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Mass Spectral Fragmentation of Benzofurazan-1-oxide

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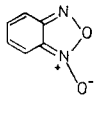
Fragmentations in the mass spectrum of benzofurazan-1-oxide have been studied using linked scan, accelerating voltage scan and mass-analysed ion kinetic energy spectrometric techniques. Major pathways involve NO$^{\cdot}$ + NO$^{\cdot}$ and NO$^{\cdot}$ + CO loss, these double losses occurring in such rapid succession as to appear 'concerted' in some experiments. Minor pathways are loss of CO_2, $C_2N_2O_2$, or $C_2HN_2O_2$ from the molecular ion. The major fragment ion, *m/z* 76, in the conventional mass spectrum is not detected in a mass-analysed ion kinetic energy spectrometric experiment with the molecular ion until collision activation is provided. The conventional electron impact spectrum invariably includes ions from benzofurazan which is produced by thermal deoxygenation in the source.

INTRODUCTION

The mass spectral fragmentation of benzofurazan-1-oxide†(⊥) has received much passing comment in the literature, but has not been studied in detail. All authors are agreed that $[M - N_2O_2]^{+\cdot}$ is a prominent ion,[1-6] and this is also the case with furazan oxides lacking the benzo fusion.[1,7] The molecular ion also loses oxygen, to a degree reported as varying from minor[1] to major[7], and nitric oxide.[5]

Three alternative pathways have been suggested for the loss of N_2O_2 from the molecular ion. Abramovitch *et al*[4] have stated that the molecular ion of **1** (*m/z* 136) loses an oxygen atom and then nitrous oxide to produce $[C_6H_4]^{+\cdot}$ (*m/z* 76). However, Fraser *et al.*[6] saw this ion *m/z* 76 arising by loss of two NO groups, one after the other, from the molecular ion. Finally, Chafin and Erickson[5] drew upon the reported[8] metastable ion for loss of N_2O_2 in a single fragmentation from benzotrifuroxan, **2**, to propose that **1** loses its furazan oxide ring (N_2O_2) directly.



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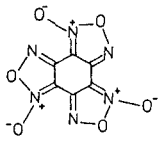

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The first two suggestions were not supported by any experimental data, while the evidence for the third is open to another interpretation. Thus, the observation of a metastable ion for N_2O_2 loss is not inconsistent with the loss of two NO groups in rapid succession,[9,10] and the two NO groups may not have come from the same furazan oxide ring in **2**.

We now report use of metastable peaks, B^2/E and B/E linked scans, accelerating voltage scans (AVS), mass-analysed ion kinetic energy spectrometry (MIKES) and collision activation (CA) to identify in detail the pathways by which the molecular ion of benzofurazan-1-oxide, and its daughters, fragment.

† The IUPAC name is 2,1,3-benzoxadiazole-1-oxide.

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EXPERIMENTAL

Materials

Benzofurazan-1-oxide was prepared by pyrolysis of 2-azidonitrobenzene[11] and was purified by vacuum sublimation (60 °C/0.1 mm). Benzofurazan was prepared by the method of Hollas and Wright[12] and then vacuum sublimed. Both compounds had melting points matching literature values, and no impurities could be detected by thin-layer chromatography (silica gel G, benzene elution).

Recording of mass spectra

Electron impact (EI) spectra were recorded with an AEI MS-30 single-beam instrument whose source was operated at 70 eV and 200 °C. Samples were introduced on a direct insertion probe, initially at room temperature. Perfluorokerosene was used as internal standard, and the DS-55 data handling system derived ion compositions which fitted the measured *m/z* values closer than 4 ppm. The spectra were also recorded photographically to obtain metastable peaks corresponding to ion decompositions in the second field-free region of the spectrometer.

For comparison purposes, a charge exchange (CE) spectrum was recorded on an MS-9 spectrometer, using argon gas (at 1 Torr). The source temperature was 160 °C and the probe temperature 25 °C. This system was used for B/E linked scans.

The B^2/E, MIKE, and MIKE/CA scans were carried out on a ZAB Model 2HF spectrometer with reverse geometry, the ions being generated by EI (70 eV).

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DISCUSSION

Thermal decomposition of benzofurazan-1-oxide

The ion m/z 120 ($[C_6H_4N_2O]^{+\cdot}$) was prominent in the EI spectrum (see Table 1). When an insertion probe with no temperature controller was used, the ion abundance varied greatly (20–85% of base peak) from sample to sample. This behaviour indicated thermal decomposition to benzofurazan, and both the reported major ions (m/z 120, 90, 64 and 63) and metastable ions (m^* 67.5, 57.0, and 44.2)[13–15] were present in our spectrum. Thermal decompositions of related compounds (*N*-oxides of quinolines and isoquinolines) in mass spectrometer sources are well documented.[16]

The extent of thermal deoxygenation on the probe was substantially reduced by using a cooled probe, or by producing the ions via CE with argon (see Table 1). However, the ions corresponding to benzofurazan (see Table 3) were not altogether eliminated. It was therefore necessary to establish which ions actually belonged to the benzofurazan-1-oxide by use of linked scans (B/E and B^2/E), AVS and MIKE scans.

Table 2 lists experimental results which show that the molecular ion $[C_6H_4N_2O_2]^{+\cdot}$ (m/z 136) of benzofurazan-1-oxide does not lose an oxygen atom to produce $[C_6H_4N_2O]^{+\cdot}$ (m/z 120); nor does this latter ion lose N_2O to produce the major ion m/z 76 in the benzofurazan oxide spectrum. The fragmentation route M–O–N_2O suggested by Abramovitch *et al.*[4] is thus disproved.

It is made clear (Tables 3 and 4) that the ion m/z 90, its daughters m/z 64 and 63, the ions m/z 104 and 77, and one of the m/z 51 ions ($[C_3HN]^{+\cdot}$), belong exclusively to the thermal decomposition product, benzofurazan. Thus, the fragmentation of the benzofurazan-1-oxide molecular ion is considerably simplified, yielding (see Table 1) only the ions m/z 106, 92, 78, 76, 75, 74, 53, 52, 51 ($[C_4H_3]^+$ only) and 50.

Table 1. Mass spectra of benzofurazan-1-oxide[a]

m/z	Ion composition	Ion intensity (%) EI[b]	EI[c]	CE (argon)[d]
136	$C_6H_4N_2O_2$	100	100	100
120	$C_6H_4N_2O$	20.1	9.2	1.8
106	C_6H_4NO	1.1	4.5	0.2
104	$C_6H_4N_2$	13.7		
92	$C_5H_4N_2$	0.1		
90	C_6H_4N	21.9	9.8	1.4
78	C_5H_4N	31.8	17.4	5.8
77	C_5H_3N	40.5	8.6	5.4
76	C_6H_4	73.6	67.9	43.0
75	C_6H_3	19.0	15.9	
74	C_6H_2	17.0	21.7	
64	C_4H_2N	19.1	11.3	1.4
63	C_5H_3	15.9	12.8	3.4
62	C_5H_2	5.5	6.9	
61	C_5H_1	4.3	5.3	
60	C_5	1.3	2.4	
53	C_3H_3N	4.6	1.9	
52	C_3H_2N	31.5	23.2	8.6
	C_4H_4	0.1		
51	C_4H_3	65.7	85.9	18.2
	C_3H_1N	18.8		
50	C_4H_2	54.0	76.8	5.4

[a] This table includes ions derived from the thermal decomposition product, benzofurazan. The benzofurazan-1-oxide spectrum has ions at m/z 136, 106, 92, 78, 76, 75, 74, 53, 52, 51 and 50 (see text).
[b] These values (MS–30 instrument) were obtained with a direct insertion probe whose temperature was not controlled, in a source at 200 °C.
[c] These results were obtained with a cooled probe (ZAB spectrometer).
[d] Results from the MS–9 spectrometer.

Table 2. Ion fragmentations in the mass spectrum of benzofurazan-1-oxide

Fragmentation (m/z)	Composition change	Evidence
136 ↠ 120		B/E; MIKES; MIKES/CA
136 → 106	$C_6H_4N_2O_2 - NO^{\cdot}$	MIKES; MIKES/CA; m^* (82.7)
136 → 92	$C_6H_4N_2O_2 - CO$	MIKES (very weak)
136 → 78	$C_6H_4N_2O_2 - NOCO$	MIKES; MIKES/CA; B^2/E
136 → 76	$C_6H_4N_2O_2 - N_2O_2$	MIKES/CA; B^2/E (very weak); AVS
136 → 52	$C_6H_4N_2O_2 - C_2N_2O_2$	MIKES (very weak); MIKES/CA; B^2/E
136 → 51	$C_6H_4N_2O_2 - C_2HN_2O_2$	MIKES/CA (very weak)
106 → 78	$C_6H_4NO - CO$	B^2/E
106 → 76	$C_6H_4NO - NO^{\cdot}$	B^2/E
79 → 78	$C_5H_5N - H^{\cdot}$	B^2/E
78 → 52	$C_5H_4N - C_2H_2$	B^2/E
78 → 51	$C_5H_4N - HCN$	m^* (33.3)
76 → 75	$C_6H_4 - H^{\cdot}$	B/E
76 → 74	$C_6H_4 - H_2$	B/E
76 → 50	$C_6H_4 - C_2H_2$	m^* (32.9); B/E
53 → 52	$C_3H_3N - H^{\cdot}$	B^2/E

Table 3. Mass spectrum (EI) of benzofurazan

m/z	Ion composition	Ion intensity (%)
120	$C_6H_4N_2O$	74.1
104	$C_6H_4N_2$	5.2
90	C_6H_4N	100
77	C_5H_3N	11.5
76	C_5H_2N	2.3
75	C_5H_1N	1.8
64	C_4H_2N	26.6
63	C_5H_3N	28.6
62	C_5H_2	5.5
51	C_3H_1N	15.9
50	C_4H_2	4.9

Table 4. Ion fragmentations in the mass spectrum of benzofurazan

Fragmentation (m/z)	Composition change	Evidence
120 → 90	$C_6H_4N_2O - NO^{\cdot}$	B/E; B^2/E, m^* (67.5)
120 ↠ 76		B/E
104 → 77	$C_6H_4N_2 - HCN$	m^* (57.0)
91 → 90	$C_6H_5N - H^{\cdot}$	B^2/E (very small)
90 → 64	$C_6H_4N - C_2H_2$	B/E
90 → 63	$C_6H_4N - HCN$	B/E; m^* (44.2)
77 → 76	$C_5H_3N - H^{\cdot}$	B^2/E

Our experiments with benzofurazan support the fragmentation pathways published by Arshadi,[13] Razmara and Waight,[14] and Pedersen and Møller.[15] We have detected additional minor ions at m/z 104 and 77, corresponding to losses of oxygen atom and hydrogen cyanide. Presumably oxygen atom loss occurs from a ring-opened nitrile oxide ion.

Fragmentations of the molecular ion of benzofurazan-1-oxide (see Table 2)

Loss of NO· and 2NO·. The loss of one NO· unit to give the ion $[C_6H_4NO]^+$, m/z 106, is attested by both MIKES and a metastable ion, and the linked scan demonstrates that this ion yields m/z 76 ($[C_6H_4]^{+\cdot}$) via a second NO· loss. This second NO· loss must follow rapidly upon the first, because the MIKES/CA, AVS and the B^2/E linked scans see the loss of two NO· units as 'concerted'. Our results thus support the published proposal[6] of successive loss of two NO· units. Given the inherent difficulty of distinguishing between a concerted loss of two fragments and two losses in rapid succession,[10] we cannot rule out the concerted loss of N_2O_2 proposed by Chafin and Erickson.[5] However, if this concerted loss does occur, then successive loss is a competing process (see Table 2).

The second NO· loss creates an odd-electron ion from an even-electron precursor. Although once thought to be 'forbidden' on energetic grounds since uncoupling of an electron pair is involved, these processes are now known to be reasonably common,[17] especially when NO· loss is involved and the ion produced has aromatic character.[18] It is, moreover, typical of these 'forbidden' fragmentations to be enhanced by CA.[17]

It is interesting that the MIKES experiment shows no evidence for unimolecular decomposition of the molecular ion to yield the ion m/z 76 (see Fig. 1(a)). CA by helium (MIKES/CA experiment) does produce this daughter ion (Fig. 1(b)). In a conventional mass spectrum, most of the molecular ions must possess sufficient energy to undergo the double NO· loss, because the m/z 76 ion is the most abundant fragment.

A referee has suggested that some of the m/z 76 ion ($[C_6H_4]^{+\cdot}$) arises by ionization of benzyne, which might be a product of *thermal* decomposition of benzofurazan-1-oxide in the hot (200 °C) source. We have attempted to produce benzyne by passing benzofurazan-1-oxide over a gas–liquid chromatography column (3% OV-17, 3 m) at 200 °C in a nitrogen stream, without success. Analysis of the effluent (based on anthracene internal standard) indicated 85% recovery and 15% deoxygenation to the furazan. No biphenylene (the expected benzyne dimer) or other product was detected.

NO· and CO loss. The evidence presented in Table 2 suggests that the daughter ion $(C_5H_4N)^+$ can arise by both successive fragmentation (m/z 136 − NO· → 106; 106 − CO → 78) and a 'concerted' process (m/z 136 − NOCO → 78). As discussed under 'Loss of NO· and 2NO·' above, the 'concerted' process may well be two fragmentations in rapid succession.

It will be suggested below that the intermediate ion m/z 106 is not structurally identical with the one which can lose NO· to yield m/z 76.

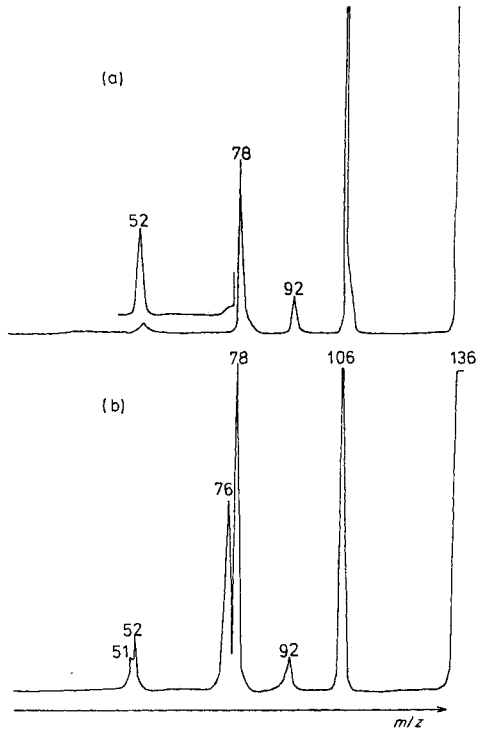


Figure 1. MIKES experiments with the molecular ion, m/z 136, of benzofurazan-1-oxide (a) without collision activation, (b) with helium (2×10^{-7} Torr) in second collision cell.

Minor pathways. The most sensitive of the techniques used, MIKES, detected loss of CO_2, yielding an ion m/z 92 of very low abundance. No daughters of it were found. There is also evidence of $C_2N_2O_2$ loss, and when the molecular ion was collisionally activated, the fragment $C_2HN_2O_2$ was lost.

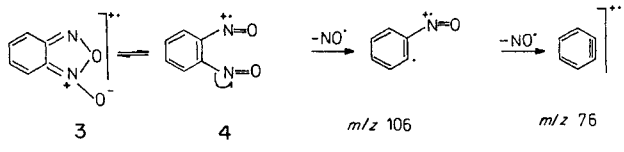
Other fragmentations

The subsequent fragmentations of the ions m/z 78 and 76 are unexceptional, involving losses of such fragments as C_2H_2, HCN and hydrogen (see Table 2).

Possible structures of ions

Fragmentation of the molecular ion would be achieved most readily from a ring-opened structure, presumably the dinitroso form which has frequently been postulated for reactions fo the neutral molecule.[19]

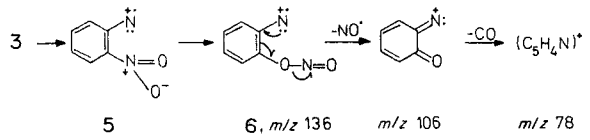
The alternative fragmentation of the molecular ion involves NO· and CO loss, and we suggest Scheme 2 to accommodate the structural reorganization required for CO loss. It is a straightforward adaptation of the thermal ring-opening recently observed by us[20] for a



Scheme 1. Loss of NO· units from benzofurazan-1-oxide molecular ion.

pyridofurazan oxide to produce an *ortho*-nitropyridylnitrene.

These suggestions imply that there are four isomeric structures (**3**, **4**, **5** and **6**) for the molecular ion, and that



Scheme 2. Loss of NO· and CO from benzofurazan-1-oxide molecular ion.

NO· loss produces two different ions $[C_6H_4NO]^+$ at m/z 106. One of these ions fragments via NO· loss to produce m/z 76 (Scheme 1), while the other loses CO to produce the ion at m/z 78.

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