Electron-Transfer Reactions of $C_{60}F_{48}$

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An area of increasing interest in fullerene chemistry is the electrochemistry of fullerenes and their derivatives. Electrochemical studies in various solvent systems have demonstrated that C_{60} can be reduced at a relatively positive potential to its radical anion[1,2] and that its degenerate LUMOs can accept up to six electrons.[3] Among the fullerene derivatives, higher fluorofullerenes are particularly interesting.[4] Higher fluorofullerenes have been reported by Taylor et al.[5] to be unstable in some solvent systems, and Adcock et al.[4a] found them to be relatively strong oxidizing and fluorinating reagents. In addition, Hettich et al. found that the electron affinities of highly fluorinated fullerenes are almost 1.5 eV[6a] higher than those of the parent fullerenes and that doubly charged anions of $C_{60}F_x$ (x = 48 and 46) can be generated in the gas phase by sequential electron capture[6b] and studied by mass spectrometry. Those results demonstrated that the electronic properties of the higher fluorofullerenes are very different from those of the fullerenes. However, the electrochemical behavior of fluorofullerenes has not been determined, and the precise mechanism[4a] of the chemical redox reactions of fluorofullerenes remains to be elucidated. We now report the first cyclic voltammetric[7] study of $C_{60}F_{48}$ and the characterization of the products formed in the successive addition of electrons to $C_{60}F_{48}$ in solution by various electron donors using electrospray mass spectrometry (ES-MS).[9]

Cyclic voltammograms (CVs) of $C_{60}F_{48}$ in a CH_2Cl_2 solution are shown in Figure 1. The reduction of $C_{60}F_{48}$ to its anion radical (wave I in Figure 1a) occurs at $E_{1/2}$ = –0.43 V with respect to the 9,10-diphenylanthracene (DPA)/9,10-diphenylanthracene radical cation ($DPA^{\bullet +}$) reference redox couple used in this experiment, or *0.79 V* with respect to the SCE. The peak current ratio, i_{pa}/i_{pc}, of 0.98 and the peak separation, ΔE_p, of 66 mV (ΔE_p of the $DPA/DPA^{\bullet +}$, a reversible couple, is 80 mV) indicated that $C_{60}F_{48}$ undergoes a reversible[11] reduction to form $C_{60}F_{48}^{\bullet -}$. The reduction potential of $C_{60}F_{48}$ is *1.38 V more positive* than that of the first reduction wave of C_{60},[7] indicating that $C_{60}F_{48}$ is much easier to reduce than C_{60}. Moreover, this potential is also more positive than that of most other neutral organic electron acceptors known to the authors.

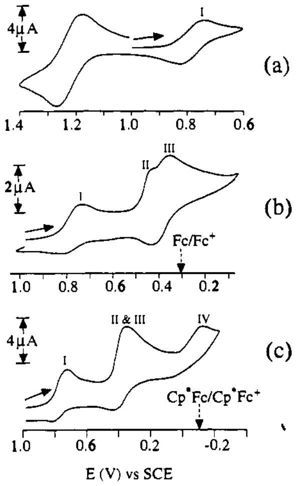

Figure 1. Cyclic voltammograms of a 0.5 mM solution of $C_{60}F_{48}$ in CH_2Cl_2, with (a) the potential scanned at 0.2 V/s and reversed at 0.6 V vs SCE; (b) the potential scanned at 0.05 V/s and reversed at 0.04 V; and (c) the potential scanned at 0.2 V/s and reversed at –0.24 V. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.08 M). Arrows indicate the starting potentials and the initial scan directions. In part a, the oxidation wave of DPA is also shown. The redox potentials of Fc/Fc^+ and Cp^*Fc/Cp^*Fc^+ are indicated by the dotted arrows for reference of the ES-MS experiments described in the text.

$C_{60}F_{48}$ should be able to oxidize I^- to I_2 in CH_2Cl_2, since the reduction potential of $C_{60}F_{48}$ is more positive than the oxidation potentials of I^-/I_3^- (0.26 V vs SCE[12]) and I_3^-/I_2 (0.65 V vs SCE[12]). Indeed, Adcock and co-workers[4a] found that fluorofullerenes can liberate I_2 from NaI in acetone, but it was not determined if I_2 was formed via a simple redox reaction producing $C_{60}F_{48}^{\bullet -}$ as the anionic product. To determine the anionic product of this reaction, a flow injection reaction[13] was carried out on line with ES-MS.[15] In this experiment, $C_{60}F_{48}$ (20 pmol) undergoes an electron-transfer reaction with I^- present in the solution (81 μM tetrabutylammonium iodide), and the anionic products of the reaction, if stable over the time frame of the experiment (in this case ~20 s), are detected by ES-MS. The only peak in the mass spectrum (not shown), which appears at *m/z* 1632,

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(6) (a) Hettich, R.; Jin, C.; Compton, R. N. *Int. J. Mass Spectrom. Ion Processes,* in press. (b) Jin, C.; Hettich, R.; Compton, R.; Tuinman, A.; Derecskei-Kovacs, A.; Marynik, D. S.; Dunlap, B. I. *Phys. Rev. Lett.*, submitted.

(7) All the electrochemical experiments were performed in a drybox, using a PAR 273 potentiostat. A 2-mm-diameter Pt disk electrode was used as the working electrode, a Pt mesh as the counter electrode, and a Ag wire as the quasi-reference electrode. All potentials were referenced to the $DPA/DPA^{\bullet +}$ couple (1.22 V vs SCE[8]). The half-wave potential of the first reduction of C_{60} was measured with respect to that of $DPA/DPA^{\bullet +}$ and then referenced to SCE, and the resulting value, –0.59 V vs SCE, is in good agreement with the literature value, –0.56 V vs SCE.[2] About 80% of the solution resistance was compensated.

(8) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1973; Vol. II.

(9) All the ES-MS experiments were carried out using a Finnigan-MAT ion trap mass spectrometer modified for atmospheric sampling.[10] For a review of ES-MS, see: Fenn, J. B.; Mann, M.; Meng, C. K.; Wang, S. K.; Whitehouse, C. M. *Mass Spectrom. Rev.* **1990,** *9,* 37.

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(13) The instrumental setup for the flow injection experiments has been detailed elsewhere.[14] Since the same CV waves as those in Figure 1 (except the oxidation wave of DPA) can be observed in an electrochemical experiment conducted in ambient atmosphere, species observed by ES-MS which was performed in ambient atmosphere should correspond to the same ones produced in the chemical reduction reactions in the solution.

(14) Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L. *Anal. Chem.* **1991,** *63,* 2064.

(15) The electrospray process does not normally ionize the analyte directly. Rather, ES assists the transfer of ionic analyte species in solution into the gas phase.

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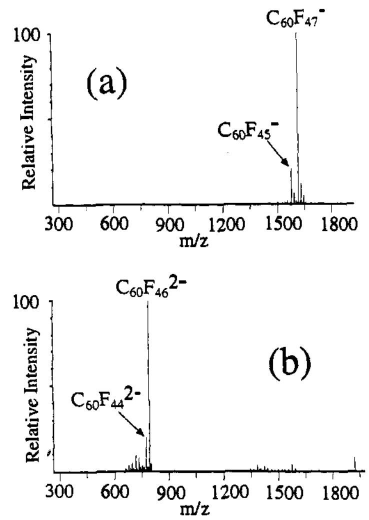

Figure 2. Electrospray mass spectra obtained in flow injection experiments using (a) ferrocene (Fc) and (b) decamethylferrocene (Cp*Fc) as the electron donor species in the carrier solutions. The peaks corresponding to $C_{60}F_{45}^-$ and $C_{60}F_{44}^{2-}$ are fragment ions, formed by collision-induced dissociation of $C_{60}F_{47}^-$ and $C_{60}F_{46}^{2-}$, respectively, in the atmospheric-sampling interface of the ES-MS instrument.[22]

corresponds to $C_{60}F_{48}^{\bullet-}$, demonstrating that $C_{60}F_{48}$ can oxidize I^- in CH_2Cl_2 and confirming our CV observation that $C_{60}F_{48}^{\bullet-}$ is the stable anionic product (solution lifetime > 20 s).[16]

A CV scan toward a more negative potential at a scan rate of 0.05 V/s produced the second reduction wave of $C_{60}F_{48}$ (wave II in Figure 1b), with a peak potential, E_{pc}, of 0.44 V vs SCE. No anodic wave was observed at scan rates up to 1 V/s when the potential scan was reversed right after wave II, indicating that $C_{60}F_{48}^{2-}$ undergoes a following chemical reaction. However, the product formed from the chemical reaction of $C_{60}F_{48}^{2-}$ appears to be reduced at a potential very close to that of the second wave (E_{pc} of wave III is 0.37 V) and reoxidized during the scan reversal even at a relatively slow scan rate of 0.05 V/s. The ΔE_p of wave III was measured to be 67 mV, suggesting that wave III is reversible and that this product is stable in solution at this scan rate. To verify this reaction scheme, a second flow injection experiment was performed using ferrocene (Fc) as the electron donor, since the redox potential of Fc/Fc^+ (0.31 V[11]) is beyond wave III. Shown in Figure 2a is the ES mass spectrum obtained following an injection of 50 pmol of $C_{60}F_{48}$ into a flowing stream of CH_2Cl_2/164 μM Fc. The base peak in this spectrum appears at *m/z* 1613, which corresponds in mass to $C_{60}F_{47}^-$. On the basis of this observation, it seems that, following the second reduction, $C_{60}F_{48}^{2-}$ loses F^- to form $C_{60}F_{47}^-$, which can then be reduced to $C_{60}F_{47}^{2-}$ (wave III).[18]

$C_{60}F_{47}^{2-}$ can be further reduced to $C_{60}F_{47}^{3-}$, yielding an irreversible CV wave at an E_{pc} of −0.12 V vs SCE (Figure 1c[20]). In an attempt to identify the product formed during the reduction of $C_{60}F_{47}^{2-}$, a third flow injection experiment was conducted using decamethylferrocene (Cp*Fc) as the reducing agent. The redox potential of Cp*Fc/Cp*Fc$^+$ is −0.11 V vs SCE,[21] which is very close to the peak potential of wave IV. Therefore, it should be possible to reduce $C_{60}F_{48}$ to generate $C_{60}F_{47}^{3-}$ with Cp*Fc. The ES mass spectrum in Figure 2b was obtained following an injection of 60 pmol of $C_{60}F_{48}$ into a stream of CH_2Cl_2/400 μM Cp*Fc. The base peak in this spectrum, which appears at *m/z* 797, corresponds to $C_{60}F_{46}^{2-}$, suggesting that $C_{60}F_{47}^{3-}$ undergoes a rapid loss of F^- in solution to form $C_{60}F_{46}^{2-}$. Compared to $C_{60}F_{47}^-$, $C_{60}F_{46}^{2-}$ was found to be more stable in solution. $C_{60}F_{46}^{2-}$ was the base peak in a mass spectrum recorded by continuously infusing a mixture of Cp*Fc and $C_{60}F_{48}$ ([Cp*Fc]:[$C_{60}F_{48}$] = 4:1), but the mass spectrum recorded by continuously infusing a mixture of Fc and $C_{60}F_{48}$ contained a number of lower mass species which increased in abundance with time in the mass spectrum, indicating the occurrence of further chemical reactions. Further reduction of $C_{60}F_{46}^{2-}$ yielded a broad irreversible wave at ca. −0.65 V vs SCE. The peak height of this wave is about 4 times as great as that of wave I, and no anodic wave was associated with this reduction wave, suggesting that $C_{60}F_{46}^{2-}$ probably undergoes a complicated multiple electron-transfer/fluoride-loss reaction.

On the basis of the CV behavior and the ES mass spectra discussed above, we propose the following EECEEC mechanism[11] for the first four reduction reactions of $C_{60}F_{48}$:

$$\begin{array}{lc}
C_{60}F_{48} + e^- \rightleftarrows C_{60}F_{48}^{\bullet-} & \mathrm{E} \\
C_{60}F_{48}^{\bullet-} + e^- \rightleftarrows C_{60}F_{48}^{2-} & \mathrm{E} \\
C_{60}F_{48}^{2-} \rightarrow F^- + C_{60}F_{47}^- & \mathrm{C} \\
C_{60}F_{47}^- + e^- \rightleftarrows C_{60}F_{47}^{2-} & \mathrm{E} \\
C_{60}F_{47}^{2-} + e^- \rightleftarrows C_{60}F_{47}^{3-} & \mathrm{E} \\
C_{60}F_{47}^{3-} \rightarrow C_{60}F_{46}^{2-} + F^- & \mathrm{C}
\end{array}$$

$C_{60}F_{46}^{2-}$, as the final product in the above scheme, is the first organic dianion formed by multiple electron-transfer reactions in solution observed in the gas phase by ES-MS.

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Supplementary Material Available: Mass spectrum of $C_{60}F_{48}^{\bullet-}$, simulated voltammograms of $C_{60}F_{48}$, and UV/visible spectrum of a $C_{60}F_{48}$/ferrocene solution (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) An ES mass spectrum obtained by spraying a $C_{60}F_{48}$ sample dissolved in CH_2Cl_2 shows a base peak at *m/z* 1632. The origin of the radical anion in the absence of a reducing agent in solution is believed to be due to the electrochemical phenomenon inherent in the ES process.[17] The abundance of $C_{60}F_{48}^{\bullet-}$ is two times greater when I^- is added to the solution than when the compound is sprayed from CH_2Cl_2 alone, indicating that I^- is more efficient in reducing $C_{60}F_{48}$ than the ES process.

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(18) The reason that the ES mass spectrum did not show a peak at *m/z* 807 ($C_{60}F_{47}^{2-}$) is probably that $C_{60}F_{47}^{2-}$ is an intermediate which has a strong tendency to reduce or reoxidize (its oxidation peak potential, E_{pa} of wave III, is 0.41 V vs SCE). In the positive ion mode, only very stable dications formed by chemical oxidation reactions can be observed in the gas phase.[19]

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(20) Note in Figure 1c, wave II shifted to a more negative potential and merged with wave III at a higher scan rate (0.2 V/s for Figure 1c versus 0.05 V/s for Figure 1b), because wave II is associated with a following chemical reaction.[11]

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