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Direct Analysis of C_{60} and Related Compounds with Electrospray Mass Spectrometry

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Without performing any charge transfer chemical reaction, C_{60} and its derivatives could be analyzed directly by electrospray mass spectrometry. Oxidation or reduction at the metal/solution interface of the probe tip was probably responsible for the formation of these radical cations and anions. This technique appeared to be superior to desorption chemical ionization and fast-atom bombardment ionization in the analysis of C_{60} derivatives because the mass spectra were characterized by molecular ions with little or no fragmentation.

Since its discovery in 1985,[1] C_{60} has been one of the most intensively studied molecules in organic and organometallic chemistry; many C_{60} derived molecules, including those with great potential in material science and medicine, have been synthesized. Mass spectrometry has played a key role not only in the discovery but also in the characterization of C_{60}.[2] A variety of ionization techniques such as electron impact (EI), chemical ionization, desorption chemical ionization (DCI), fast-atom bombardment (FAB), and laser desorption have all been used to characterize C_{60} and its derivatives.[3–9] The analysis of C_{60} derivatives appears to be much more difficult than analysis of C_{60} itself; many C_{60} related compounds degrade easily under most ionization conditions. Therefore, the observation of ions with *m/z* values different from those of the expected analytes could be the result of either incomplete purification or degradation under ionization. An ideal ionization technique would be one that produced only the molecular and/or pseudomolecular ions, with little or no fragmentation. The structure of the sample can then be further investigated by collision-induced dissociation of the molecular ions.

Electrospray ionization (ESI) has been one of the major foci of mass spectrometry in the past few years. This technique is known for giving 'soft' ionization and for its ability to analyze biopolymers. Unfortunately, not all types of compounds can be analyzed by ESI. In ESI, electrical energy is used to assist the transfer of ions initially present in solution into the gas phase at atmospheric pressure for mass spectrometric analysis. Therefore, compounds that are ionic or that can be ionized through acid–base reactions in solution are most suitable for ESI analysis. To expand the utility of ESI to so called 'ESI-inactive' compounds, chemical derivatization has received considerable attention as a useful approach for converting ESI-inactive compounds to ESI-active analytes.[10, 11]

Fullerenes are neutral and non-polar molecules and therefore are considered not amenable to ESI. Several approaches, including tagging C_{60} with crown ether,[12, 13] amination,[14] and oxidation–reduction in solution with chemical reagents,[15–17] have all been used for making these compounds suitable for analysis by ESI. In this paper, results are presented to show that C_{60} and related derivatives can be analyzed directly by ESI-MS, without any requirement for pre-ionization in solution.

EXPERIMENTAL

C_{60} (>99.9%) was purchased from Materials & Electrochemical Research Corporation (Tucson, AZ, USA). Aziridine and cyclopentadiene adducts of fullerene were synthesized as described respectively by Nogami *et al.*[18] and Howard *et al.*[19] All electrospray mass spectra were obtained using a Fisons (Manchester, UK) Platform quadrupole mass spectrometer. Analyte solutions (approximately 10^{-3} M) were infused directly into the ESI chamber by a syringe pump at a flow rate of 5–15 μL/min through a 0.01 in i.d. PEEK (polyether ether ketone) tubing that connected via a union to a 35 cm stainless-steel capillary tubing of 130 μm i.d. (220 μm o.d.). This tubing functioned as the spray needle and the voltages applied to this capillary tubing were +(2.5–4.5) and −(2.5–4.5) kV for positive ions and negative ions respectively. The 220 μm o.d. stainless-steel tubing passed through a 350-μm i.d. (635-μm o.d.) stainless-steel tubing and ESI nebulizing gas (nitrogen) was supplied through the connection tee and travelled between these two stainless-steel tubings. Nitrogen drying gas at 80 °C, at a flow rate of 3 L/min, assisted the solvent vaporization. Electrosprayed charged liquid droplets in the atmospheric-pressure chamber drift toward the skimmer (at ground potential) under the influence of the electric field. The ions emitted from the charged droplets were sampled into the vacuum system and analyzed by the quadrupole mass spectrometer.

RESULTS AND DISCUSSION

It is generally believed that generating radical cations or anions of neutral analytes, via charge transfer chemical reaction in solution, is a necessary step for their detection in ESI-MS. There have been many reports on the analysis of C_{60} by ESI-MS and, because C_{60} was considered to be an ESI-'inactive' compound, most reports described the formation of radical cations or anions via chemical reactions.[15–17] However, when C_{60} was analyzed directly by ESI-MS in the present work, it was somewhat surprising to see that radical cations as well as anions of C_{60} were observed (Fig. 1). These experiments suggested that C_{60} and related compounds could be analyzed directly by positive- and negative-ion ESI, without any preformed ion requirement.

More than half-a-dozen C_{60} derivatives have been analyzed directly by positive and negative ESI, and typical ESI spectra of C_{60} derivatives are shown in Fig.

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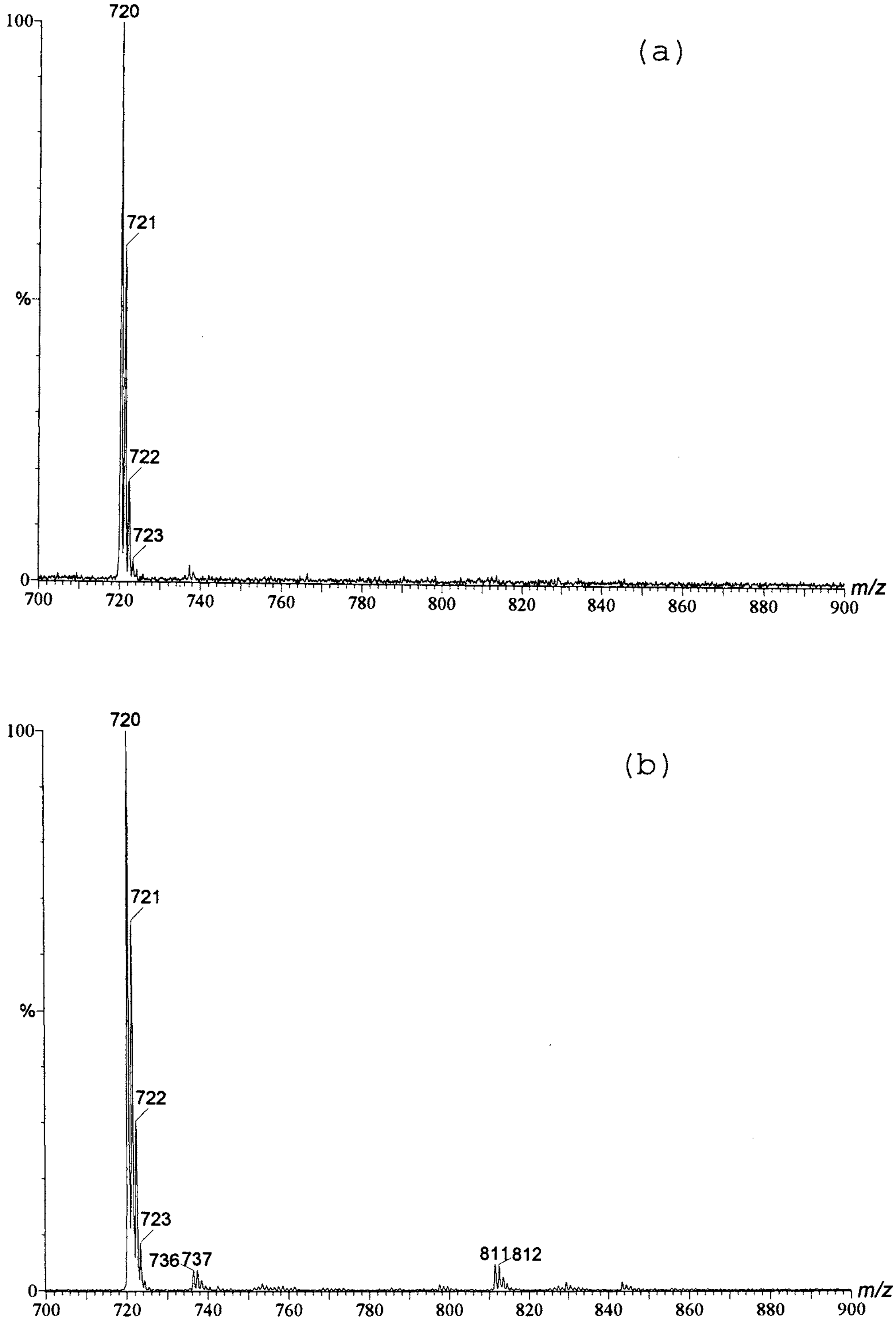

Figure 1. (a) Positive- and (b) negative-ion ESI mass spectra of C_{60} in toluene. The ions at *m/z* 736 and *m/z* 811 in (b) correspond to $C_{60}O^-$ and $C_{60}(PhCH_2)^-$, respectively.

2. Both positive- and negative-ion mass spectra were characterized by molecular ions with little or no fragmentation. Prior to ESI analysis, our analysis of many C_{60} derivatives suggested that desorption chemical ionization (DCI) in the negative-ion mode (electron-capture negative chemical ionization) was often better than other conventional techniques in producing molecular ions.[20] The observation of strong molecular ion signals in ESI spectra indicated that ESI might be superior to negative-ion DCI in the analysis of C_{60} related compounds. Among the C_{60} compounds studied, the merits of ESI in comparison with negative DCI were best demonstrated with the analysis of $C_{60}(C_5H_6)_n$. Under negative DCI, the only ion recorded in the spectra corresponded to the starting material (C_{60}), and no ions related to molecular weights of complete molecules were detected. Because heat was used to evaporate the sample in DCI, and the $C_{60}(C_5H_6)_n$ species were the products of a Diels–Alder reaction, the observation of only $C_{60}^{+\bullet}$ ions was more likely the result of a thermally induced retro Diels–Alder reaction. Much better quality spectra, however, were obtained with ESI as shown in Fig. 3. The intense peaks at *m/z* 786, 852 and 918 correspond

to the molecular ions of $C_{60}(C_5H_6)_n$, with values of n of 1, 2 and 3.

Electrochemical reaction has been proposed as the mechanism for the formation by ESI of radical cations from alkyl-substituted metalloporphyrins, polycyclic aromatic hydrocarbons, and other compound types.[21,22] Since pretreatment with reductant (or oxidant),[16,17] or mixing with reductant (or oxidant) before spraying,[15] was not used in the present approach, electrochemical reaction (reduction or oxidation) could be the major, if not the only, mechanism responsible for the formation of radical ions before spraying. The intensity of the C_{60} signal did not change significantly with the use of different solvents; thus, generating solvent ions which then exchange charge with C_{60} was believed not to be a major mechanism for the formation of these radical ions. The nature of the solvents, however, did affect the quality of the spectra. For example, the spectra obtained using methanol + toluene as the solvent were more complicated than those using toluene as the

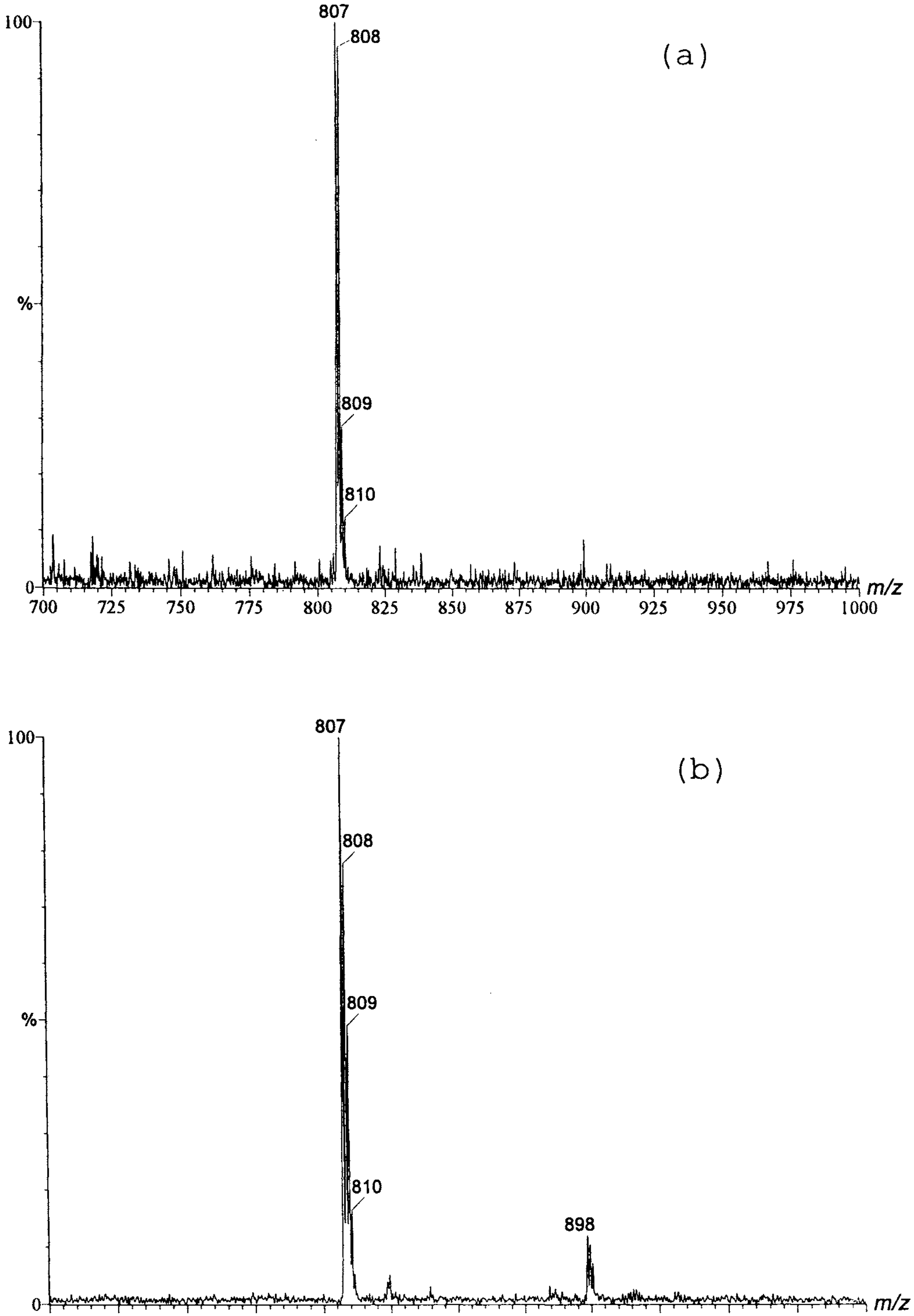

Figure 2. (a) Positive- and (b) negative-ion ESI mass spectra obtained from a fullerene aziridine ($C_{60}NCO_2C_2H_5$) solution (toluene was used as the solvent). The ion at *m/z* 807 corresponds to the molecular ion. The ion at *m/z* 898 in (b) corresponds to the pseudomolecular anion $C_{60}NCO_2C_2H_5(CH_2Ph)^-$.

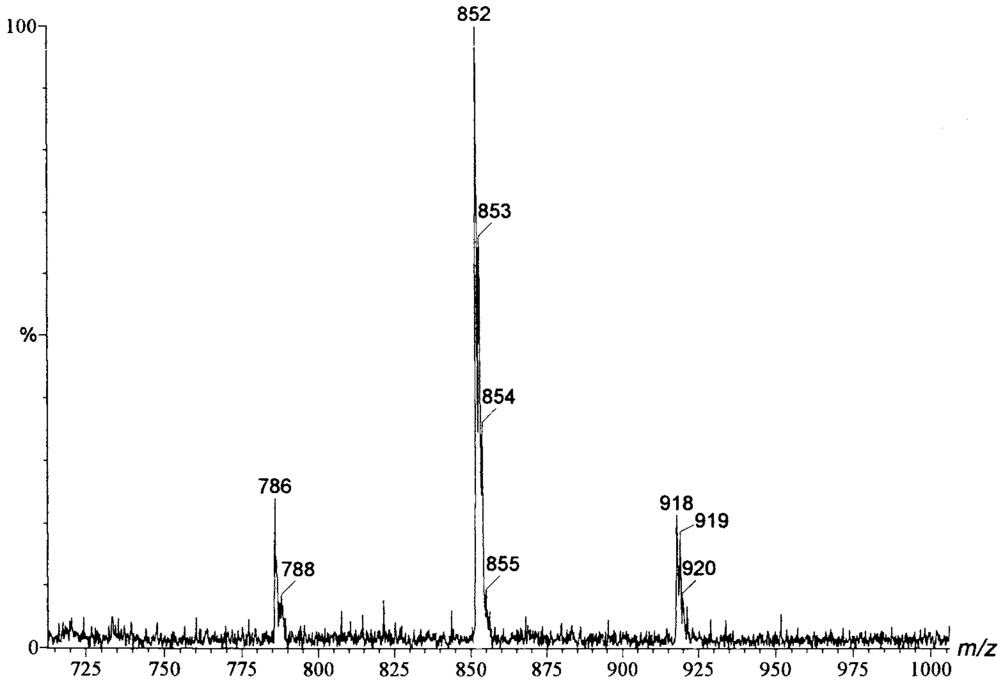

Figure 3. Positive-ion ESI mass spectrum obtained from a $C_{60}(C_5H_6)_n$ solution (toluene was used as the solvent).

solvent, because many higher mass ions resulting from the reaction of C_{60} (or C_{60} derivatives) with methanol were also observed.

The instrument used in this study was a Fisons Platform quadrupole mass spectrometer. Whether or not these radical ions could be observed using other ESI instruments was not certain, because the formation of radical ions might be instrument dependent. For example, even with the treatment of C_{60} with iodine or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) before ESI analysis, radical cations of C_{60} were not observed in the work of Hiraoka and co-workers.[16] Moreover, radical cations of naphthalene were observed in this laboratory but not in the work of Van Berkel *et al.*[21] Work in this respect is in progress and it is believed that the understanding of the instrumental conditions required for the formation of these radical ions should be useful for the analysis of other neutral and nonpolar compounds by ESI.

In conclusion, we have investigated the approach of analyzing C_{60} and related compounds directly using ESI. Our results with more than half-a-dozen C_{60}-related compounds suggested that ESI was superior to EI, DCI, and FAB in the analysis of these compounds and, more importantly, that C_{60} related compounds can be analyzed directly with ESI without any requirement for preformed ions in solution. These findings provide an easy and useful approach for the characterization of fullerenes and related compounds.

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