

Dual Mechanisms for the Fragmentation of 1-Benzoylbenzotriazole upon Electron Impact

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The electron impact induced fragmentation of 1-benzoylbenzotriazole has been studied by ^{13}C labelling experiments. It has been found that the loss of CO from the $[\text{M}-\text{N}_2]^{+\cdot}$ ions proceeds by two routes; about 78% of the ions decompose via the molecular ions of the corresponding thermal fragmentation product, 2-phenylbenzoxazole, and 22% via those of the corresponding photochemical fragmentation product, 6-phenanthridone.

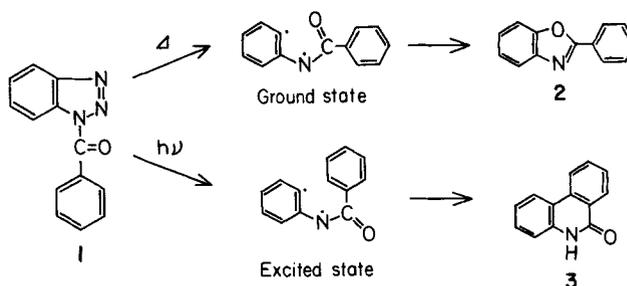
INTRODUCTION

Although most mass spectral reactions are interpreted by consideration of the ground state electronic configurations of the reacting ions, in connection with the charge localization concept Williams and Beynon argued that the ions in two different electronic states can 'communicate' with each other and different reactions may occur from different excited electronic states.¹ This concept is probably applicable not only to molecular ions but also to fragment ions. We now report that the behaviour of the $[\text{M}-\text{N}_2]^{+\cdot}$ ions produced by electron impact ionization of 1-benzoylbenzotriazole seems to provide evidence of participation of an electronically excited state in the fragmentation processes.²

Many investigations concerning fragmentation mechanisms of benzotriazoles upon electron impact have been reported.³ We have also examined the behaviour of $[\text{M}-\text{N}_2]^{+\cdot}$ ions produced by loss of nitrogen from the molecular ions of various benzotriazoles in comparison with that of the biradicals ($\text{M}-\text{N}_2$) produced by photochemical or thermal reactions, and have concluded that the fragmentation processes upon electron impact resemble those of the thermal reactions rather than photochemical ones.⁴

1-Benzoylbenzotriazole (**1**) loses nitrogen upon heating to give a biradical which then cyclizes to yield 2-phenylbenzoxazole (**2**). In this reaction no 6-phenanthridone (**3**), another cyclization product, is detected.⁵ On the other hand, **1** loses nitrogen upon irradiation to give 6-phenanthridone through an alternative biradical and no 2-phenylbenzoxazole is produced.⁶ This sharp contrast between the thermal and photochemical reactions of **1** implies that the electronic configurations of the intermediate biradicals, which may control the subsequent reactions, must be different from each other: one may be a ground state configuration and the other an excited state. A problem then arises as to whether the fragmentation upon electron impact proceeds through a radical ion $[\text{M}-\text{N}_2]^{+\cdot}$ with an electronic configuration similar to either

of these biradicals, although the multiplicities of these intermediates are different from each other (doublet vs. singlet or triplet). This report discusses evidence for the participation in the fragmentation of the process via an excited state, as well as the ground state species.



Scheme 1

EXPERIMENTAL

Mass spectra

The 70 and 20 eV spectra were measured on a Hitachi RMU-6M single focusing mass spectrometer. Samples were introduced via a direct insertion probe. Source and sample temperatures were 220 and 120 °C respectively. The ionizing current was 80 μA and the accelerating voltage 3.2 kV.

Materials

1-Benzoylbenzotriazole (**1**) and its ^{13}C labelled analogue (**1a**) were prepared by acylation of 1H-benzotriazole with benzoyl chloride and with ^{13}C labelled benzoyl chloride respectively. For the preparation of the labelled compound commercially available ^{13}C labelled benzoic acid ($\text{C}_6\text{H}_5^{13}\text{COOH}$, isotopic purity 90.3%, purchased from Prochem., BOC Ltd) was used as the starting material.

2-Phenylbenzoxazole (**2**) and its ^{13}C labelled analogue (**2a**) were prepared from *o*-aminophenol and benzoic acid (labelled and unlabelled) according to the standard method.⁷

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6-Phenanthridone (**3**) was synthesized by photochemical cyclization of *o*-chlorobenzanilide, which was prepared from *o*-chloroaniline and benzoic acid according to Tsujimoto's procedure.^{8a} A mixture of benzoic acid (269 mg) and thionyl chloride (2 cm³) was heated under reflux for 2 h. A solution of *o*-chloroaniline (1 cm³) in CH₂Cl₂ (5 cm³) was added to the cooled solution and the mixture was allowed to stand for 2 h. The solution was washed with 1 M NaOH and then evaporated. The residue (141 mg) was dissolved in acetone (150 cm³) and the resulting solution was irradiated with a low pressure mercury lamp (6 W) for 19 h under nitrogen. The solvent was removed and the residue was chromatographed on silica gel. Elution with ethyl acetate gave a solid. Crystallization from EtOH gave 6-phenanthridone (82 mg, overall yield 19%, m.p. 291–292.5 °C (lit.^{8b} 293 °C)).

The labelled 6-phenanthridone (**3a**) was obtained by a similar method starting from the labelled benzoic acid.

RESULTS AND DISCUSSION

Figure 1 summarizes the 70 eV spectra of **1**, **2** and **3**. The spectrum of **1** indicates that the molecular ion of **1** (*m/z* 223) loses nitrogen (*m/z* 195, *m*^{*} 170.5) followed by expulsion of carbon monoxide (*m/z* 167, *m*^{*} 143.0). The compositions of these ions have been confirmed by accurate mass measurements.^{4a} It is obvious from this series of fragmentations that the structure of the [M–N₂]⁺ ion should be a cyclized one such as **2** or **3**. The mass spectra of **2** and **3** resemble each other; both exhibit loss of CO (*m/z* 167, *m*^{*} 143.0) from the molecular ions (*m/z* 195). From the external standard method based on these mass spectra it is difficult to deduce whether the fragmentation processes of **1** proceed via the molecular ion of **2** or **3**. In order to differentiate those two processes we have synthesized ¹³C labelled analogues of **1**, **2** and **3** (**1a**, **2a** and **3a** respectively as shown below and have

examined their mass spectra. The results are summarized in Tables 1 and 2.

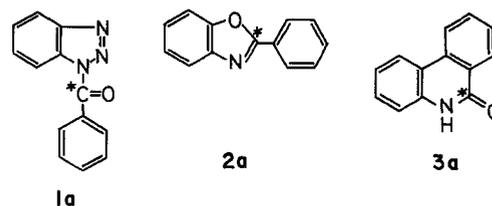
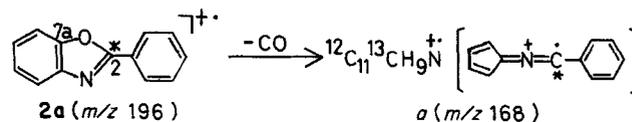


Table 3 summarizes the isotopic purities of ¹³C labelled ions observed in each cluster of ions after correction of the contribution from isotope peaks due to ¹³C natural abundance. The ¹³C isotopic purity (88.0%) of the molecular ions of **2a** is the same as that of the benzoic acid used for the synthesis of **2a** within experimental error. Since the 89.4% isotopic purity of the [M–CO]⁺ ions (*a*, *m/z* 167–168) is the same as that of the molecular ions, the carbon lost as CO should not be C-2 carbon but C-7a bearing oxygen in the benzene ring as shown below.



On the other hand, although the isotopic purity (89.3%) of the molecular ions of **3a** (*m/z* 195–196) is the same as that of **2a**, that of the fragment ions (*b*, *m/z* 167–168) derived from loss of CO is zero. This means that the labelled carbon in **3a** is completely ejected as ¹³CO during the fragmentation process as shown below.

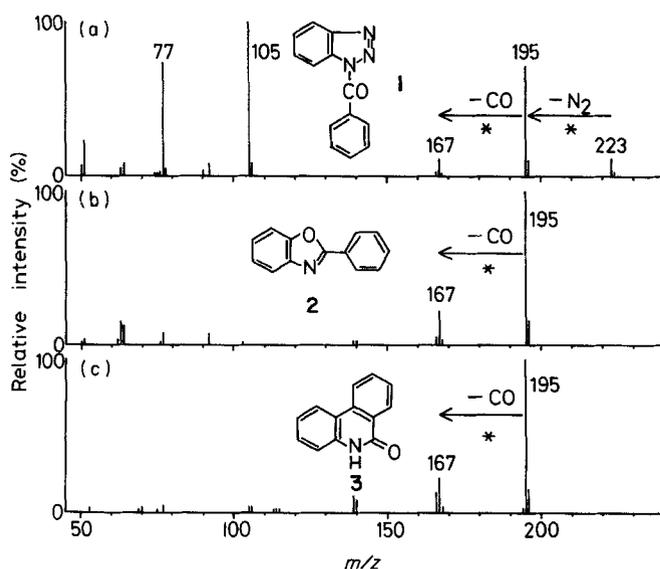
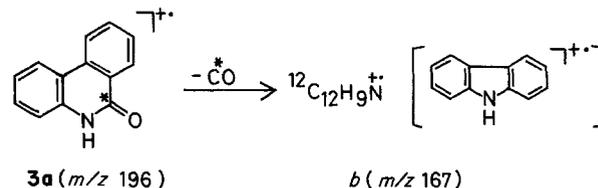


Figure 1. The 70 eV mass spectra of (a) 1-benzoylbenzotriazole (**1**), (b) 2-phenylbenzoxazole (**2**), and (c) 6-phenanthridone (**3**).

Table 1. Relative abundance of major ions in the 70 eV mass spectra of **1**, **2**, **3** and their ¹³C labelled analogues^a

	1	1a	2	2a	3	3a
<i>m/z</i> 225		16.7				
224	17.1	100				
223	100	11.7				
<i>m/z</i> 198		2.2		1.2		2.0
197	2.5	15.0	1.1	14.4	3.2	14.6
196	18.0	100	15.3	100	17.3	100
195	100	12.1	100	13.3	100	14.1
194	1.1		0.9		2.5	
<i>m/z</i> 169		14.0		12.4		
168	15.0	100	13.5	100	17.4	15.6
167	100	63.4	100	31.5	100	100
166	28.3	29.0	20.7	4.8	56.3	57.8
165	4.7	3.2			5.4	5.9

^a The figures represent the relative intensities of peaks compared with the most abundant peak in each cluster of ions.

Table 2. Relative abundance of major ions in the 20 eV mass spectra of 1, 2, 3 and their ¹³C labelled analogues^a

<i>m/z</i>	1	1a	2	2a	3	3a
<i>m/z</i> 225		16.2				
224	16.0	100				
223	100	13.2				
<i>m/z</i> 198		2.7		1.2		2.2
197	1.3	15.7	1.5	13.7	1.4	14.6
196	15.7	100	15.7	100	15.2	100
195	100	13.3	100	12.3	100	13.1
194	0.9		0.5		1.7	
<i>m/z</i> 169		12.7		13.2		
168	14.8	100	14.2	100	16.6	14.0
167	100	63.7	100	28.6	100	100
166	25.1	25.4	17.0	4.4	42.4	42.1
165	3.5				3.3	

^a See footnote to Table 1.

In the case of **1a** the isotopic purities of the molecular ions (*m/z* 223–224) and the [M–N₂]⁺ ions (*m/z* 195–196) are 89.3 and 89.8% respectively, indicate that no expulsion of the labelled carbon occurs during this fragmentation. However, the isotopic purity of the ions [M–N₂–CO]⁺ (*m/z* 167–168) derived from the subsequent loss of CO is only 69.6%, which indicates that a part of the ¹³C labelled carbon is ejected in the process. These results seem to indicate that the molecular ions of **1a** decompose competitively via two processes (paths A and B) as shown in Scheme 2. On the basis of the isotopic purities of those fragment ions the contributions of paths A and B are estimated to be 78% and 22% respectively. (The relative ratio of the contributions from the two paths

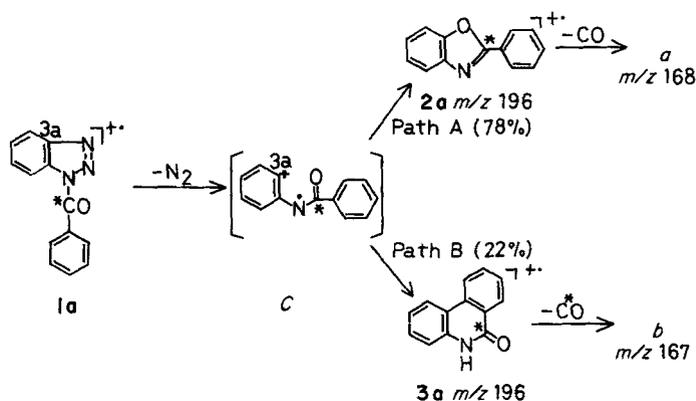
Table 3. The isotopic purities of each cluster of ions in the mass spectra of ¹³C labelled compounds, 1a, 2a and 3a

<i>m/z</i>	70 eV			20 eV		
	1a	2a	3a	1a	2a	3a
223–224	89.3			88.1		
195–196	89.8	88.0	89.3	88.5	87.8	88.7
167–168	69.4	89.4	0	68.3	88.9	0

was calculated from A : B = 69.6 : (89.8 – 69.6) = 78 : 22).

The 20 eV mass spectra of the labelled compounds **1a**, **2a** and **3a** are similar to those of the 70 eV spectra (see Table 3). Similar results are obtained in the case of 20 eV spectra, for which the contributions of paths A and B are 77% and 23% respectively.

At this stage it may be of use to correlate the fragmentations with molecular orbital considerations. In general, pericyclic reactions are controlled by the symmetry and the degree of interactions of the frontier molecular orbitals of the reacting species, i.e. HOMO for ground state thermal reactions and LUMO for excited state photochemical reactions.⁹ According to the extended Hückel calculations on the radical cation *c* the atomic bond population of the C–3a–O bond is bonding in the ground state, while it is antibonding in the excited state.^{4a} Referring to the general rule and the results of calculations we suggest that since paths A and B correspond to the thermal and photochemical cyclization of the intermediate diradicals shown in scheme 1, the intermediate radical cation *c* produced upon electron impact possibly consists of two species; one (major) has a ground state configuration and the other (minor) an excited state.

**Scheme 2****Acknowledgements**

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