a major pathway involving the loss of OH as in the fragmentation of nitroarenes.[15] This was evident by a lack of a major peak at *m/z* 17. A neutral loss experiment for *m/z* 17 was run on TNAZ. It showed peaks at *m/z* 100, 73 and 47 (Fig. 7). However, the peaks at *m/z* 83 and 56 were minor, indicating that the neutral loss of 17 u from *m/z* 100 and 73 were not major pathways. The neutral loss of 17 u from *m/z* 47 was merely a loss of OH from HNO_2.

CONCLUSIONS

The base peak in the TNAZ spectra, at *m/z* 46 $[NO_2]^+$, originates from the nitramine group. Pathways to the larger ions (*m/z* 146/145) involve an initial neutral loss of either NO_2 or HNO_2 from the nitrocarbon group. Intense peaks at *m/z* 99 and 100 indicate a further loss of NO_2 or HNO_2 from the $N—NO_2$ bond. The

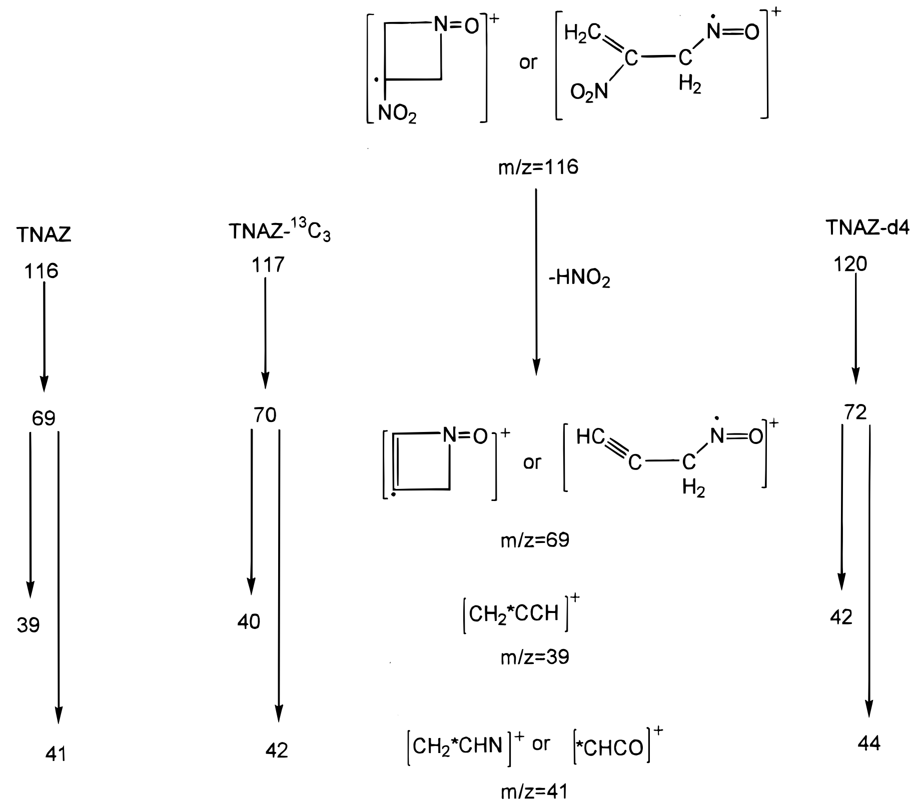


Figure 5. Fragmentation of TNAZ fragment of m/z 116.

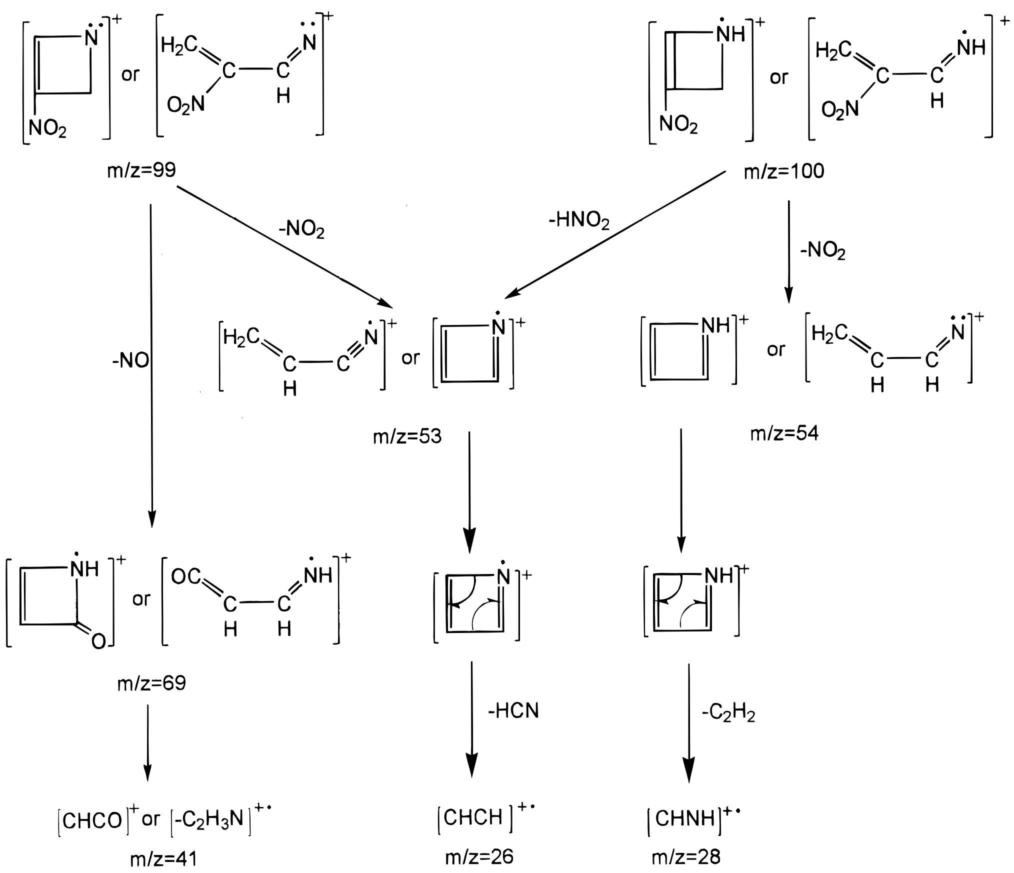


Figure 6. TNAZ fragmentation: medium fragments.

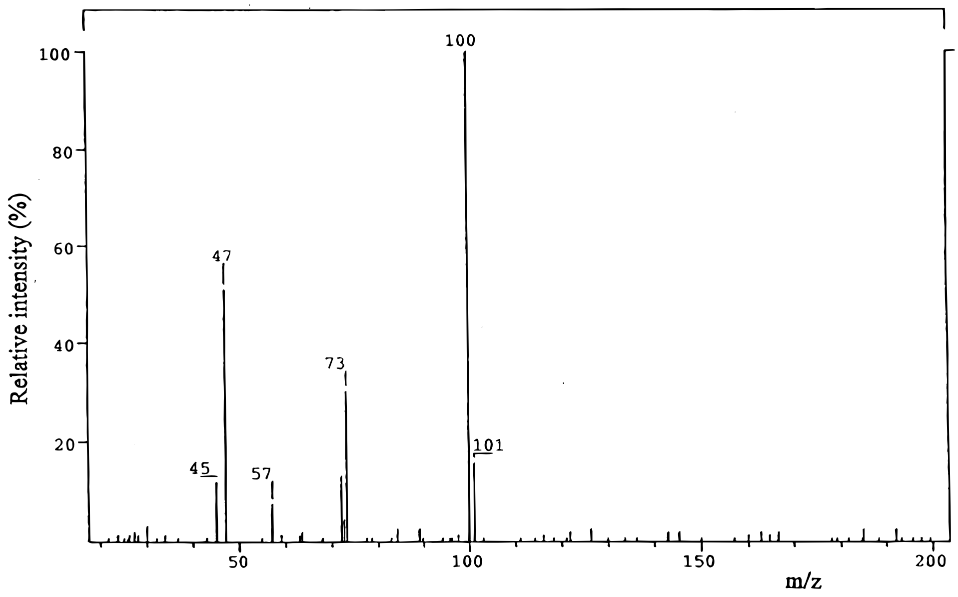


Figure 7. Mass spectrum of neutral loss of 17 u.

fragment at *m*/*z* 30, $[NO]^+$, could originate from $N—NO_2$ or $C—NO_2$ bonds. No evidence was seen for loss of CH_2NNO_2 or CH_2NNO as with RDX or HMX or for loss of OH as is seen with nitroarenes.

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