Electrochemical Studies of the Protonation of C\textsubscript{60}\textsuperscript{-} and C\textsubscript{60}\textsuperscript{2-}

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Cyclic voltammetric reduction of C\textsubscript{60} to the radical anion, C\textsubscript{60}\textsuperscript{-}, is unaffected by the presence of weak proton donors in o-dichlorobenzene, indicating that the monoanion is a weak base. Further reduction to the dianion results in a drastic increase in basicity, and an estimate of the acidity of the conjugate acid, C\textsubscript{60}H\textsuperscript{+}, is obtained. Bulk electrolysis studies allow further characterization of the monoanion properties, including an estimate of the acidity of C\textsubscript{60}H\textsuperscript{+} relative to triflic acid. The dianion can be titrated in acetonitrile by triflic acid to form an orange solution that FAB mass spectral analysis indicates is C\textsubscript{60}H\textsubscript{2}. Spectrophotometric titration of the anions reveals two new, distinct species, which we attribute to C\textsubscript{60}H\textsuperscript{+} and C\textsubscript{60}H\textsuperscript{2+}.

Introduction

We describe here the effects of added proton donors on the electroreduction of C\textsubscript{60} in acetonitrile and o-dichlorobenzene (ODCB) solutions and discuss the acid/base properties of the one- and two-electron reduction products. The hydrogenation of fullerene has been of interest, beginning with the initial report of C\textsubscript{60}H\textsubscript{36} as the dominant Birch reduction product. The synthesis of C\textsubscript{60}H\textsubscript{2} has been accomplished by both hydroborane and metal/acid reductions, with chromatographic purification yielding >90% hydrogenated fullerene. The electrochemistry of C\textsubscript{60}H\textsubscript{2} is reported to be very similar to C\textsubscript{60} with a slight negative shift in reduction potentials. The EPR of the free radical C\textsubscript{60}H\textsuperscript{+} (equivalent to the protonated radical anion) prepared by photolysis of solutions of C\textsubscript{60} in benzene in the presence of thiophenol and either tri-n-butyl tin hydride or 1,2-cyclohexadiene has also been reported. This radical has also been formed by reacting C\textsubscript{60} with hydrogen atoms followed by matrix isolation in cyclohexane at 77 K or neon at 4 K. Hydrogenated C\textsubscript{60} should also result from protonation of C\textsubscript{60}\textsuperscript{-} and C\textsubscript{60}\textsuperscript{2-}; both are conveniently prepared by electroreduction. The effects of protonation on the cyclic voltammetry (CV) of C\textsubscript{60} should allow estimation of thermodynamic and kinetic parameters from shifts in waves and changes in wave shape. Such studies can be complicated in acetonitrile, however, by the insolvability of C\textsubscript{60} and the limited solubility of the reduced forms (depending on the supporting electrolyte cation). In o-dichlorobenzene, the neutral C\textsubscript{60}, monoanion, and dianion forms are slightly soluble.

Experimental Section

Cyclic voltammetric studies were carried out at a gold microelectrode (diameter, 25 or 60 \textmu m) in ODCB with 0.1 M tetra-n-butylammonium tetrafluoroborate (TBABF\textsubscript{4}) using a BAS 100A electrochemical analyzer. A platinum mesh served as the counter electrode, and a silver wire was used as a quasireference electrode. All potentials were referenced to and are reported versus the ferrocene/ferricenium (Fc/Fc\textsuperscript{+}) couple. ODCB (Aldrich, HPLC grade) was used as received. TBABF\textsubscript{4} (SACHEM, electrometric grade) was dried in a vacuum oven and stored in a helium drybox. C\textsubscript{60} was extracted from enriched soot (Texas Fullerenses, Houston, TX) using silica/activated carbon flash chromatography. All solutions were prepared in a helium drybox and sealed in an air-tight electrochemical cell. Trifluoromethane sulfonic acid (triflic acid, 99.9% Aldrich) and benzoic acids were used as received.

Cyclic voltammetry was used to measure the effects of added proton donors on the electroreduction of C\textsubscript{60} in acetonitrile and o-dichlorobenzene (ODCB) solutions and discuss the acid/base properties of the one- and two-electron reduction products. The hydrogenation of fullerene has been of interest, beginning with the initial report of C\textsubscript{60}H\textsubscript{36} as the dominant Birch reduction product. The synthesis of C\textsubscript{60}H\textsubscript{2} has been accomplished by both hydroborane and metal/acid reductions, with chromatographic purification yielding >90% hydrogenated fullerene. The electrochemistry of C\textsubscript{60}H\textsubscript{2} is reported to be very similar to C\textsubscript{60} with a slight negative shift in reduction potentials. The EPR of the free radical C\textsubscript{60}H\textsuperscript{+} (equivalent to the protonated radical anion) prepared by photolysis of solutions of C\textsubscript{60} in benzene in the presence of thiophenol and either tri-n-butyl tin hydride or 1,2-cyclohexadiene has also been reported. This radical has also been formed by reacting C\textsubscript{60} with hydrogen atoms followed by matrix isolation in cyclohexane at 77 K or neon at 4 K. Hydrogenated C\textsubscript{60} should also result from protonation of C\textsubscript{60}\textsuperscript{-} and C\textsubscript{60}\textsuperscript{2-}; both are conveniently prepared by electroreduction. The effects of protonation on the cyclic voltammetry (CV) of C\textsubscript{60} should allow estimation of thermodynamic and kinetic parameters from shifts in waves and changes in wave shape. Such studies can be complicated in acetonitrile, however, by the insolvability of C\textsubscript{60} and the limited solubility of the reduced forms (depending on the supporting electrolyte cation). In o-dichlorobenzene, the neutral C\textsubscript{60}, monoanion, and dianion forms are slightly soluble.

Electroreduction of C\textsubscript{60} to the radical anion, C\textsubscript{60}\textsuperscript{-}, is unaffected by the presence of weak proton donors in o-dichlorobenzene, indicating that the monoanion is a weak base. Further reduction to the dianion results in a drastic increase in basicity, and an estimate of the acidity of the conjugate acid, C\textsubscript{60}H\textsuperscript{+}, is obtained. Bulk electrolysis studies allow further characterization of the monoanion properties, including an estimate of the acidity of C\textsubscript{60}H\textsuperscript{+} relative to triflic acid. The dianion can be titrated in acetonitrile by triflic acid to form an orange solution that FAB mass spectral analysis indicates is C\textsubscript{60}H\textsubscript{2}. Spectrophotometric titration of the anions reveals two new, distinct species, which we attribute to C\textsubscript{60}H\textsuperscript{+} and C\textsubscript{60}H\textsuperscript{2+}.

Results

Proton Reduction in ODCB. Studies of the protonation of the fullerene anions are complicated by direct reduction of acids at the electrode at potentials where C\textsubscript{60} reduction occurs, depending on acid strength and concentration. Figure 1 shows the reduction of triflic and benzoic acids at concentrations used to study the

![Figure 1. Proton reduction in 0.1 M TBABF\textsubscript{4}/ODCB at 25\textmu m-diameter electrodes; scan rate, 25 mV/s. (A): (1) 6.6 mM triflic acid at Pt; (2) 6.6 mM triflic acid at Au; (3) 6.9 mM benzoic acid at Au. (B): (1) 6.6 mM triflic acid at Pt; (2) 3.3 mM triflic acid at Pt. Fc (\sim 1 mM) was added to all solutions as an internal reference. Zero current at ca. -0.3 V.](#)
earlier studies of C60- solutions in liquid ammonia, where addition
of benzoic acid strongly affects the second C60 reduction wave. When 1.25:1 ratio benzoic acid is present (curve 3), a steady-state voltammogram of 1.26 mM C60 in 0.1 M TBABF4/ODCB at a 25-μm-diameter Au electrode; scan rate, 25 mV/s: (1) no acid added; (2) 1.58 mM triflic acid added (1.25:1 ratio).

addition of benzoic acid dramatically alters the voltammogram at both fast and slow scan rates (Figures 2 and 3). Additional electron-transfer steps are indicated by the higher currents after proton donor addition. In Figure 2, an ECE mechanism is indicated:

C60- + e- = C602- E (1)

C602- + RCOOH = C60H+ + RCOO- C (2)

C60H+ + e- = C60H2+ E (3)

Thus protonation of C602- to C60H+ produces a species that is immediately reduced at potentials near the second wave with addition of another electron. The protonation process is not complete since 0.84 equiv of benzoic acid does not result in an increase in current of an additional 0.84 equiv. An estimate of the equilibrium constant for the chemical step eq 2 can be obtained from the current ratio and is approximately K = 0.09. This estimate assumes the additional current (1.96 vs 1.63 nA) results from the formation and reduction of C60H+, eqs 2 and 3.

Voltammograms at higher acid ratios (8.4:1) indicate more than a quadrupling of the current at the second reduction wave indicative of a multiple ECE... sequence. This is illustrated by the series of reactions eqs 1–3 followed by

C60H2+ + RCOOH = C60H2+ + RCOO- C (4)

C60H2+ + e- = C60H22- E (5)

Thus multiple reduction and protonation steps occur at potentials around -1.4 V vs Fc/Fc+. This sequence ends when the proton equilibrium is reached or the reduction potential of the hydrofullerene species moves to more negative potentials. After a cycle through the C602- wave in the presence of acid, the ferrocene oxidation current seen on reversal decreases. This suggests processes accompany the reduction that cause deposition of a film on the electrode, probably the salt of an insoluble hydrofullerene or perhaps an aggregation product.

The effect of acid on the four reduction waves of C60 accessible in the potential window of the ODCB solvent is shown in Figure 4. In curve 1, a steady-state voltammogram of 1.26 mM C60 shows four reversible waves before the solvent reduction. In the voltammogram taken after the addition of 1 μL of triflic acid (1.58 mM, 1.25:1 acid/C60) (curve 2), the first reduction wave remains unperturbed, except for a small contribution of direct proton reduction, but a dramatic increase is seen in the remaining reduction waves, and the steady-state character is lost. Additional peaks are present at potentials similar to those reported for.

fullerene protonations. As shown, particularly for stronger acids, proton reduction can complicate interpretation of the cyclic voltammetric (CV) behavior at the first C60 reduction wave. Although we did not study the reduction of acids in ODCB in any depth, we might note that the reduction of a given acid occurs at about the same potentials at Pt and Au electrodes. Thus, CV studies were limited to those utilizing lower concentrations of weak acids and, hence, as discussed below, to C602- protonation.

Cyclic Voltammetry—First Wave. The reduction of C60 to the stable radical anion, C60-, is clearly indicated by a reversible wave at a gold electrode in ODCB (curve 1 in Figures 2–4). Weaker acids, e.g., benzoic or maleic acid, are not reduced until more negative potentials and hence do not interfere with the first C60 reduction wave. However, no change is seen in the height or shape of this wave in the presence of these acids (Figure 2), even at slower scan rates where steady-state voltammograms are observed (Figure 3). The effect of direct proton reduction on the voltammogram is shown clearly in Figure 3B as the small slope evident on the plateau of the C60 wave. These results, indicating lack of reaction of C60- with weaker acids, are in accord with earlier studies of C60- solutions in liquid ammonia, where addition of strong acid (NH4+?) did not affect the CV behavior, indicating lack of protonation of the radical anion in this solvent.14 We conclude from these results that C60- is a very weak base.

Cyclic Voltammetry—Second Wave. Addition of a weak acid does affect the second C60 reduction wave, C602- generation, demonstrating the effect of protonation of the dianion. The

Figure 2. Cyclic voltammograms of 0.82 mM C60 in 0.1 M TBABF4/ODCB at a 60-μm-diameter Au electrode at a scan rate of 3.0 V/s, where linear diffusion behavior is obtained: (1) no acid added; (2) 0.69 mM benzoic acid present (0.84:1 ratio); (3) 3.5 mM benzoic acid present (4.2:1 ratio); (4) 6.9 mM benzoic acid present (8.4:1 ratio).

Figure 3. Steady-state cyclic voltammograms of 0.82 mM C60 in 0.1 M TBABF4/ODCB at a 25-μm-diameter Au electrode; scan rate, 25 mV/s. (A): (1) no acid added; (2) 0.69 mM benzoic acid present (0.84:1 ratio). (B): (1) no acid added; (2) 6.9 mM benzoic acid present (8.4:1 ratio).

Figure 4. Steady-state cyclic voltammogram of 1.26 mM C60 in 0.1 M TBABF4/ODCB at a 25-μm-diameter Au electrode; scan rate, 25 mV/s: (1) no acid added; (2) 1.58 mM triflic acid added (1.25:1 ratio).
triflic acid (HT), the strongest simple proton donor known, is similar in acidity and electrochemistry to Cm-. And third, oxidation currents are proportional to the concentrations of HCso' before any additional protonation steps, and the CmH- formed is shown in Figure 5. In-situ spectrophotometric titration of 0.23 mM Cm- with 2.2 mM triflic acid: (1) no acid; (2) 0.61:1 triflic acid added; (3) 1.22:1 triflic acid added; (4) 1.53:1 triflic acid added; (5) 2.14:1 triflic acid added. ODCB has a sharp peak near 1140 nm.

hydrofullerenes. The reference ferrocene current on sweep reversal is decreased, again indicating that protonation products block the electrode.

**Bulk Electrolysis—Protonation of the Monoanion.** To investigate the reaction of Cm- with strong acid, bulk electrolysis was carried out to the monoanion in ODCB with TBABF4 electrolyte. UV-vis-near-IR spectroscopy was used to monitor Cm-, which has a strong, characteristic near-IR peak at 1078 nm. A 200-μL portion of the 0.9 mM monoanion solution was transferred to a sealed cuvette with a Teflon septum under an inert atmosphere and diluted with ODCB to 800 μL. Triflic acid (2.0 mM) in ODCB under nitrogen was used to titrate the monoanion. Spectra were recorded initially and after 50, 100, 125, and 175 μL of total titrant was added (acid/Cm- ratios of 0.61, 1.22, 1.53, and 2.14, Figure 5). The maximum 20% dilution effect is small compared to the effect of the proton donor. The decrease of the monoanion absorbance corresponds to the addition of triflic acid to form CmH:

An additional electrolysis to the monoanion (with a small amount of dianion) was carried out, with the protonation monitored by the steady-state voltammetry after addition of successive 0.2 equiv of triflic acid. As long as most of the triflic acid is deprotonated, no significant contribution of direct protonation at the electrode occurs. The series of steady-state voltammograms at different stages of the Cm-—triflic acid titration is shown in Figure 6. These data can be used to calculate the acidity of HCm' with three assumptions. First, the reduction and oxidation currents are proportional to the concentrations of HCm' and Cm-, respectively. Second, all of the residual Cm-2 protonates before any additional protonation steps, and the CmH- formed is similar in acidity and electrochemistry to Cm-. And third, triflic acid (HT), the strongest simple proton donor known, is assumed to act as a strong acid in ODCB. Under these assumptions, the following equilibrium is obtained for the reaction

\[
\text{HCm}^+ + \text{T} \rightleftharpoons \text{Cm}^- + \text{HT}
\]

and \(K_a = [\text{H}^+] [\text{Cm}^-] / [\text{HCm}']\) is \(4 \times 10^{-4}\) (Table 1). This indicates that HCm' is a fairly strong acid, 3 orders of magnitude weaker than triflic acid under these conditions. These results are also consistent with the very weak basicity of Cm- indicated in the CV experiments and by the lack of reaction with weak acids.

Previous work on simple hydrofullerenes has encountered many problems in achieving good mass spectra with conversion to the parent Cm prevalent. Mass spectral analysis of the product of the electrochemically monitored titration was performed using FAB ionization from a nitrobenzyl alcohol matrix. Both negative and positive ion collection modes show higher than isotopically expected peaks at 721 when compared to a C60 spectrum (Figure 7). While protonation is a commonplace ionization pathway for even pure C60, the negative ion peak at 721 is 86% of the C60 peak. This extra 20% above isotopic abundance found with pure C60 indicates that some of the HCm' must remain intact to be ionized negatively. Considering the strong acidity of HCm' and therefore the weakness of the C—H bond, it is not surprising to see most of the mass spectrum at 720. The peaks near 746 in the negative ion collection mode are the result of clustering of the acid/electrolyte present in the solution.

**Bulk Electrolysis—Protonation of the Dianion.** Bulk electrolysis was also used to investigate the dianion in acetonitrile solution again with near-IR spectroscopy used to follow concentrations of the various species. The dianion has a broad

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**TABLE 1: Calculation of HCm' Acidity from Data in Figure 6**

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<th>acid/Cm- ratio</th>
<th>fraction of HCm'</th>
<th>(K_a \times 10^{-4})</th>
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<tr>
<td>0.224</td>
<td>0.155</td>
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<td>1.024</td>
<td>0.571</td>
<td>3.4</td>
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*Average \(K_a = (4.2 \pm 0.9) \times 10^{-4}; pK_a = 3.4 \pm 0.1.\)
characteristic absorbance at 952 nm (Figure 8). When 1 equiv of triflic acid is added, the near-IR spectrum of the resulting product clearly resembles that of C₆₀⁻ with a prominent peak at 1078 nm. Two possibilities emerge, a redox reaction or a protonation (C₆₀²⁻ + H⁺ = C₆₀⁻ + H₂) or C₆₀³⁻ + H⁺ = C₆₀H⁺.

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References and Notes


