

## Electrochemical Studies of the Protonation of $C_{60}^-$ and $C_{60}^{2-}$

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Cyclic voltammetric reduction of  $C_{60}$  to the radical anion,  $C_{60}^-$ , 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,  $C_{60}H^-$ , is obtained. Bulk electrolysis studies allow further characterization of the monoanion properties, including an estimate of the acidity of  $C_{60}H^-$  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  $C_{60}H_2$ . Spectrophotometric titration of the anions reveals two new, distinct species, which we attribute to  $C_{60}H^-$  and  $C_{60}H^{2-}$ .

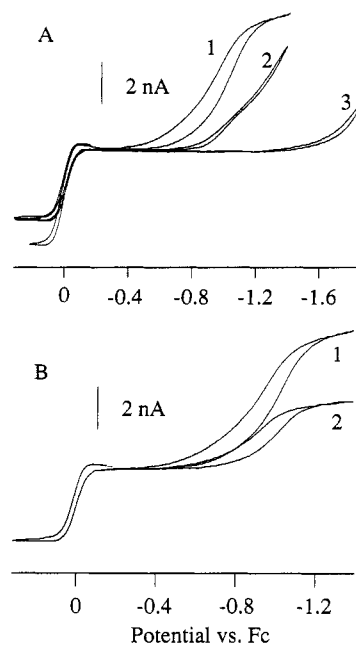
### Introduction

We describe here the effects of added proton donors on the electroreduction of  $C_{60}$  in acetonitrile and *o*-dichlorobenzene (ODCB) solutions and discuss the acid/base properties of the one- and two-electron reduction products. The hydrogenation of fullerenes has been of interest, beginning with the initial report of  $C_{60}H_{36}$  as the dominant Birch reduction product.<sup>1,2</sup> The synthesis of  $C_{60}H_2$  has been accomplished by both hydroborane<sup>3</sup> and metal/acid<sup>4</sup> reductions, with chromatographic purification yielding >90% hydrogenated fullerene.<sup>4</sup> The electrochemistry of  $C_{60}H_2$  is reported to be very similar to  $C_{60}$  with a slight negative shift in reduction potentials.<sup>4,5</sup> The EPR of the free radical  $C_{60}H^\cdot$  (equivalent to the protonated radical anion) prepared by photolysis of solutions of  $C_{60}$  in benzene in the presence of thiophenol and either tri-*n*-butyl tin hydride or 1,4-cyclohexadiene has also been reported.<sup>6</sup> This radical has also been formed by reacting  $C_{60}$  with hydrogen atoms followed by matrix isolation in cyclohexane at 77 K<sup>7</sup> or neon at 4 K.<sup>6</sup> Hydrogenated  $C_{60}$  should also result from protonation of  $C_{60}^-$  and  $C_{60}^{2-}$ ; both are conveniently prepared by electroreduction. The effects of protonation on the cyclic voltammetry (CV) of  $C_{60}$  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 insolubility of  $C_{60}$  and the limited solubility of the reduced forms (depending on the supporting electrolyte cation).<sup>8–10</sup> In *o*-dichlorobenzene, the neutral  $C_{60}$ , monoanion, and dianion forms are slightly soluble.<sup>11</sup>

### Experimental Section

Cyclic voltammetric studies were carried out at a gold microelectrode (diameter, 25 or 60  $\mu$ m) in ODCB with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) 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<sup>+</sup>) couple. ODCB (Aldrich, HPLC grade) was used as received. TBABF<sub>4</sub> (SACHEM, electrometric grade) was dried in a vacuum oven and stored in a helium drybox.  $C_{60}$  was extracted from enriched soot (Texas Fullerenes, Houston, TX) using silica/activated carbon flash chromatography.<sup>12</sup> 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.

Bulk electrolysis studies were carried out in a two-compartment cell in the drybox using a platinum foil working electrode with



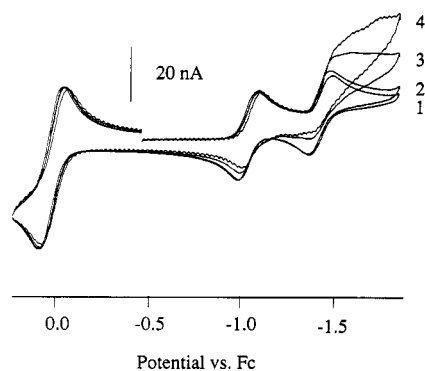
**Figure 1.** Proton reduction in 0.1 M TBABF<sub>4</sub>/ODCB at 25- $\mu$ m-diameter electrodes; scan rate, 25 mV/s. (A): (1) 6.6 mM triflic acid at Pt; (2) 6.6 mM triflic acid at Au; (3) 6.9 mM benzoic acid at Au. (B): (1) 6.6 mM triflic acid at Pt; (2) 3.3 mM triflic acid at Pt. Fc ( $\sim$ 1 mM) was added to all solutions as internal reference. Zero current at ca.  $-0.3$  V.

a silver wire reference electrode and a platinum mesh counter electrode separated from the working and reference electrodes by a fine porosity frit. The MeCN/ $C_{60}$  slurry, saturated with (0.035 M) potassium perchlorate (KClO<sub>4</sub>) or 0.05 M TBABF<sub>4</sub> electrolytes, was stirred vigorously with two Teflon stir bars during electrolysis using a Princeton Applied Research (PAR) 173 potentiostat and a PAR 179 coulometer. Other bulk electrolyses used ODCB as the solvent.<sup>13</sup> Acids were added to aliquots of the anion solutions and sealed for FAB mass spectral analysis using nitrobenzyl alcohol as the matrix. Additional aliquots of the anion solutions were used for titration studies using an Olis-17 UV-vis-near-IR spectrometer.

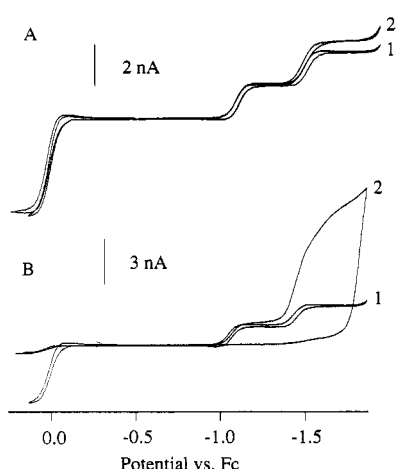
### Results

**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  $C_{60}$  reduction occurs, depending on acid strength and concentration. Figure 1 shows the reduction of triflic and benzoic acids at concentrations used to study the

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**Figure 2.** Cyclic voltammograms of 0.82 mM  $C_{60}$  in 0.1 M TBABF<sub>4</sub>/ODCB at a 60- $\mu$ m-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).

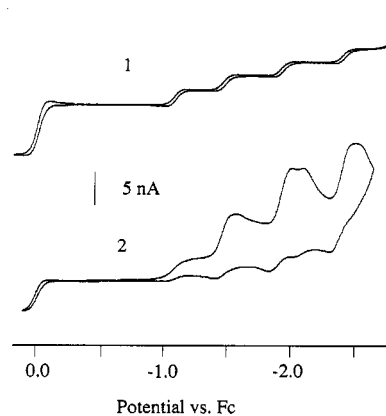


**Figure 3.** Steady-state cyclic voltammograms of 0.82 mM  $C_{60}$  in 0.1 M TBABF<sub>4</sub>/ODCB at a 25- $\mu$ m-diameter Au electrode; scan rate, 25 mV/s. (A): (1) no acid added; (2) 0.69 mM benzoic acid present (0.84:1 ratio). (B): (1) no acid added; (2) 6.9 mM benzoic acid present (8.4:1 ratio).

fullerene protonations. As shown, particularly for stronger acids, proton reduction can complicate interpretation of the cyclic voltammetric (CV) behavior at the first  $C_{60}$  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  $C_{60}^{2-}$  protonation.

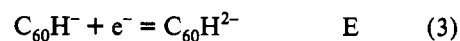
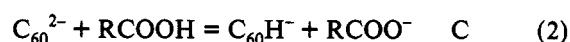
**Cyclic Voltammetry—First Wave.** The reduction of  $C_{60}$  to the stable radical anion,  $C_{60}^-$ , is clearly indicated by a reversible wave at a gold electrode in ODCB (curve 1 in Figures 2–4). Weaker acids, e.g., benzoic or maleic acid, are not reduced until more negative potentials and hence do not interfere with the first  $C_{60}$  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  $C_{60}$  wave. These results, indicating lack of reaction of  $C_{60}^-$  with weaker acids, are in accord with earlier studies of  $C_{60}^-$  solutions in liquid ammonia, where addition of strong acid ( $NH_4^+$ ) did not affect the CV behavior, indicating lack of protonation of the radical anion in this solvent.<sup>14</sup> We conclude from these results that  $C_{60}^-$  is a very weak base.

**Cyclic Voltammetry—Second Wave.** Addition of a weak acid does affect the second  $C_{60}$  reduction wave,  $C_{60}^{2-}$  generation, demonstrating the effect of protonation of the dianion. The



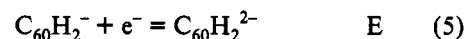
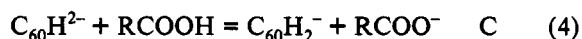
**Figure 4.** Steady-state cyclic voltammogram of 1.26 mM  $C_{60}$  in 0.1 M TBABF<sub>4</sub>/ODCB at a 25- $\mu$ m-diameter Au electrode; scan rate, 25 mV/s: (1) no acid added; (2) 1.58 mM triflic acid added (1.25:1 ratio).

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:



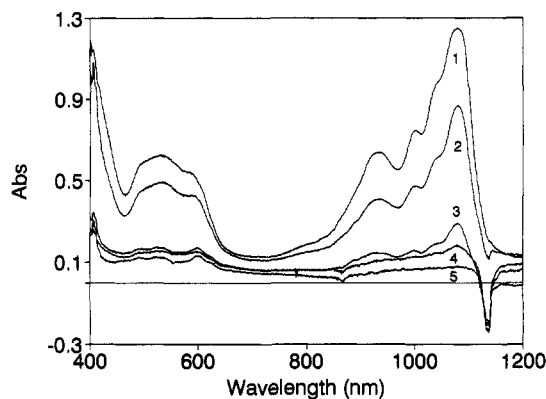
Thus protonation of  $C_{60}^{2-}$  to  $C_{60}H^-$  produces a species that is immediately reduced at potentials near the second wave with addition of another electron. The protonation process is not complete since 0.84 equiv of benzoic acid does not result in an increase in current of an additional 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  $C_{60}H^-$ , 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

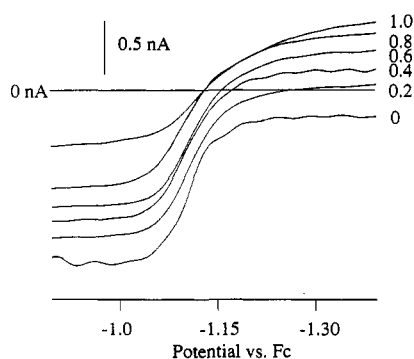


Thus multiple reduction and protonation steps occur at potentials around  $-1.4$  V vs Fc/Fc<sup>+</sup>. This sequence ends when the proton equilibrium is reached or the reduction potential of the hydrofullerene species moves to more negative potentials. After a cycle through the  $C_{60}^{2-}$  wave 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  $C_{60}$  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  $C_{60}$  shows four reversible waves before the solvent reduction. In the voltammogram taken after the addition of 1  $\mu$ L of triflic acid (1.58 mM, 1.25:1 acid/ $C_{60}$ ) (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



**Figure 5.** In-situ spectrophotometric titration of 0.23 mM  $C_{60}^-$  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.



**Figure 6.** Steady-state cyclic voltammograms of 0.99 mM  $C_{60}^-$  solution at a 25- $\mu$ m Au electrode: scan rate, 25 mV/s; 0, 0.2, 0.4, 0.6, 0.8, and 1.0 ratios of triflic acid added.

hydrofullerenes.<sup>34</sup> The reference ferrocene current on sweep reversal is decreased, again indicating that protonation products block the electrode.

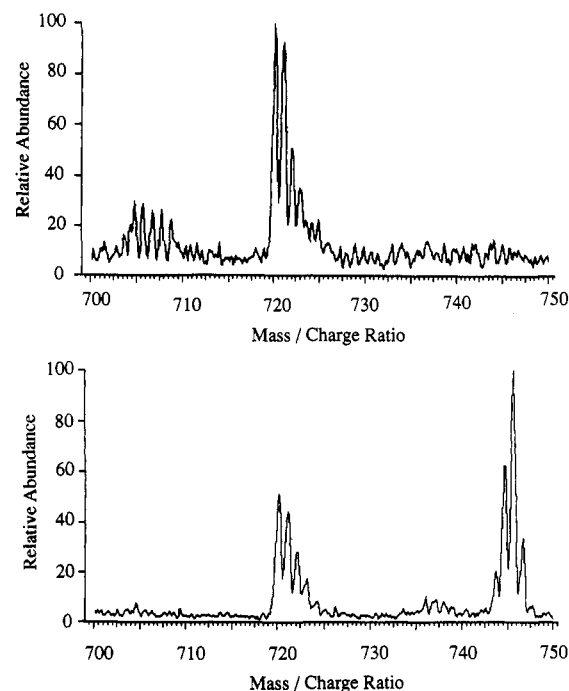
**Bulk Electrolysis—Protonation of the Monoanion.** To investigate the reaction of  $C_{60}^-$  with strong acid, bulk electrolysis was carried out to the monoanion in ODCB with TBABF<sub>4</sub> electrolyte.<sup>13</sup> UV-vis-near-IR spectroscopy was used to monitor  $C_{60}^-$ , which has a strong, characteristic near-IR peak at 1078 nm.<sup>15</sup> A 200- $\mu$ L 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  $\mu$ L. 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  $\mu$ L of total titrant was added (acid/ $C_{60}^-$  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  $C_{60}H^+$ .

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 proton reduction at the electrode occurs. The series of steady-state voltammograms at different stages of the  $C_{60}^-$ -triflic acid titration is shown in Figure 6. These data can be used to calculate the acidity of  $HC_{60}^+$  with three assumptions. First, the reduction and oxidation currents are proportional to the concentrations of  $HC_{60}^+$  and  $C_{60}^-$ , respectively. Second, all of the residual  $C_{60}^{2-}$  protonates before any additional protonation steps, and the  $C_{60}H^-$  formed is similar in acidity and electrochemistry to  $C_{60}^-$ . And third, triflic acid (HT), the strongest simple proton donor known, is

**TABLE 1: Calculation of  $HC_{60}^+$  Acidity from Data in Figure 6**

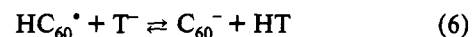
acid/ $C_{60}^-$ ratio	fraction of $HC_{60}^+$	$K_a \times 10^{-4}$ <sup>a</sup>
0.224	0.155	3.8
0.424	0.246	5.5
0.624	0.354	4.9
0.824	0.491	3.5
1.024	0.571	3.4

<sup>a</sup> Average  $K_a = (4.2 \pm 0.9) \times 10^{-4}$ ;  $pK_a = 3.4 \pm 0.1$ .



**Figure 7.** Fast atom bombardment mass spectra of solution resulting from addition of excess triflic acid to  $C_{60}^-$  ( $C_{60}H^+$ ). (A, Top) positive ion collection mode; (B, Bottom) negative ion collection mode.

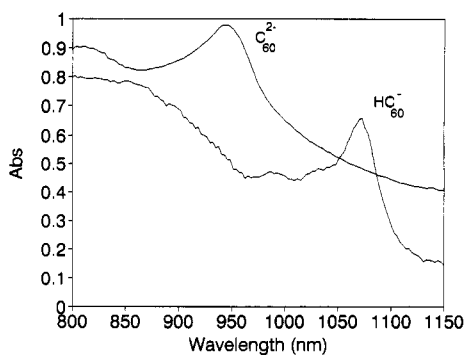
assumed to act as a strong acid in ODCB. Under these assumptions, the following equilibrium is obtained for the reaction



and  $K_a = [H^+][C_{60}^-]/[HC_{60}^+]$  is  $4 \times 10^{-4}$  (Table 1). This indicates that  $HC_{60}^+$  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  $C_{60}^-$  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  $C_{60}$  prevalent.<sup>2,3</sup> 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  $C_{60}$  spectrum (Figure 7). While protonation is a commonplace ionization pathway for even pure  $C_{60}$ , the negative ion peak at 721 is 86% of the  $C_{60}$  peak. This extra 20% above isotope abundance found with pure  $C_{60}$  indicates that some of the  $HC_{60}^+$  must remain intact to be ionized negatively. Considering the strong acidity of  $HC_{60}^+$  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<sup>13</sup> again with near-IR spectroscopy used to follow concentrations of the various species. The dianion has a broad



**Figure 8.** Near-IR spectra of the 300  $\mu$ L dianion diluted to 1.2 mL from an electrolysis of 5.6 mg of  $C_{60}$  slurry in 8.2 mL of 0.035 M  $KClO_4/MeCN$  before and after 1:1 addition of triflic acid.

characteristic absorbance at 952 nm<sup>15</sup> (Figure 8). When 1 equiv of triflic acid is added, the near-IR spectrum of the resulting product clearly resembles that of  $C_{60}^-$  with a prominent peak at 1078 nm. Two possibilities emerge, a redox reaction or a protonation ( $C_{60}^{2-} + H^+ = C_{60}^- + H^+$  or  $C_{60}^{2-} + H^+ = C_{60}H^-$ ). Since  $C_{60}H^-$  might have a spectrum similar to  $C_{60}^-$ , the results do not distinguish the two alternatives.

FAB mass spectral analysis of the dianion after addition of a 4:1 excess of triflic acid, however, helps to confirm the hydrofullerene pathway. The product after addition was a soluble orange solution with no undissolved solid. The largest mass spectral peak in the fullerene region was at 722, corresponding to  $C_{60}H_2$ , very similar to that obtained by Cahill.<sup>3</sup> The 720 and 721 mass peak abundances were 95 and 78% of the 722 peak, respectively.

### Discussion

The results presented here demonstrate that  $C_{60}^-$  is a very weak base. This is consistent with the radical anion being a large anion with delocalized electronic charge and thus resembling other very weak bases, e.g.,  $ClO_4^-$  and  $BF_4^-$ . The possibility for dimerization of  $C_{60}H^-$  has been raised.<sup>6,7</sup> In this work, no direct evidence was found to support a dimerization scheme. Indeed, if dimerization was present, we would expect to see its effect on

the electrochemistry, spectroscopy, and mass spectra. In contrast, the dianion is a relatively strong base. A new method of producing  $C_{60}H_2$  via bulk electrolysis to  $C_{60}^{2-}$  followed by protonation is proposed as an alternative to the free radical methods currently used. Stepwise protonation of the dianion indicated the first protonation is easier than the second, as expected. This agrees with the results reported by Wudl<sup>16</sup> under very different conditions ( $LiHC_{60}$  in alcohol/aqueous solutions).

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