

MASS SPECTROMETRIC STUDY OF SUBSTITUTED 5- OR 4-NITRO- 1,2,3-TRIAZOLE 1-OXIDES

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A mass-spectrometric study of substituted 5- or 4-nitro-1,2,3-triazole 1-oxides showed the feasibility of using mass spectrometry for identifying 5-amino- and 5-alkylamino-2-methyl-4-nitro-1,2,3-triazole 1-oxides and their 4-amino-5-nitro isomers.

Keywords: nitro-1,2,3-triazole 1-oxides, mass spectra, molecular ions, fragmentation, electron impact.

Analysis of studies of the mass spectra of heterocyclic N-oxides [1] has shown that the data on the fragmentation of these compounds in the literature are contradictory. Thus, some authors consider that the distinguishing feature of the mass spectra of N-oxides is the presence of a strong $[M^+ - 16]$ peak, which can serve as a diagnostic test for the N-oxide group [2-4]. This conclusion emerged from a study of the mass spectra of N-oxides of substituted quinolines [2] and phenazines [3] as well as pentachloropyridine 1-oxide and pentachloropyridine [4]. High intensity for the $[M^+ - 16]$ peak was also observed in the mass spectra of substituted 1,2,4-triazole 4-oxides [5, 6]. However, Grigg and Odell [7] reported that this peak is insignificant for pyrroline N-oxide and 2-alkylpyridine 1-oxides.

Prior to our work, there were no mass spectrometric studies of 1,2,3-triazole 1-oxides. Mass spectral data with indication of the presence of $[M]^+$, $[M^+ - 16]$ or $[M^+ - 17]$ appeared only in the work of Begtrup [8, 9].

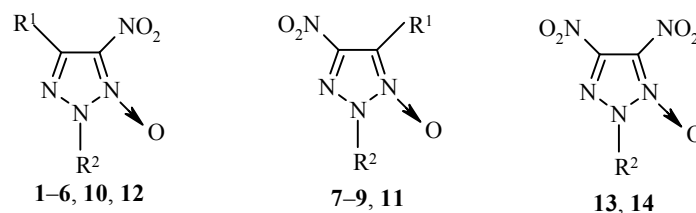
In a continuation of an investigation on the properties of substituted nitrotriazole N-oxides, we studied the behavior of these compounds upon electron impact, elucidated the direction of their fragmentation, and established, if possible, the rules of decomposition.

In the present work, we studied the mass spectra of substituted 5- or 4-nitro-1,2,3-triazole 1-oxides **1-12** (see Table 1).

Molecular ion peaks were observed in all the mass spectra of the compounds studied. These oxides may be divided into two major groups relative to the nature of the further electron impact fragmentation.

Group I contains 4-amino- and 4-alkylamino-2-methyl-5-nitrotriazole 1-oxides **1-6** (see Table 1). Analysis of the mass spectra of these compounds suggested the following fragmentation scheme, which accounts for the origin of the strongest peaks in the mass spectra:

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TABLE 1. Mass Spectra of Substituted 5- or 4-Nitro-1,2,3-triazole 1-Oxides **1-14**

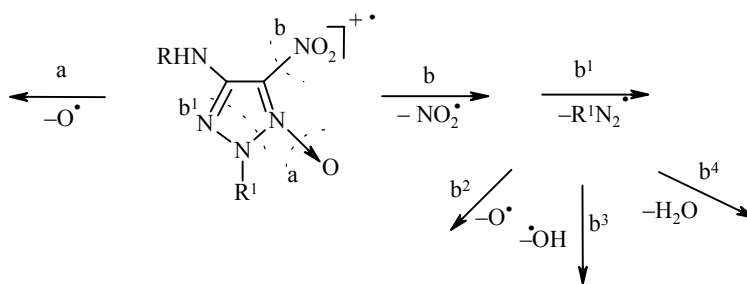
Com- pound	R ^{1*}	Mass spectra, <i>m/z</i> (<i>I</i> _{rel} , %)									
		[M] ⁺	[M - O] ⁺ (a)	[M - OH] ⁺	[M - NO ₂] ⁺ (b)	[M - NO ₂ - AlkN ₂] ⁺ (b ¹)	[b ¹ - O] ⁺ (b ²)	[b ¹ - OH] ⁺ (b ³)	[b ¹ - H ₂ O] ⁺ (b ⁴)	AlkN ₂ ⁺	AlkN ₂
1	NH ₂	159 (13)	143 (20)	—	113 (21)	71 (17)	55 (17)	54 (19)	53 (19)	43 (100)	42 (65)
2	MeNH	173 (21)	157 (1)	—	127 (48)	85 (50)	69 (48)	68 (18)	67 (12)	43 (100)	42 (20)
3	EtNH	187 (36)	171 (3)	—	141 (61)	99 (97)	83 (10)	82 (10)	81 (22)	43 (100)	42 (35)
4	MeNH	187 (55)	171 (5)	—	141 (73)	85 (76)	69 (11)	68 (100)	67 (44)	57 (23)	56 (78)
5	EtNH	201 (31)	185 (14)	—	155 (55)	99 (52)	83 (50)	82 (40)	81 (65)	57 (100)	56 (62)
6	PrNH	229 (32)	213 (4)	—	183 (46)	113 (100)	97 (15)	96 (13)	95 (19)	71 (85)	70 (52)
7	NH ₂	159 (67)	143 (3)	—	113 (15)	71 (4)	55 (9)	54 (19)	53 (31)	43 (18)	42 (100)
8	MeNH	173 (25)	157 (4)	156 (9)	—	85 (5)	69 (19)	68 (14)	67 (15)	43 (100)	42 (22)
9	EtNH	187 (23)	171 (40)	170 (25)	—	99 (0.5)	83 (4)	82 (13)	81 (12)	43 (100)	42 (20)
10	MeO	174 (27)	158 (3)	—	128 (59)	86 (46)	70 (46)	69 (6)	—	43 (100)	42 (23)
11	MeO	174 (82)	—	—	128 (10)	86 (4)	70 (22)	69 (11)	68 (5)	43 (100)	42 (18)
12	N ₃	185 (76)	169 (5)	—	—	97 (13)	81 (5)	—	—	43 (100)	42 (28)
13 ^{*2}	—	189 (21)	173 (4)	—	143 (23)	—	—	—	—	—	—
14 ^{*3}	—	265 (1)	249 (2)	248 (3)	—	—	—	—	—	—	—

* **1-3, 7-13** R² = Me, **4, 5** R² = Et, **6** R² = Pr, **14** R² = CH₂C₆H₅.

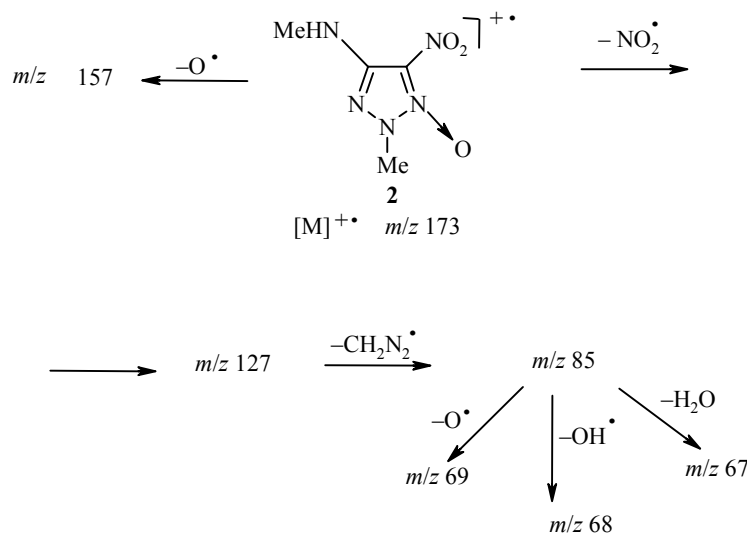
*² The mass-spectra also contains ion peaks, *m/z* (*I*_{rel}): 97 (100) [M - NO₂ - NO₂]⁺, 55 (3) [97 - CH₂N₂]⁺, 39 (18)

[55 - O]⁺, 38 (7) [55 - OH]⁺.

*³ The spectrum also contains peaks: *m/z* (*I*_{rel}): 91 (100) [CH₂C₆H₅]⁺, 77 (10) [C₆H₅]⁺.



This scheme appears as follows for 2-methyl-5-nitro-1,2,3-triazole 1-oxide (**2**):



The major ions formed as the result of these processes are given in Table 1.

These results indicate that the $[M - O]^+$ ion peak is present in all the mass spectra of **1-16** but has low intensity and, thus, cannot be characteristic.

The predominant fragmentation pathway involves initial loss of NO_2^\bullet from the molecular ion followed by loss of a neutral molecule of the corresponding diazoalkane. It is precisely this direction of fragmentation, which, in our view, is an important feature of all the triazole N-oxides studied **1-12** and, thus, the corresponding peaks may be used as characteristic for this type of compound.

We should note that charge is localized upon loss of a neutral diazoalkane molecule predominantly on the remaining fragment. However, an alternative charge distribution is also observed. All the mass spectra show peaks for the ions of the corresponding diazoalkanes and their protonated forms.

Partial pyrolysis is apparently observed for **5, 6, 8, and 9** under the mass-spectral conditions, which complicates the overall picture without, however, eliminating the major fragmentation directions.

Group II combines 5-amino- and 5-alkylamino-2-methyl-4-nitro-1,2,3-triazole 1-oxides **7-9** and isomeric 5-nitro derivatives **1-3**.

The fragmentation of **7-9** is generally similar to the fragmentation of the triazole N-oxides in Group I. Their mass spectra contain strong molecular ion peaks and the formation of $[M - O]^+$ ions is found for all these compounds. The loss of NO_2^\bullet from the molecular is also apparently common for both isomers. However, the corresponding ions from the 4-nitro isomers are much less stable than from the 5-nitro isomers. Thus, the $[M - NO_2]^+$ ion peaks in the mass spectra of triazole N-oxides in Group I are much stronger than the molecular ions in contrast to Group II compounds.

The $[M - \text{NO}_2]^+$ peak for 5-amino-2-methyl-4-nitro-1,2,3-triazole 1-oxide (**7**) is less intense than the molecular ion peak. The analogous peaks are lacking in the mass spectra of compounds **8** and **9** with alkyl substitution of the amino group. However, peaks are found in the spectra of **8** and **9**, which correspond to the consecutive loss of NO_2^\cdot and diazomethane from the molecular ion $[M - \text{NO}_2 - \text{CH}_2\text{N}_2]^+$. This finding suggests that the $[M - \text{NO}_2]^+$ ions formed from **8** and **9** are extremely unstable and are formed in such insignificant amounts that they are not seen in the mass spectra.

A special feature of the mass spectral behavior of 5-alkylamino derivatives **8** and **9** is the loss of a hydroxyl from the molecular ion, which may be explained by the migration of a proton, probably from the alkyl group and not from the nitrogen atom of the alkylamino group to the oxygen atom of the N-oxide fragment through a five- or six-membered state (McLafferty rearrangement [10]). Evidence for this hypothesis is found in the lack of an $[M - \text{OH}]^+$ peak in the mass spectrum of **7**, which is unsubstituted at the amino group.

The mass spectra of 5-nitro isomers **2-6** also lack the $[M - \text{OH}]^+$ peak due to the large distance between the N-oxide oxygen atom and the alkylamino group when the molecule has planar structure.

The intensity of the peaks of the diazomethane ion peaks and especially the peaks for protonated diazomethane is much greater for Group II compounds **7-9** than for Group I triazole N-oxides, while the intensity of the $[M - \text{NO}_2 - \text{CH}_2\text{N}_2]^+$ ion peaks is less for **7-9**.

Partial pyrolysis is also observed for Group II triazole N-oxides under mass-spectral conditions.

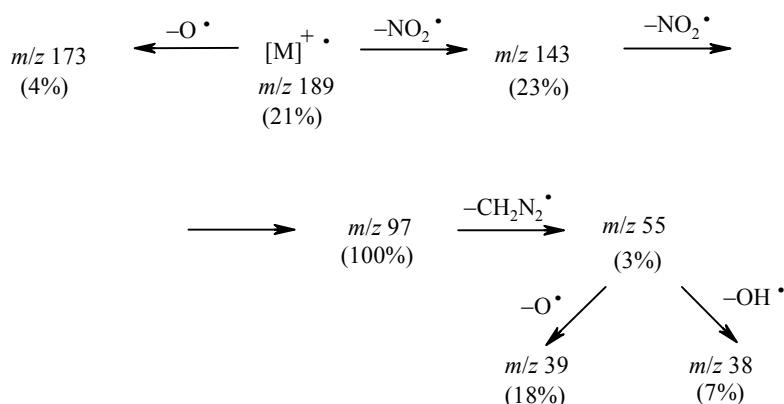
The fragmentation of 4- and 5-methoxy derivatives of 2-methyl-5- (**10**) and 2-methyl-4-nitro-1,2,3-triazole N-oxides (**11**) proceeds similarly to the scheme established for the alkylaminonitro isomers except that the $[M - \text{O}]^+$ and $[M - \text{OH}]^+$ ion peaks are lacking in the mass spectrum of the 5-methoxy isomer.

Comparison of the intensities of the major ion peaks for the methoxy derivatives shows the same trend as in the case of the alkylamino isomers for the intensity ratio of the $[M]^+$ and $[M - \text{NO}_2]^+$ peaks.

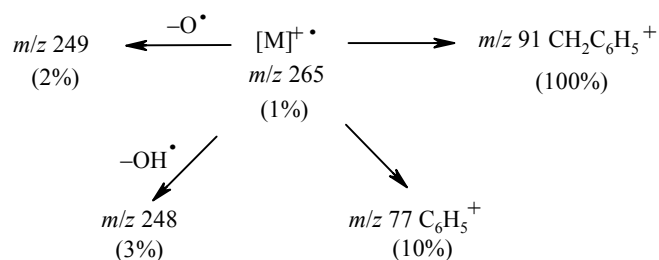
The mass spectrum of 4-azido-5-nitro-1,2,3-triazole 1-oxide (**12**) contains a strong molecular ion peak, while the intensity of the $[M - \text{O}]^+$ peak is only 5%. The $[M - \text{NO}_2]^+$ peak is lacking in this spectrum but peaks are observed for ions corresponding to consecutive dissociation $[M - \text{NO}_2 - \text{CH}_2\text{N}_2]^+$. The peak with m/z 43 is the strongest peak, while the intensity of the diazomethane peak is only 28%.

The mass spectrometric study of 2-methyl-4,5-dinitro-1,2,3-triazole 1-oxide (**13**) showed that the behavior of this compound upon electron impact differs somewhat from the behavior of the corresponding 4-alkylamino derivatives.

The formation of the major fragmentation ions may be explained as follows:



The molecular ion peak of 2-benzyl-4,5-dinitro-1,2,3-triazole 1-oxide (**14**) has low intensity. The mass spectrum also has $[M - \text{O}]^+$ and $[M - \text{OH}]^+$ peaks, which might have been expected by analogy with previous results [6, 7, 11, 12]. The strongest peaks are found for aromatic tropylium and phenyl ions. The fragmentation of the compound upon electron impact may be given by the following scheme:



Hence, the electron impact decomposition of substituted nitro-1,2,3-triazole 1-oxides proceeds largely through a common scheme. The slight differences are a function of the nature of the substituents.

EXPERIMENTAL

The mass spectra were taken on a Varian CH-6 mass spectrometer with direct sample inlet into the ion source. The ionizing electron energy was 70 eV. The accelerating voltage was 1.75 kV and the emission current was 100 mA.

The methods for preparation of **1-14** were described in our previous work [13-16].

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