Positive Electron Impact and Chemical Ionization Mass Spectra of Some Nitramine Nitrates

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The positive electron impact (EI) and isobutane chemical ionization (CI) mass spectra of six nitramine nitrates were studied with the aid of some accurate mass measurements. In the EI spectra, β fission relative to both the nitramine and nitrate ester is important. In the CI spectra a major ion occurs at $[MH - 45]^+$ and was found to be mainly due to $[M + 2H - NO_2]^+$. All of the compounds except N-(2 hydroxyethyl)-N-(2',4',6'-trinitrophenyl)nitramine nitrate gave an $[MH]^+$ ion. The $[MH - 45]^+$ ion in the isobutane CI mass spectra of tetryl is also due to $[M + 2H - NO_2]^+$.

INTRODUCTION

Nitramines and nitrate esters are commonly encountered in explosives and propellant technology and nitramine nitrates may have similar applicability. Some nitramine nitrates (1) have recently been synthesised¹ by the reaction of N_2O_5 with small-ring nitrogen heterocycles:



Structural identification of the compounds was confirmed by both nuclear magnetic resonance and mass spectrometry.

EXPERIMENTAL

The compounds were prepared by the reaction of the appropriate aziridine or azetidine with N_2O_5 :

- $\begin{array}{cccc} n & R & R^{1} \\ 1: & 0 & n-C_{4}H_{9} & H & RMM & 207 \end{array}$
- N-butyl-N-(2'-hydroxyethyl)nitramine nitrate 2: 1 CH_2CH_2CN H RMM 218
- N-(2-cyanoethyl)-N-(3'-hydroxylpropyl)nitramine nitrate
- 3: 0 CH₂CH₂CN CH₃ RMM 218 N-(2-cyanoethyl)-N-(2'-hydroxypropyl)nitramine nitrate
- 4: 0 Picryl H RMM 362 N-(2-hydroxyethyl)-N-(2',4',6'-trinitrophenyl)nitramine nitrate

- 5: N,N'-bis(2-hydroxyethyl)nitramine nitrate (DINA), RMM 240, O₂NOCH₂CH₂N(NO₂)CH₂CH₂ONO₂ was prepared from [NCH₂CH₂OH.
- 6: N,N'-bis(2-hydroxyethyl)-N,N'-dinitrooxamide (NENO), RMM 356,
 O₂NOCH₂CH₂CH₂N(NO₂)COCON(NO₂)-CH₂CH₂ONO₂, was prepared from [NCOCON]].

Compounds 5 and 6 have already been synthesized by other routes.

Instrumental conditions

All spectra were obtained on a VG 7070 EQ mass spectrometer with a DEC PDP8 data system. The source temperature was 200 °C and the accelerating potential was 6 kV. Positive electron impact (EI) mass spectra were obtained at 50 eV and trap current 100 μ A. Positive chemical ionization (CI) mass spectra were obtained using isobutane as reagent gas at a source housing pressure of 2 × 10⁻⁵ mbar (1 bar = 10⁵ Pa), electron energy 50 eV and emission current 1 mA.

Compound 1 was introduced in a 20 mm deep silica sample tube on the solids probe heated to 120 °C. All the other compounds were placed in 2 mm deep silica cups at the end of a solid silica rod that projected from the front end of the solids probe, so the sample reached just to the source cavity and was heated by contact with the source block. Although not true direct exposure mass spectrometry,² much less decomposition was observed than with the sample tube in the conventional position.

Accurate mass measurement was performed using the data system peak matching facility at resolution 4000 (10% valley definition) against perfluorokerosene (PFK), except for the accurate CI mass measurements of 4, which were carried out at resolution 10 000 against PFK and $[MH]^+$ of di-*n*-butyl phthalate.

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RESULTS AND DISCUSSION

EI mass spectra

The most abundant and structurally important ions are shown in Table 1. No ions were seen at M - 47 ([M $-HNO_2$ ⁺) and only with 3 was a weak [M $-NO_2$] ion observed. α -Fission of the nitrate ester results in the $[M - NO_3]^+$ ion and with loss of the nitramine nitro group leads to the $[M - N_2O_5]^+$ ion. All of the compounds showed some ions corresponding to nitramine and nitrate ester β -fission and further ions corresponding to loss of NO, NO₂ and HNO₂ from the β -fission product. ions. As expected,³ ions were not seen at M - 1 and M - 15 due to nitrate ester β -fission. Ions corresponding to the nitrate ester moiety resulting from nitramine α -fission were present only in some of the compounds and then only at very low intensity. The ion at m/z 42 is always an intense ion when the molecule has methylene groups on either side of the nitramine; this was confirmed by accurate mass measurement to be $[C_2H_4N]^+$. For dimethylnitramine the ion at m/z 42 has the proposed structure $[CN_2=N=CH_2]^{+4}$ The $[C_2H_4N]^+$ ion is also prominent in the EI mass spectra of diethylnitramine⁵ and would result from β -fission on both sides of the nitramine. In the EI mass spectra of nitrate esters, $[NO_2]^+$ is a major ion and a minor ion

in the EI mass spectra of simple nitramines such as diethylnitramine.^{3,5} In these nitramine nitrates $[NO_2]^+$ is a major ion and probably results primarily from the nitrate ester. A summary of these proposed fragmentation processes for 2 is shown in Scheme 1.

In the EI mass spectra of 6 the highest mass ion observed was $[C_4H_4N_3O_7]^+$ (observed mass 206.005; calculated 206.005) due to α -fission of the nitramine. The next highest mass ion was $[CH_2N_3O_4]^+$ (1%) (observed mass 120.003; calculated 120.004) and must result from a rearrangement reaction. Similar ions have been seen in the spectra of other nitrate esters,⁵ e.g. in the EI mass spectra of 1-nitro-2-hydroxylbutyl nitrate, $O_2NCH_2CH(ONO_2)CH_2CH_3$, a minor ion was observed as [CH₂N₂O₄]^{+•} (observed mass 106.006; calculated 106.002).

The highest mass observed in the EI spectra of 4 corresponded to M - 45 due to $[C_6H_7N_5O_7]^+$ ([M + H] $(-NO_2]^+$ (observed mass 317.023; calculated 317.024). The ion was always seen over a range of source temperatures and probe conditions. The base peak is at m/z241 owing to nitrate ester β -fission of the m/z 317 ion. The ion at m/z 75 was composed primarily (95%) of $[CH_3N_2O_2]^+$ (observed mass 75.020; calculated 75.019) with 5% of $[C_2H_3O_3]^+$ (observed mass 75.003; calculated 75.008). There are many ions below m/z 212 due to fragmentation of the 2,4,6-trinitrophenyl ion, similar to those seen for other 2,4,6-trinitroaromatic compounds.

Table 1. The most abundant and structurally important ions in the EI mass spectra of nitramine nitrates 1-6

	m/z (relative abundance)						
tonic species	1	2	3	4	5	6	
M+	207(0.1)						
[M - 45] ⁺	• •			317(5)			
$[M - NO_3]^+$	145(1)	156(1)	156(8)	300(0.1)	178(1)		
$[M - N_2 O_5]^+$	99(1)	110(1)	110(2)	254(0.2)	132(1)		
Nitrate ester β -fission 1 °	76(4)	76(3)	90(7)	76 ^b (29)	76(1)	76(7)	
Nitrate ester β -fission 1 ^a	131 (89)	142(4)	128(62)	286(3)	164(41)	. ,	
Nitrate ester β -fission 1° – NO ₂	85(27)	96(6)	82(30)	240(41)	118(5)		
Nitrate ester β -fission 1 * -HNO ₂	84(100)	95(2)	81(6)	239(4)	117(5)		
Nitramine β -fission 2°	43°(90)	40(4)			d	đ	
Nitramine β -fission 2°	164(2)	178(8)			đ		
Nitramine β -fission 2 ^a – NO ₂	118(1)	132(3)			d		
Nitramine β -fission 2° – HNO ₂	117(1)	131(2)			d		
Nitramine β -fission 1°	d	128(33)	đ	ď	đ		
Nitramine β -fission 1° – NO ₂	d	82(12)	d	d	d		
Nitramine β -fission 1° – HNO ₂	d	81 (9)	đ	đ	d		
Nitramine β -fission 1 ^a	d	. ,	d	d	đ		
Nitramine a-fission	57(32)	54(31)	54(17)	212(3)		206(9)	
[NO ₂] ⁺	46(72)	46(69)	46(54)	46(100)	46(100)	46(100)	
m/z 42	42(94)	42(100)	42(100)	42(1)	42(99)	42(3)	
m/z 30 ^e	30(35)	30(40)	30(14)	30(78)	30(16)	30(17)	
Other major ions	70(16)	86(40)	43(17)	241(100)		56(21)	
	89(19)	56(41)		75(42)		29(6)	
	56(24)			. ,		· · ·	
	29(40)						

27(24) ^a β -Fission 1 = between nitrate ester and nitramine; β -fission 2 = on the non-nitrate ester chain.

^b $CH_2NO_3: C_2H_4O_3: CH_4N_2O_2 (100:30:10)$. ^c $C_3H_5N: C_3H_7 (100:5)$.

^d Same ion as nitrate ester β -fission. ^e Mainly NO and CH₂O.



Isobutane CI mass spectra

All of the compounds except 4 gave an $[MH]^+$ ion but only in 5 was it the base peak. Adduct ions $[M + NO_2]^+$ and $[M + 30]^+$ were also sometimes observed. The major ions in all the spectra were due to various combinations of losses of H, NO, NO₂ and NO₃ from $[MH]^+$. Other ions were due to nitrate ester and nitramine β -fission and also subsequent loss of nitrogen oxides. NO₂ was present in all the spectra and formed the base peak of 6. The highest mass observed for 4 was at m/z 358.066 (5%) due to $[M + C_3H_7 - HNO_2]^+$ (calculated mass 358.063). All of the compounds showed an ion at $[MH - 45]^+$ of about equal or greater intensity than the ions at $[MH - 46]^+$ or $[MH - 47]^+$. Its accurate mass was determined for 1, 4 and 5 and also for 1,3-dihydroxypropane dinitrate (7) and N-methyl-N-(2,4,6-trinitrophenyl)nitramine (tetryl) (8).⁵ The results are given in Table 2.

Yinon² proposed the $[MH - 45]^+$ ion for tetryl to be $[MH - CH_3NO]^+$ or possibly $[MH - OH - CO]^+$; accurate mass measurement has shown that this is not the case and that for other nitro and nitrate ester compounds the $[MH - 45]^+$ ion is likely to be due to $[MH + H - NO_2]^+$.

Table 2. Accurate mass determinations of the [MH - 45]⁺ ion in the CI spectra of some nitramines, nitrate esters and nitramine nitrates

$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Atomic			Intensity relative		
1 163.105 $C_6H_{15}N_2O_3$ 163.108 59 $[M + 2H - NO]$ 4 318.030 $C_6H_6N_5O_9$ 318.032 a $[M + 2H - NO]$ 5 196.062 $C_4H_{10}N_3O_6$ 196.062 10 $[M + 2H - NO]$ 5 196.022 $C_3H_6N_3O_7$ 196.021 5 $[M + H - CH_3N]$ 7 122.044 $C_2H_1N_2O_2$ 122.045 54 $[M + 2H - NO]$	Compound	Observed Mass	composition	Calculated mass	to [MH]+ (%)	Species	
4 318.030 $C_6H_6N_5O_9$ 318.032 ^a $[M + 2H - NO]$ 5 196.062 $C_4H_{10}N_3O_6$ 196.062 10 $[M + 2H - NO]$ 5 196.022 $C_3H_6N_3O_7$ 196.021 5 $[M + H - CH_3]$ 7 122.044 $C_2H_2N_2O_2$ 122.045 54 $[M + 2H - NO]$	1	163.105	$C_{6}H_{15}N_{2}O_{3}$	163.108	59	[M + 2H - NO ₂]+	
5 196.062 $C_4H_{10}N_3O_6$ 196.062 10 $[M + 2H - NO_5$ 5 196.022 $C_3H_6N_3O_7$ 196.021 5 $[M + H - CH_3N_5]$ 7 122.044 $C_2H_2N_2O_2$ 122.045 54 $[M + 2H - NO_5]$	4	318.030	C ₆ H ₆ N ₅ O ₉	318.032	a	$[M + 2H - NO_2]^+$	
5 196.022 $C_3H_6N_3O_7$ 196.021 5 $[M + H - CH_3H_6N_3O_7$ 122.044 $C_2H_2N_2O_2$ 122.045 54 $[M + 2H - NO_2$	5	196.062	C₄H ₁₀ N ₃ O ₆	196.062	10	$[M + 2H - NO_2]^+$	
7 122.044 C.H.N.O. 122.045 54 [M+2H-NO	5	196.022	C ₃ H ₆ N ₃ O ₇	196.021	5	$[M + H - CH_3NO]^+$	
	7	122.044	$C_3H_6N_4O_7$	122.045	54	[M + 2H - NO ₂] ⁺	
8 243.037 C ₇ H ₇ N ₄ O ₆ 243.036 ^b [M+2H-NO	8	243.037	C ₇ H ₇ N ₄ O ₆	243.036	b	$[M + 2H - NO_{2}^{-}]^{+}$	

^b Base peak; at resolution 6000 no other ions at m/z 243 seen.

The base peak in the mass spectrum of 4 is at MH - 90 (observed mass 273.046, corresponding to $C_7H_7N_5O_7$; calculated 273.047), due to $[MH + H - NO_2 + H - NO_2]^+$ with 5% of m/z 273.097, $C_6H_{13}N_6O_5$ (calculated mass 273.095), corresponding to the reduction of three nitro groups to the corresponding amine. The reduction of a nitro group to an amine has been observed² in the CI mass spectra of other trinitroaromatic compounds when water is used as the reagent gas.

The $[MH - 45]^+$ ion in these compounds is therefore due mainly to the addition of further hydrogen and loss of NO₂. The $[MH - 45]^+$ ion seen in CI and direct CI mass spectra of tetryl and other explosives² may also be due to this mechanism.

CONCLUSIONS

The EI fragmentation of nitramine nitrates is dominated by β -fission relative to both the nitramine and nitrate ester groups. $[NO_2]^+$ is always intense and where $CH_2=N=CH_2$ can be formed this is also a prominent ion. In isobutane chemical ionization, $[MH]^+$ is present for all the compounds except 4. An ion at MH – 45 present in the spectra of all the compounds was primarily $[M + 2H - NO_2]^+$. This ion is also present in the CI mass spectrum of tetryl and some nitrate esters and could account for the $[MH - 45]^+$ ion seen in the CI mass spectra of other explosive compounds.

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