

UNIQUE ANIONIC SPECIES REVEALED IN THE MASS SPECTROMETRY OF FULLERENE SYSTEMS

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Electrospray mass spectrometry (EMS) in the negative-ion mode has proven most useful in the identification of the anionic species derived directly from the fullerenes as well as via adduct systems formed by nucleophilic attack.¹⁻⁵ In addition to C₆₀ and C₇₀, the higher fullerenes studied include C₇₆, C₇₈, C₈₂, C₈₄, C₈₆, C₈₈, C₉₀, C₉₂, C₉₄, C₉₆ and C₉₈.

With benzene or 1,2-dichlorobenzene as solvent the fullerenes show varying capacity for electron attachment in the electrospray process, with most forming a monoanion, but only two, C₈₄ and C₉₀, forming appreciable quantities of a dianion. The C₉₀²⁻ dianion is shown as the most stable under mass spectrometric conditions.

Nucleophilic attack by CN⁻ is facilitated by suitable solvent mixtures such as fullerene in 1,2-dichlorobenzene and NaCN in dimethylformamide. All fullerenes studied form the mono- and di-adduct species C_n(CN)⁻ and C_n(CN)₂²⁻, while only the smaller fullerenes form C_n(CN)_m⁻ for m = 3, 5 and C_n(CN)_m²⁻ for m = 4, 6. These are all even-electron species. The most prominent odd-electron species formed are C₆₀(CN)₂⁻ and C₇₀(CN)₂⁻ where the former is revealed by the collision-induced dissociation of its dimer [C₆₀(CN)₂]₂²⁻, which is an anion-anion complex unusually stable in the high-vacuum environment.

MOPAC calculations using the AM1 approximation have been used to explore the structures and energetics of these anionic systems.

References

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