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# Gas-Phase Observation of Multiply Charged $C_{60}$ Anions

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Gas-phase observation of $C_{60}{}^{1-}$, $C_{60}{}^{3-}$, and $C_{60}{}^{4-}$ anions generated at platinum and gold electrodes and detected by electrochemical/electrospray mass spectrometry is reported. The anions were electrochemically generated from solutions of $C_{60}$ dissolved in toluene/acetonitrile as well as from reduction of $C_{60}$ films on gold electrode surfaces. The gas-phase observation of $C_{60}{}^{3-}$ and $C_{60}{}^{4-}$, despite the fact that they have negative electron affinities, is a result of a Coulombic barrier to electron loss. The fact that $C_{60}{}^{2-}$ was not detected in these experiments is ascribed to its limited solubility under the reaction conditions. These studies, which demonstrate the gas-phase kinetic stability of $C_{60}{}^{3-}$ and $C_{60}{}^{4-}$, illustrate the promise of electrochemical/electrospray mass spectrometry for the study of metastable anions.

## Introduction

One of the most interesting aspects of fullerene chemistry is the ease with which these remarkable molecules accommodate negative charges. It has been said that the electron-accepting ability of $C_{60}$ is its most characteristic chemical property.[1] The fact that $C_{60}$ has three low-lying degenerate unoccupied molecular orbitals allows stepwise electrochemical[2−11] or alkali metal reduction[12−18] to produce fulleride anions with up to six negative charges.[1,19] Salts of $C_{60}$ with up to three negative charges have been isolated[20−22] and the ease of generating $C_{60}{}^{2-}$ has led to its use as a reagent in the synthesis of disubstituted fullerenes.[23,24]

Although it is clear that these multiply charged fullerides exhibit remarkable stability in solution, their observation in the gas phase has been problematic. Thus, while $C_{60}{}^{1-}$ is readily detected in negative ion mass spectrometry[1,4,7,25,26] and $C_{60}{}^{2-}$ has been observed by laser desorption mass spectrometry,[27] gas-phase detection of fullerides with more that two negative charges has proved elusive. A consideration of the electron affinities (EAs) of $C_{60}$ provides a simple rational for this fact. Thus, while the first EA is quite positive at 2.66 eV[28] and the second EA has been calculated to be positive, higher EAs are calculated to be negative.[29] The fact that $C_{60}{}^{2-}$ is only observed under extremely energetic conditions while dianions of higher fullerenes are much more common in negative ion spectrometry has been attributed to more positive EAs for these molecules and the ability of the larger fullerenes to mitigate Coulombic repulsion.[30,31] Dianionic adducts of $C_{60}$ with F[32,33] and CN[34] attached are also readily observed.

It is certainly true that negative EAs will render multiply charged fulleride anions metastable and difficult to generate by electron attachment. However, multianions often exhibit a Coulombic barrier to electron loss that can temporarily stabilize $M^{n-}$ anions with negative $n$th EAs.[35−37] Since negatively charged $C_{60}$ anions are readily generated electrochemically, it seemed to us that electrochemistry/electrospray mass spectrometry (EC/ESMS)[38−41] would be an ideal technique for the detection of multiply charged $C_{60}$ anions in the gas phase. Although both ESMS and EC/ESMS have been used to study $C_{60}$ anions in the gas phase, neither $C_{60}{}^{3-}$ nor $C_{60}{}^{4-}$ has been detected in these studies. We now report EC/ESMS studies of $C_{60}$ in which these metastable polyanions are observed.

## Experimental Section

**Chemicals.** $C_{60}$ was obtained from MER Corporation and used as received. Methanol, acetonitrile, *o*-dichlorobenzene (DCB), nitric acid, 98% sulfuric acid, and 49% hydrofluoric acid were purchased from Fischer Scientific Co. Acetonitrile was distilled from $CaH_2$ before use. Tetrabutylammonium tetrafluoroborate ($TBABF_4$), tetrabutylammonium perchlorate ($TBAClO_4$), sodium tetraphenylborate ($NaBPh_4$), and tetraethylammonium tetrafluoroborate ($TEABF_4$ ) were obtained from Aldrich Chemical Co. and used as received. All solutions were degassed with grade 5.0 Ar gas.

**Instrumentation.** All data were collected with a VG-Trios-2000 quadrupole electrospray mass spectrometer. The mass spectra were acquired in negative-ion mode co-adding 50 scans at a scan rate of 0.5 scan/s. The ES tip voltage was −2.89 kV, the source temperature was 60 °C for $CH_3CN$ and 110 °C for DCB, and the cone voltages were typically ca. −20 V. The solutions were pumped with a syringe pump at a flow rate of 5.0 mL/h.

The electrochemical cell is made from a cylindrical Pyrex tube with the solution flowing around a spherical platinum or gold working electrode into a cupped Pyrex collection tube. This cupped collection assembly leads to the mass spectrometer through a fused silica capillary. The working electrode potentials were applied by using a Bioanalytical System Inc. CV-27 potentiostat. A platinum-mesh counter electrode and a Ag/AgCl reference electrode (connected to the cell through a double salt bridge) were used. All potentials are quoted versus aqueous Ag/AgCl. Literature values for $C_{60}$ reduction potentials[19] have been converted to potentials vs Ag/AgCl.

Before use, the working electrodes were cleaned by rinsing sequentially with distilled water, 49% hydrofluoric acid, piranha[42] solution, distilled water, HPLC grade methanol, and fresh acetonitrile.

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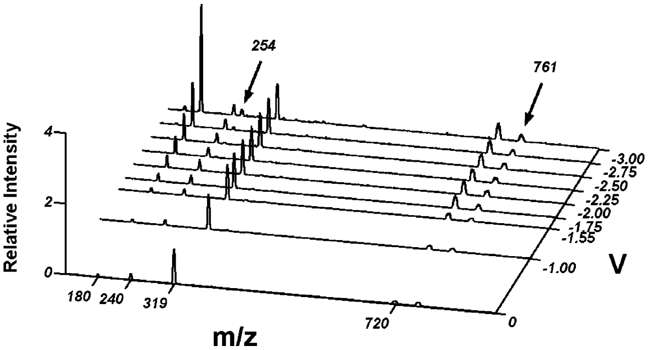


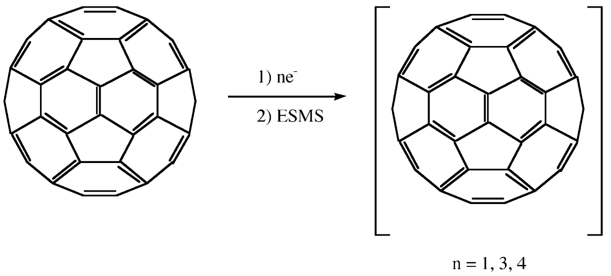
**Figure 1.** 3-D plot EC/ESMS mass spectra of dissolved $C_{60}$ as a function of applied electrochemical cell potential. The spectra are normalized to the intensity of the internal standard, $BPh_4^{1-}$ (*m/z* 319).

**EC/ESMS Studies of $C_{60}$ Solutions.** In these experiments $C_{60}$ was dissolved in different solvent mixtures with supporting electrolytes and $NaBPh_4$ as the internal standard. One solvent system used was 5:1 toluene/acetonitrile with $TBABF_4$ or $TEABF_4$ as supporting electrolyte. The EC/ESMS experiments were then carried out as the solution with dissolved $C_{60}$ flowed over the platinum electrode into the mass spectrometer. A second solvent system used $C_{60}$ dissolved in DCB with $TEABF_4$ as the supporting electrolyte. In these experiments a gold working electrode was used. In another experiment, a bulk electrolysis of a 5:1 toluene/acetonitrile with $TBABF_4$ solution of $C_{60}$ produced $C_{60}^{3-}$. This solution was then transferred anaerobically via syringe to the electrospray probe.

**EC/ESMS Studies of $C_{60}$ Films.** A film of $C_{60}$ was formed by repeatedly dropping a solution of $C_{60}$ dissolved in methylene chloride onto a gold electrode and drying in air. The coated electrodes were then immersed in the cell containing acetonitrile and $TBAClO_4$ as the supporting electrolyte or a 1:1 acetonitrile/toluene mixture with $TBABF_4$. Under these conditions dissolution of $C_{60}$ from the electrode by the solvent was minimal as evidenced by the fact that the characteristic color of $C_{60}$ was not observed in the solution after exposure to the coated electrode for 12 h.

## Results and Discussion

**EC/ESMS Studies of $C_{60}$ in Solution.** It was found that a 5:1 mixture of toluene and acetonitrile with $TBABF_4$ as a supporting electrolye and $NaBPh_4$ as an internal standard was a satisfactory solvent for $C_{60}$ EC/ESMS experiments. This solution was placed in an electrolysis cell and the applied potential was decreased incrementally from 0.0 to −3.4 V. The solution was continuously sprayed into the mass spectrometer. Figure 1 shows a three-dimensional plot of observed mass spectra as a function of the applied potential on the cell. The peaks have all been normalized to the intensity of the internal standard. It can be seen that small amounts of $C_{60}^{1-}$, $C_{60}^{3-}$, and $C_{60}^{4-}$ are detected at 0.0 V. The concentrations of all of these anions increase when the voltage is made more negative with $C_{60}^{4-}$ showing the most dramatic increase in intensity. In none of these experiments were we able to see evidence for $C_{60}^{2-}$. In addition, a peak at *m/z* 761, corresponding to the adduct of $C_{60}^{1-}$ and acetonitrile, was observed. Since it is thought that electrospray sources function as a type of electrochemical cell,[26] it is not surprising that small amounts of fulleride anions are observed when spraying $C_{60}$ solution from the cell at 0.0 V applied potential. The fact that these peaks increase with increasing applied cell voltage provides evidence for their electrochemical formation in solution and subsequent transport into the gas phase (eq 1). That the gas-phase ions are stable for the transport through the quadrupole mass spectrometer implies that the lifetimes are in excess of 0.5 ms.



(1)

That we observe no $C_{60}^{2-}$ in these experiments is puzzling. Given the ease with which this species is generated electrochemically, it must be formed initially in our experiments. While it is possible that $C_{60}^{2-}$ is rapidly removed by a chemical reaction, it is difficult to imagine a solution reaction exclusive to $C_{60}^{2-}$ that would not also remove other negatively charged $C_{60}$ species. Hence, we hypothesize that our failure to observe $C_{60}^{2-}$ in the gas phase results from the fact that this anion is simply insoluble under our reaction conditions and is thus not sprayed into the gas phase. In support of this hypothesis, it has been reported that $C_{60}^{1-}$ and $C_{60}^{2-}$ are far less soluble in acetonitrile than $C_{60}^{3-}$ and $C_{60}^{4-}$ when $TBA^+$ is the counterion.[43]

There is also evidence that $C_{60}^{1-}$ and $C_{60}^{2-}$, but not $C_{60}^{3-}$, form insoluble films with the $TBA^+$ counterion under certain conditions.[43] Thus, with a $TBA^+$ counterion, $C_{60}^{3-}$ is quite soluble in acetonitrile. However, electrooxidation of a solution of $C_{60}^{3-}(TBA^+)_3$ results in the formation of insoluble films of $C_{60}^{2-}(TBA^+)_2$. In the reverse of this process in $CH_3CN$, a film of $C_{60}$ may be electrochemically reduced to a film of $C_{60}^{1-}TBA^+$, thence to a film of $C_{60}^{2-}(TBA)_2^+$, and finally to a solution of $C_{60}^{3-}$. Although our experiments have been carried out in toluene−acetonitrile rather than in pure acetonitrile, it seems reasonable that films of $C_{60}^{2-}(TBA)_2^+$ may also form in our solvent system preventing the observation of the dianion in the gas phase.

In an attempt to solubilize $C_{60}^{1-}$ and $C_{60}^{2-}$ and observe these species by EC/ESMS, a solution of $C_{60}$ in DCB was reduced at a gold electrode at applied potentials ranging from 0 to −1.5 V. These experiments did not show fulleride anions at 0.0 V. However, small amounts of $C_{60}^{1-}$ appeared at −0.8 V and increased as the voltage was decreased to −1.5 V. This experiment does not reveal the presence of $C_{60}^{2-}$ in the gas phase leading to the conclusion that this dianion is insoluble in DCB. Due to a competing reduction of DCB, it is not possible to decrease the cell voltage beyond −1.5 V in these experiments.

**EC/ESMS Studies of $C_{60}$ Films.** To examine the relationship between our EC/ESMS studies and electrochemical investigations of $C_{60}$ films, we have also studied the EC/ESMS of $C_{60}$ films. In our investigations of the EC/ESMS of $C_{60}$ in toluene−acetonitrile, the solvent system is chosen such that $C_{60}$ is soluble. Thus, spraying a fullerene solution from a cell at 0.0 V results in ionization of $C_{60}$ in the ES source and observation of fulleride anions. However, if one starts with a film of $C_{60}$ on an electrode in acetonitrile, in which $C_{60}$ is insoluble, fulleride anions should only be observed after electrochemical reduction and only those soluble in acetonitrile will be detected. Accordingly, we have studied the EC/ESMS of a film of $C_{60}$ on a gold electrode with $TBAClO_4$ as the supporting electrolyte in acetonitrile. As expected from the fact that there is no $C_{60}$ in solution, these experiments show no fulleride anions when solvent is sprayed

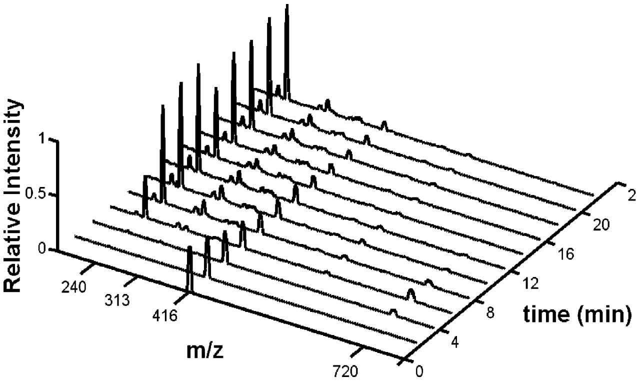


**Figure 2.** 3-D plot that shows the relative negative ion EC/ESMS intensities as a function of time for the reduction in $C_{60}$ film experiments. The potential was stepped from 0.0 V to −2.0 V in 1:1 (v/v) acetonitrile:toluene. These spectra were normalized to the largest peak. The peak at *m*/*z* 416 is $TBA(BF_4)_2^{1-}$.

from the cell at 0.0 V. Decreasing the cell voltage to −1.5 V did not result in the observation of any fulleride anions. Since this voltage is sufficient to reduce $C_{60}$ to $C_{60}^{1-}$ ($E = -0.63$ V) and $C_{60}^{2-}$ ($E = -1.01$ V), we conclude that both of these anions remain as films on the electrode consistent with previous reports. However, when the voltage is decreased to −2.5 V, sufficient to form $C_{60}^{3-}$ ($E = -1.55$ V) and $C_{60}^{4-}$ ($E = -1.80$ V), a strong peak for $C_{60}^{3-}$ at *m*/*z* 240 is observed. The observation of $C_{60}^{4-}$ at *m*/*z* 180 under these conditions is complicated by the fact that a peak at *m*/*z* 180 attributed to $ClO_4(CH_3CN)_2^{1-}$ is also observed independent of cell voltage.

In an attempt to better solubilize fulleride anions, and observe these by EC/ESMS, a film of $C_{60}$ on a gold electrode in $CH_3CN$/toluene (1:1 v/v) was reduced at −2.0 V with 1 mM $TBABF_4$ as supporting electrolyte. The $C_{60}$ film is not soluble in this solution, but its reduced anions become more soluble and detectable in ESMS. Figure 2 shows the negative ion EC/ESMS as a function of time; $C_{60}^{1-}$ appears at 4 min, quickly increases to its maximum value, and then disappears in a very short time. Meanwhile, the intensity of $C_{60}^{3-}$ increases from 6 to 22 min, and decays very slowly after that time. These studies do not reveal the presence of $C_{60}^{2-}$. The small peaks in Figure 2 at *m*/*z* 366 and above are currently unidentified. If the same experiment is carried out holding the potential at −1.0 V instead of −2.0 V, only $C_{60}^{1-}$ (*m*/*z* 720) is observed growing and decaying. Since −1.0 V is not negative enough to reduce the $C_{60}$ film to $C_{60}^{3-}$, no $C_{60}^{3-}$ is observed in these studies.

## Conclusions

The gas-phase observation of both $C_{60}^{3-}$ and $C_{60}^{4-}$ in these experiments demonstrates that these metastable polyanions may be observed in the gas phase by first generating them in solution and spraying into the gas phase. The fact that these polyanions can be observed despite the fact that they have negative EAs is attributed to a Coulombic barrier to electron loss. As in any ESMS technique, the method is successful only for those fulleride anions that are soluble. The high concentration of charge in these fulleride polyanions is expected to render them strong nucleophiles and the method promises to become a convenient way of measuring their gas-phase reactivities.

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