

AN ELECTROSPRAY FOURIER TRANSFORM ICR MASS SPECTROMETRY STUDY OF FULLERENE DERIVATIVES

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Fullerenes are non-polar molecules which are generally unsuitable for electrospray ionization mass spectrometry (ESI-MS) studies. However, fullerenes can react with many electron rich compounds to form derivatives, and some of these fullerene derivatives are ionic and polar molecules. These new fullerene derivatives are then soluble in polar solvents such as methanol or acetonitrile, therefore they become accessible to ESI-MS. We report here our electrospray Fourier transform ICR mass spectrometry studies of fullerene derivatives such as fluorinated fullerene $C_{60}F_x$ and dicarboxylic methanofullerene $[C_{60}C(COOH)_2]$.

Our experiments were carried out on a 7 Tesla Bruker BioAPEX 70e Fourier transform ICR mass spectrometer incorporating an external electrospray ionization source. Fullerene derivative samples were dissolved in the methanol at a concentration of 1 $\mu\text{g/ml}$, and both positive ions and negative ions were investigated.

The positive-ion spectrum of fluorinated C_{60} has a broad distribution of fluorinated carbon cations $C_nF_x^+$ where n ranges from 10 to 70 and x ranges from 20 to 50, indicating that fullerene cage destruction has occurred during the synthesis. The negative-ion spectrum shows many smaller fluorinated carbon ions with n ranging from 10 to 30 and x ranging from 20 to 40.

There were no positive ions observed for $C_{60}C(COOH)_2$. The negative-ion spectrum shows the first ion at a capillary exit voltage of -90 V. This ion has a mass of m/z 777, is assigned to a dissociation product ion which has lost one carboxylic acid group from the molecular ion. Higher capillary exit voltages resulted in further dissociation and gas phase ion molecule reactions (see Figure). An ion at m/z 778 which corresponds to $[C_{60}CHCOOH]^-$ forms dimer and trimer at a capillary exit voltages which range from -100 V to -220 V. Polymerization occurs probably via hydrogen bonding between neighbouring carboxyl groups as dimerization is commonly observed for natural carboxylic acids. Sustained off resonance irradiation collision induced dissociation experiment was applied to $[C_{60}CH]^-$. The CH group was lost and gave the major product ion C_{60}^- .

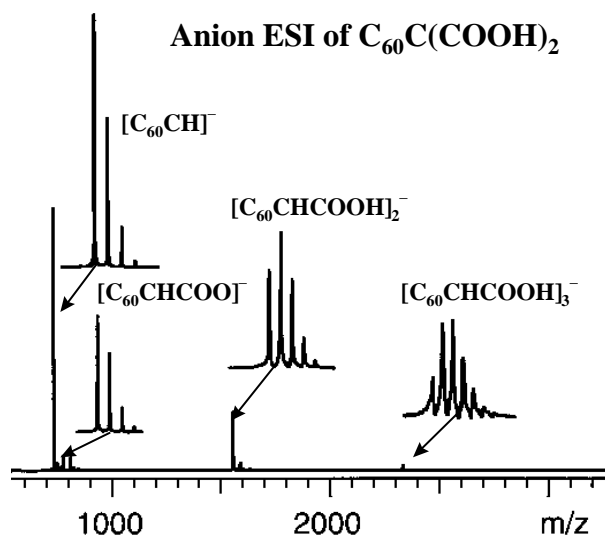


Figure. Negative-ion ESI-FTICR mass spectrum of $C_{60}C(COOH)_2$.