Random and Non-random Decomposition Modes induced by Electron Impact in Benzonitrile

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BENZONITRILE fragments specifically from its molecular ion by loss of HCN, with an intense "metastable peak" at *m/e* 56·1 corresponding to this process. With an electron beam energy in the range 25—70 ev, [2,4,6-$^2H_3$]benzonitrile (I, 95% trideuterated)[1] statistically loses HCN and DCN to give peaks at *m/e* 79 and 78 in the approximate intensity ratio 2:3† and shows "metastable peaks" at *m/e* 58·9 and 57·4 in the ratio 2:3 corresponding to these processes (Figure 1).

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† A small peak at $M-H_2CN$ in the spectrum of benzonitrile at 70 ev precludes calculation of the exact ratio.

However, as the electron beam energy is decreased from 20 to 14 ev, the peak at *m/e* 79 undergoes a steady decrease in intensity relative to *m/e* 78, even though the ratio of the appropriate "metastable peaks" remains the same within the limits of experimental error (see, for example, Figure 2). At the lower limit of this range (a nominal 14 ev), the 2 : 3 ratio of the metastables is maintained but the ratio of the ($M-$HCN) : ($M-$DCN) peaks is 1 : 70 (after correcting for ^{13}C isotopes). At a nominal 13 ev, after correcting for the ^{13}C isotope contribution, no significant loss of HCN is observed and the ratio of "metastable peaks" is also markedly reduced (~1 : 3, see Figure 3).

FIGURE 1 (70 eV)

FIGURE 2 (16 eV)

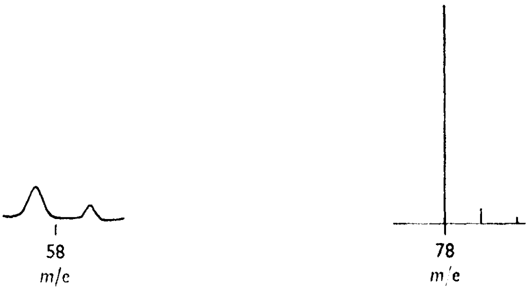
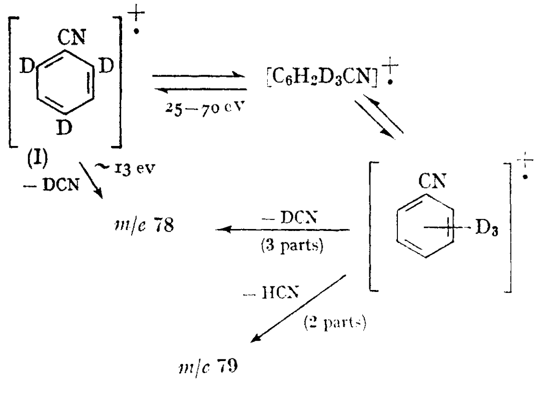


FIGURE 3 (13 eV)

Thus in the range 25—70 ev, the hydrogens and deuteriums are randomised in that form of the molecular ion which undergoes the reaction under consideration, but at 14 ev, product ions are formed in the source specifically by loss of DCN. The latter reaction is most reasonably interpreted in terms of 1,2-elimination in the [2,4,6-$^{2}H_{3}$]-benzonitrile molecular ion to give, at least initially, ionised benzyne. The observation that at 70 ev the "metastable peaks" are the same shape and abundance (on the basis of randomisation), and that this shape and magnitude of relative abundance is still observed for the specific loss of DCN at low ev, strongly suggests that random loss of HCN and DCN in the 25—70 ev range occurs from the same species, and that this species is also the one to undergo specific loss of DCN.[2]

Apparently, the appearance potential of the fragment ion due to loss of HCN is greater than that of the "metastable peak" formed by loss of HCN.[3] The rate of the randomisation reaction is so reduced at low energies that an insufficient concentration of $M-$HCN ions is formed within the source to allow detection at the collector, but this rate is still great enough to permit loss of HCN within the longer time spent by ions travelling from source to collector.‡

The above results appear to constitute the first example of removal of an isotope scrambling reaction at low voltage. The data are interpreted in terms of a reversible isomerisation in the labelled benzonitrile molecular ion (I) at 70 ev. The isomeric species must be one such that reversible equilibration will permit randomisation of hydrogens and deuteriums, and by analogy to photochemistry, the intervention of prismanes and other benzene isomers[4] can be entertained. It is equally plausible that the high-energy reversible isomerisation may precede ionisation.[5]



The behaviour of benzonitrile upon electron impact is therefore intermediate between that of

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‡ The insensitivity of the ratio of the "metastable peak" abundances to electron beam energy in the range 14—25 ev is nevertheless unusual, but possible for some combinations of relative rates of randomisation and fragmentation.

benzene[6] (in which hydrogens are randomised in the molecular ion even at 15 ev), and of substituted benzophenones and acetophenones[7] and many disubstituted aromatics[8] (in which the relative orientation of the substituent groupings is retained even at 70 ev in many of the important fragmentation reactions).

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[1] Prepared by a Sandmeyer reaction on [2,4,6-$^2H_3$]aniline (see J. Ronayne, D. H. Williams, and J. H. Bowie, *J. Amer. Chem. Soc.*, 1966, **88**, 4980).
[2] T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5021; J. H. Beynon and A. E. Fontaine, *Z. Naturforsch.*, 1967, **22a**, 334.
[3] The appearance potentials of "metastable peaks" and daughter ions are usually very similar; see, for example, H. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions", ed. F. W. McLafferty, Academic Press, New York, 1963, pp. 43—48.
[4] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.
[5] S. Meyerson, H. M. Grubb, and R. W. Vander Haar, *J. Chem. Phys.*, 1963, **39**, 1445.
[6] K. R. Jennings, *Z. Naturforsch.*, 1967, **22a**, 454.
[7] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 529.
[8] See, for example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964, ch. 9.