1:3 ratio. In the wings of the spectrum, lines can be seen due to $Fe_2(CO)_6(\mu\text{-SD})_2(\mu\text{-H})$ (triangles, circles). The unexpected presence of this hydrogen-containing isotopomer could be due to a large kinetic isotope effect. Isotopic labeling (Table I) shows the presence of two strongly interacting ^{13}C nuclei. EHMO calculations lead us to assign these interactions to two terminal CO ligands trans to the bridging hydrogen (Figure 2).[4]

Radical **3** has two bridging hydrogens (2H = 26.1 G) and a large positive g shift (Figure 1A). With D_2S a 4.1-G quintet was obtained, together with additional lines in the wings belonging to $Fe_2(CO)_6(\mu\text{-SD})(\mu\text{-H})(\mu\text{-D})$ (Figure 1B). With $Fe(^{13}CO)_5$, each line of the triplet becomes a binomial septet due to the six terminal carbonyls. With H_2Se, a radical analogous to **3** was obtained containing two equivalent iron atoms and a single selenium atom as established by isotopic enrichment (Table I).

This work is currently being extended to include the photolysis of mercaptans and disulfides with $Fe(CO)_5$. Preliminary results have shown that radicals analogous to **1**, **2**, and **3** containing bridging SR groups are formed, as well as an asymmetric species, **4**.

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[4] EHMO calculations were performed on **2a**, using the atomic coordinates of $Fe_2(CO)_6(\mu\text{-CO})_3$ with two SH groups and a hydrogen [d(FeH) = 1.5 Å] replacing the bridging CO's.

Electrochemical Reduction and Oxidation of C_{60} Films

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We describe the first electrochemical study of films of C_{60} on platinum electrodes. The cyclic voltammetry (CV) of such films in tetra-n-butylammonium $[(TBA)AsF_6]/MeCN$, showing an unusual hysteresis, differs from the CV of dissolved C_{60} and suggests that large structural or resistive changes occur on reduction. The structure of C_{60} has been investigated by a number of techniques.[1-5] The CV of C_{60} dissolved in solvents such as CH_2Cl_2 and THF shows that C_{60} is reduced easily with three reversible CV reductions at −1.07, −1.43, and −1.92 V vs Fc/Fc$^+$ (where Fc is ferrocene).[4-6] No oxidation waves were seen.

C_{60} is insoluble in MeCN so that films cast on electrode surfaces [Pt, Au, or glassy carbon (GC)] can be studied in this medium. The films were prepared by evaporation on the electrode surface of a few microliters of a solution of C_{60} in CH_2Cl_2 or benzene. Typical voltammograms[7] for the reduction of C_{60} films (Figures 1 and 2) show four reduction peaks with cathodic peak potentials (E_{pc}) at −1.17, −1.39, −1.88, and −2.24 V vs Fc/Fc$^+$. The first three peak potentials are close to those reported for dissolved C_{60}[4,6] and probably represent successive one-electron-transfer reactions. However, the behavior on scan reversal is different than that of dissolved C_{60}. The anodic peaks are displaced to potentials far positive of the cathodic peaks (ca. 0.5 V for the first wave and ca. 0.2 V for the second).

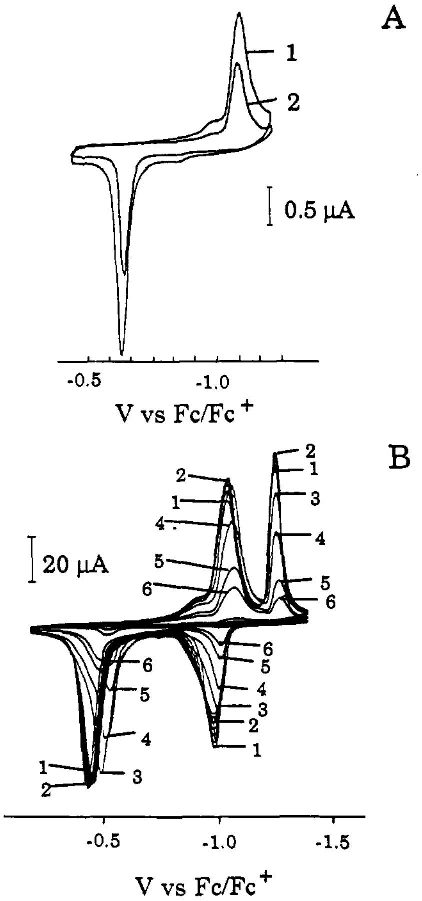

Figure 1. Cyclic voltammograms of a film of C_{60} on a platinum electrode in a solution of MeCN; supporting electrolyte: 0.1 M $(TBA)AsF_6$. Reversible reduction processes: (A) First reduction. (1) v = 200 mV/s; (2) v = 100 mV/s. (Electrode diameter: 250 μm). (B) Second reduction and effect of continuous scanning at 200 mV/s. (1) First cycle; (2) 10th cycle; (3) after 5 min; (4) after 10 min; (5) after 20 min; (6) after 25 min. (Electrode diameter: 1 mm.)

The film was stable in the presence of TBA$^+$ on Pt, Au, or GC electrodes. Continuous scanning over the first pair of waves, or over both the first and second pairs, showed small changes in peak potentials and a slow and continuous decrease in peak currents, with the waves almost gone after 2 h of scanning at 200 mV/s (Figure 1B). The film was less stable for scans beyond the third or fourth reduction waves. The peak widths at half-height, $\Delta E_{p,1/2}$ (55–70 mV for the first cathodic wave and 30–55 mV for the first anodic wave), were significantly less than those expected for a surface-confined species (91 mV)[8] at scan rates (v) below 200 mV/s. In this region of v a plot of the peak current, i_p, against v was linear and intersected the origin, as expected for a surface-confined species. To obtain a more quantitative estimate of the state of reduction of the film, a known amount of C_{60} (2 μL of 1 mM C_{60} in benzene) was dropped on a 3-mm-diameter GC

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[7] Electrochemical experiments were conducted in a glovebox under a He atmosphere. The counter electrode was a Pt foil; a Ag wire was used as a quasi-reference electrode. All potentials are referenced to the Fc/Fc$^+$ couple, which was used as an internal standard. Electrochemical experiments and working electrode fabrication followed the procedures described in the following: Garcia, E.; Kwak, J.; Bard, A. J. *Inorg. Chem.* **1988**, *27*, 4377.

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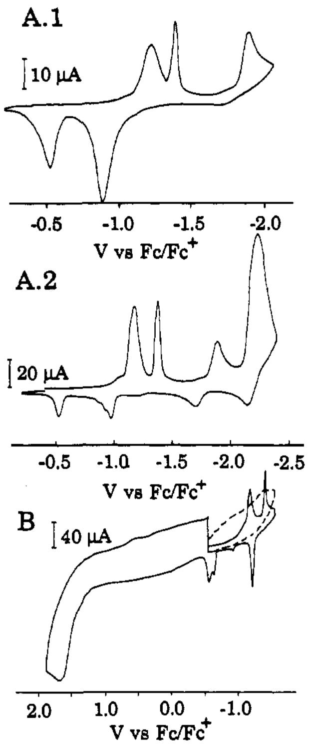

Figure 2. Cyclic voltammograms of a film of C_{60} on a platinum electrode (1-mm diameter) in a solution of MeCN [supporting electrolyte: 0.1 M $(TBA)BF_4$] showing (A) (1) third reduction; (2) fourth reduction; and (B) oxidation processes. Solid curve, first scan; dashed curve, second scan; v = 200 mV/s.

electrode. This amount represents 2.7×10^{-8} mol of C_{60}, or about 16 monolayers (assuming a 10-Å diameter of the molecule).[9] The integrated areas of the first reduction and reoxidation waves were 2.56 and 2.37 mC/cm^2, respectively, near the values expected for a one-electron transfer. Similarly the second reduction and reoxidation waves were 1.19 and 1.34 mC/cm^2, i.e., about 50% of the first waves. For a number of different electrodes, the integrated second-wave areas were typically 50–70% of the first waves. For $v \leq 200$ mV/s, the E_{pc} values were essentially independent of v, while E_{pa} shifted toward less negative values by about 90 mV (first peak) and 50 mV (second peak) with increasing v. At higher v, i_{pc} and i_{pa} increased more slowly with v and the peaks broadened, suggesting the onset of kinetic limitations in the electrode processes.

The CV behavior depended upon the nature of the cation in the supporting electrolyte. In the presence of Na^+, Cs^+, or TEA^+ (tetraethylammonium) the waves decreased markedly after a few scans over the first reduction and reoxidation waves. However, with THA^+ (tetra-*n*-hexylammonium) or TOA^+ (tetra-*n*-octylammonium) very stable films were obtained.

A scan of the C_{60} film in 0.1 M $(TBA)BF_4$/MeCN toward positive potentials showed an oxidation wave at about +1.6 V vs Fc/Fc$^+$ (Figure 2B). No cathodic wave was associated with this oxidation wave, and after cycling over this wave, the electroactivity of the film was diminished, suggesting instability of the oxidized C_{60}.

The first reduction and reoxidation waves are separated by about 0.5 V, are narrower than the usual surface waves, and shift relatively little at small v. Similar waves showing hysteresis, although with significantly smaller splittings, have been found for several systems, e.g., TTF–TCNQ films,[10-13] and were attributed to large structural rearrangements of the surface films following the electron-transfer process. Resistance changes in the films occurring during the redox processes may also be important. Thus we propose the following scheme for the first reduction and reoxidation waves:

$$\begin{tikzcd} (C_{60})_A + TBA^+ + e \arrow[r, shift left] & (TBA^+C_{60}^-)_A \arrow[l, shift left] \arrow[d] & \text{reduction wave} \\ (C_{60})_B + TBA^+ + e \arrow[u] \arrow[r, shift left] & (TBA^+C_{60}^-)_B \arrow[l, shift left] & \text{oxidation wave} \end{tikzcd}$$

A and B represent two different structural forms, where B is more stable for the reduced film and A is the stable form of the C_{60} film. The large splitting between the waves implies significant energies of reorganization for both forms and suggests that the C_{60} films are highly organized. A similar mechanism could be proposed for the second reduction and reoxidation waves, which show smaller splittings. C_{60} deposited on indium tin oxide displays a UV band (344 nm) slightly shifted from that in solution.[2] Upon reduction [at the first wave in MeCN/$(TBA)BF_4$] the band shifts by 6 nm to longer wavelengths. The C_{60} film is not stable after extended reduction at the first and second waves, or briefer reduction at the third and fourth waves, or upon oxidation of C_{60}. These preliminary studies also suggest that tetra-*n*-alkylammonium cations are important in stabilization of the reduced film. Additional studies are under way to probe the properties of C_{60} films and elucidate the mechanism of their redox processes.

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Template-Directed Modification of Single-Stranded DNA by Psoralen-Tethered Oligonucleotides: Sites of Photoadduct Formation Analyzed by Sequence-Specific and Sequence-Random Cleavage

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Numerous agents have been targeted to react sequence specifically with single-stranded[1] or double-stranded[2] nucleic acids

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