Appearance Energy of Benzonitrile Fragment Cations Under Low Energy Electron Impact

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Synopsis Dissociative ionisation of benzonitrile (C_6H_5CN) is studied under low-energy electron impact to map the energy dependence of its various dissociation channels. Instrument-specific appearance energies ranging from 14.8 to 23.7 eV were estimated for all prominent primary and secondary channels. An attempt is made to correlate the variation in appearance energy with isomerisation, the sequence of dehydrogenation, ring opening and the formation of cyanopolyynes cations.

Cold interstellar clouds such as TMC-1 are rich in nitrogen-bearing molecules, the most abundant of which are the cyanopolyynes ($HC_{2n+1}N$). The same cloud also hosts benzonitrile (C_6H_5CN), the first aromatic ring detected by radio astronomy [1]. Threshold coincidence studies indicate that the benzonitrile radical cation dissociates through many parallel channels, yielding fragments such as HC_3N [2]. However, the complete fragmentation network, including the order in which the channels open and how they are interconnected, has not yet been fully established. In this work, we investigate the dissociative ionisation of benzonitrile by electron impact, using appearance energy measurements to identify the fragmentation channels and determine their onsets.

Electron impact ionisation often leaves the target molecular species in an ionized as well as internally excited state. This internal energy then governs the statistical disassociation process in the parent cation. When this transfer exceeds the ionisation energy, a molecular ion is formed, and any energy beyond that is retained as internal excitation that can drive fragmentation. Tuning the electron energy from 11 to 30 eV controls which fragmentation channels. The yield of each ion as a function of electron energy was recorded and used to determine its appearance energy.

The appearance energy (AE) of a fragment ion is the lowest energy at which it is observed in an experiment, whereas the threshold energy is the true, instrument-independent minimum energy required to form that fragment. Therefore, over and above the threshold energy, additional instrument-specific internal energy, called the kinetic shift, is required to make the decay product ions observable in a given setup. Thus, it can safely be assumed that AE $\approx$ TE + kinetic shift. This distinction is important for benzonitrile because its channels differ in mechanism.

AEs were obtained for fragment ions from *m/z* 26 to 102. The parent ion (*m/z* 103) appears at 11 eV. The lowest AEs correspond to *m/z* 76 (14.8 eV) and *m/z* 77 (15.3 eV). Several fragments follow an unexpected order in which the more dehydrogenated ion appears at lower energy than the less dehydrogenated one: *m/z* 101 (17.7 eV) before *m/z* 102 (18.9 eV), *m/z* 63 (16.6 eV) before *m/z* 64 (17.8 eV) and *m/z* 65 (18.1 eV). In addition, the *m/z* 75 curve shows two kinks, indicating two formation routes: directly from the parent ion, and by H loss from *m/z* 76 also stating one of the structure is cyclic and the other is linear.

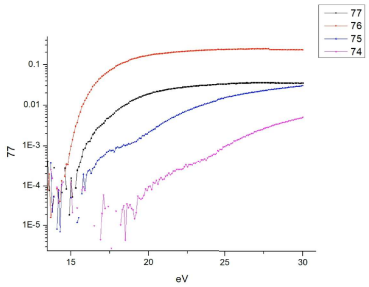


Figure 1. The m/z 75 ion (HC_5N^+, a cyanopolyyne cation) shows a double kink, indicating two formation pathways.

References

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