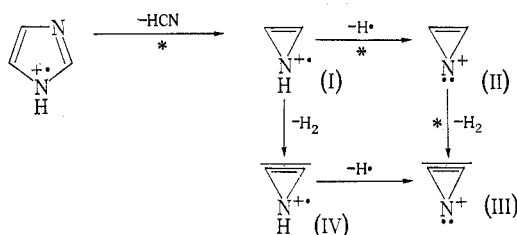


THE MASS SPECTRA OF IMIDAZOLE AND 1-METHYLIMIDAZOLE*

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The mass spectra of a series of substituted imidazoles have recently been reported,¹ and the electron-impact induced fragmentation of imidazole itself stated to produce ultimately the azirine§ cation (II). Our investigation of a similar series of imidazoles supports the fragmentation mechanisms proposed by Bowie *et al.*, but shows that the azirine cation is only the ultimate fragmentation product of imidazole if the ionizing electrons have energies in the range of approx. 17–26 eV. At higher energies the ion (II) further loses a hydrogen molecule giving (III) (C₂N)⁺. In addition, the ion (IV) (C₂HN⁺) is produced, probably by the loss of a hydrogen molecule from (I) (C₂H₃N⁺), and this may lose a hydrogen radical leading once more to (III). A metastable peak (denoted as *) at 37.05 m.u. indicates that at least one of the steps (I) → (IV) and (IV) → (III) is taking place. This fragmentation scheme is depicted in Scheme 1.



Scheme 1

Since both the loss of HCN from the imidazole molecular ion and the further loss of a hydrogen radical do not occur by specific processes, it seemed desirable to investigate the loss of a hydrogen molecule from (I). The peak of m/e 40 in the mass spectrum of 1-*d*-imidazole consisted of two ions in the ratio of 50 : 1. The most intense of these, C₂H₂N⁺, can have arisen either by the loss of HCN followed by D[•] from imidazole-*d*₁, or by the successive losses of DCN and H[•]. However, the weaker of these, C₂DN⁺, can only have been formed from 1-*d*-imidazole by loss of HCN, followed by H₂. The intensities of the ions C₂HN⁺ and C₂DN⁺ were in the ratio of 16 : 1. This suggests that the loss of a hydrogen molecule from (I) is largely a specific process, involving the 1-hydrogen in imidazole. In order to rule out the possibility of this result being biased by an isotope effect, the spectrum of 2,4,5-trideuterioimidazole

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§ Bowie *et al.*¹ referred to (II) as the aziridine cation.

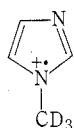
¹ Bowie, J. H., Cooks, R. G., Lawesson, S.-O., and Schroll, G., *Aust. J. Chem.*, 1967, **20**, 1613.

was examined. In this case the order of the relative intensities ($C_2NH^{+\cdot}$) : ($C_2ND^{+\cdot}$) was reversed to 1 : 10. The structures shown in Scheme 1 for (I), (II), (III), and (IV) could equally well be written in open-chain forms and in fact the open form of (I), $\ddot{H}\ddot{C}^+-NH=\dot{C}H$, might explain the specific loss of hydrogen to give (IV), $\ddot{C}=\ddot{N}^+=\dot{C}H \leftrightarrow \dot{C}=\ddot{N}^+-\ddot{C}H$. We have noted the formation of the ions (III) and (IV) in the spectra of a large series of imidazoles and in the spectrum of pyrazine.

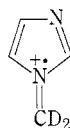
TABLE 1
MASS SPECTRUM OF METHYL DEUTERATED 1-METHYLIMIDAZOLE

m/e	Intensity	Composition	m/e	Intensity	Composition
85	100%	$C_4H_3D_3N_2$	54	0.2%	C_2DN_2
84	7	$C_4H_2D_3N_2$	53	0.8	C_3H_3N
83	14	$C_4H_3D_2N_2$	53	1	C_3HDN
58	7	$C_3H_3D_3N$	52	1.2	C_3H_2N
57	4.5	C_3HD_3N	51	0.8	C_3HN
56	12	$C_3H_2D_2N$	50	0.2	C_3N
55	2.5	C_3H_3DN	45	21	C_2HD_3N
54	1	C_3H_2DN			

We have also studied the fragmentation of the 1-methylimidazole molecular ion. The ion $C_2D_3HN^+$ present in the spectrum of (V) (see Table 1) and the absence of any significant ions at m/e 44 or m/e 43 shows clearly that none of the deuterium atoms of the methyl group are involved in the loss of $\cdot CH_2CN$. Since C2 and C5 have been shown¹ to be involved in this process, it seems likely that C3 may also be involved. We were also able to show that (V) lost either a deuterium radical to give M—D (VI) or a hydrogen radical. The intensities of the M—D and M—H peaks



(V)



(VI)

were in the ratio of 68 : 32. Since it has been shown¹ that 5-*d*-1-methylimidazole undergoes a relative 24% loss of deuterium and 76% loss of hydrogen, it is likely that only the hydrogens on C5 and the 1-methyl group are involved.

The peak at m/e 55 in the spectrum of (V) consisted only of $C_3H_3DN^+$, which was shown by the presence of the appropriate metastable peaks to have arisen from the molecular ion by loss of deuterium followed by the loss of DCN. Though (V) loses HCN rather than DCN, the M—D ion (VI) produced from (V) does lose a DCN fragment and could also have lost HCN to form the ion of m/e 56 ($C_3H_2D_2N^+$). However, at least some of this latter ion has been shown, by the presence of a metastable peak, to arise by the loss of a deuterium radical from $C_3H_2D_3N^+$.

Experimental

The mass spectra were determined with an A.E.I. MS9 mass spectrometer operating at 70 eV. Spectra were measured by the direct inlet procedure as the use of the heated inlet system caused some loss of deuterium. Exact mass measurements were made on all peaks mentioned, with resolving power sufficient to distinguish D from H₂ in all fragment ions.

1-Methyl-d₃-imidazole

Imidazole (0.5 g) in sodium ethoxide (3.5 ml ethanol; 0.18 g sodium) was treated with methyl-d₃ iodide (1.15 g) during 1 hr at 0°. The solvent was removed at 15° and after 12 hr, the residue was extracted with chloroform, and the extracts dried with anhydrous sodium sulphate and filtered. The concentrated chloroform extract was passed through an alumina column to remove any unmethylated product, the eluate was concentrated to dryness, and the residue sublimed under vacuum to yield 1-methyl-d₃-imidazole (0.4 g; b.p. 70–80° 1.5 mm).

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