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Energy-Dependent Electrospray Ionization Mass Spectrometry

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Background

Electrospray ionization mass spectrometry (ESI-MS) has revolutionized the study of a vast array of compounds previously inaccessible to gas-phase analysis. Electrospray is a soft ionization technique that causes little or no fragmentation of a sample. This is ideal for simple mass analysis and isotope matching of low M_w compounds, but also allows the accurate mass determination of high mass molecules (e.g. proteins) from m/z data of each of the charge states of the molecular ion. Minimizing fragmentation also simplifies the interpretation of mixtures, which may otherwise be impossible with the presence of fragment ions.

Collision-induced dissociation (CID) in an ESI source (MS) or collision cell (MS/MS) can be used to impart energy to the ions, leading to the formation of fragment ions. Voltages in the source or collision cell can be ramped to control the level of fragmentation, providing useful structural information. However, this produces a vast quantity of data, which can prove unwieldy to handle, interpret, and present. Energy-dependent electrospray ionization mass spectrometry (EDESI-MS) provides a simple and effective solution by presenting the information acquired by CID at all voltages in a compact, 2D format.[1]

Method and Applications

Full experimental details for collecting EDESI spectra can be found in ref. [1]. In simple terms, a spectrum is recorded at each setting of collision energy and the spectra are combined to generate an ion intensity map. The EDESI-MS/MS spectrum showing the fragmentation pattern of glutamic acid is presented in Figure 1. The upper graph is a summation of all spectra, and on the right is a breakdown graph of the major ions.[2] The presentation of both the 1D graphs and the 2D map proves useful in the assignment of fragment ions, allowing their relative stabilities to be easily extracted.

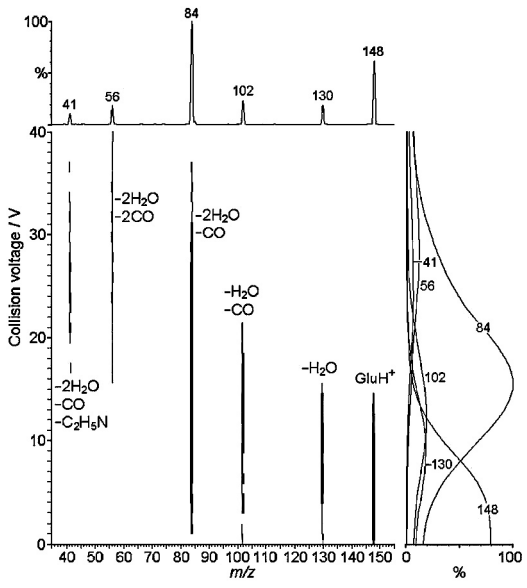

Fig. 1. EDESI-MS/MS spectrum of protonated glutamic acid in MeOH/H_2O/HCOOH.

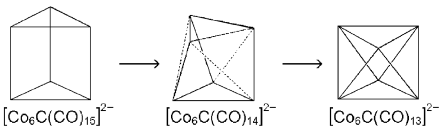

Fig. 2. Diagram showing the metal core rearrangement of $[Co_6C(CO)_{15}]^{2-}$.

EDESI-MS experiments have also been carried out on a number of charged or chemically derivatized compounds, such as transition metal carbonyl clusters,[3] organometallic complexes,[4] and simple organic molecules,[1] although the technique is fully applicable to any sample which undergoes CID. EDESI-MS is also effective for the rapid screening of complex product mixtures.[5] Significant variations in ion intensity on EDESI spectra show how certain molecules rearrange.[6] For example, in the EDESI spectrum of $[Co_6C(CO)_{15}]^{2-}$, the peak corresponding to $[Co_6C(CO)_{14}]^{2-}$ is very weak, attributed to the instability of this species. Upon loss of two CO ligands, the metal core of $[Co_6C(CO)_{15}]^{2-}$ rearranges from a trigonal prism to an octahedron (Fig. 2), as demonstrated by X-ray diffraction studies, while $[Co_6C(CO)_{14}]^{2-}$ has never been isolated. The additional structural details that EDESI-MS can provide may prove particularly useful, especially where full structural characterization from single crystal X-ray diffraction is impossible.

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