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Electrochemically-Reversible, Single-Electron Oxidation of C_{60} and C_{70}

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Since the large-scale method for the preparation of the fullerenes became available in 1990,[1] its rich redox chemistry has been explored by many.[2-7] Of particular interest has been its cathodic electrochemistry,[2-5] in part due to the observation of superconductivity for some of the triaionic states of C_{60}.[8] While the cathodic electrochemistry has proven to be very rich, culminating last year in the observation of C_{60}^{6-},[4-6] its anodic electrochemistry remains largely unexplored.[3,7,9]

The first reported study of the anodic electrochemistry of C_{60} of which we are aware was really performed for a film of this compound, not for C_{60} in solution.[7] A chemically-irreversible oxidation wave for this film was detected in 0.1 M $(TBA)BF_4$/MeCN at +1.6 V vs Fc/Fc$^+$.[7] Not only was there a total lack of a corresponding cathodic wave for this oxidative process, but also, repeated cycles resulted in diminished electroactivity of the film. These results were interpreted as resulting from the chemical instability of the oxidized C_{60}. The next report of the anodic electrochemistry of C_{60} and C_{70} of which we are aware appeared shortly after.[3] In this work, cyclic and differential pulse voltammograms (CV and DPV, respectively) revealed chemically-irreversible oxidation waves at $E_{ox} = +1.30$ V vs Fc/Fc$^+$ for both fullerenes.[3] The oxidations remained irreversible at scan rates of up to 50 V/s and at temperatures down to –15 °C[3]. More importantly, the peak current intensities for these irreversible oxidations were about 4 times larger than the corresponding one-electron quasireversible waves for the cathodic processes.[3] This 4:1 relative ratio was confirmed by controlled-potential coulometry of both C_{60} and C_{70}, which indicated that four electrons were abstracted at a potential of +1.44 V vs Fc/Fc$^+$[3]. These results led the authors to conclude also that the oxidized fullerenes were chemically unstable, even on the time scales associated with fast scan rates and at low temperatures. They did not offer explanations for the unusual observation of a four-electron anodic wave. It should be pointed out that gas-phase reactions attributed to C_{60}^{+}, C_{60}^{2+}, and C_{60}^{3+} have been reported by numerous authors.[9]

The last report of anodic electrochemistry of mixtures containing C_{60} and C_{70} appeared very recently.[10] This is the only report in which a claim is made about having observed chemically-reversible oxidations of these fullerenes in solution. However, these authors did not quantify their assertions of chemical reversibility using anodic and cathodic peak currents. Their results, which were obtained in CH_2Cl_2 and in mixtures of CH_2Cl_2 with dimethylamine (DMA) at –65 °C, indicated that the anodic processes occurred in two steps, each one corresponding to a two-electron process, thus leading to an overall oxidation to a tetracationic state. They stressed the agreement of these results with those of Kadish et al.,[3] who only observed four-electron oxidations of the fullerenes. The only other report of reversible anodic electrochemistry of a fullerene of which we are aware is for a totally different system, C_{76}.[11]

Either OSWV[12] or CV of C_{60} in 0.1 M $(TBA)PF_6$/TCE at room temperature exhibits a chemically-reversible, one-electron oxidation wave at +1.26 V vs Fc/Fc$^+$ at room temperature, see Figures 1a–d.[13] Figure 1b shows this reversible anodic wave along with the reversible first cathodic wave corresponding to the formation of the monoanion radical of C_{60}. It can be clearly appreciated that these two waves have the same current intensity, indicating that they both correspond to the transfer of the same number of electrons. This result is also evident from the OSWV result shown in Figure 1d. Under identical conditions, a one-electron, chemically-reversible oxidation is also observed for C_{70}, see Figures 1e–h. The chemically-reversible oxidation of C_{70} occurs 60 mV more negative than that for C_{60}, at +1.20 V vs Fc/Fc$^+$. To our knowledge, this is the first report of a chemically-reversible, one-electron oxidative process for either one of these fullerenes. Both oxidations are electrochemically quasireversible, with $\Delta E_{pp} \simeq 80$ mV. It should be pointed out that although the BAS-100W analyzer is presumably compensating 100% for solution internal resistance, ΔE_{pp} is also 80 mV for the ferrocene added as an internal potential standard, see Figures 1c–f. The sizable and measurable 60-mV potential difference between the oxidation potentials of these two fullerenes contradicts the observations previously reported in benzonitrile,[3] in which both fullerenes were reported to have the same oxidation potential of +1.30 vs Fc/Fc$^+$. The potential difference between the first cathodic and the first anodic waves for these fullerenes (which can be interpreted as a measure of the energy difference between the HOMO and the LUMO in solution) is 2.32 V for C_{60} and 2.22 V for C_{70}.

To establish the chemical reversibility of the first oxidation wave of C_{60} and C_{70}, the corresponding anodic and cathodic currents for this couple were measured as a function of the scan

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(13) All experiments were conducted under high-vacuum conditions, ~10^{-5} mmHg. The C_{60} sample was extracted from soot purchased from Strem Chemicals, Inc. and purified by column chromatography according to the procedure described in ref 14. The C_{70} sample, used as received, was 98% guaranteed minimum purity, vacuum-dried material and was purchased from MER Corp. TCE (99%) was purchased from Aldrich and dried first by refluxing over $CaCl_2$ under a nitrogen atmosphere for 3 days before use. Typically, 1 mg of C_{60} or C_{70} in 3 mL of TCE was placed in a home-built high-vacuum electrochemical cell.[4] Predried 99% pure TCE was further dried over P_2O_5, deareated by three freeze–pump–thaw cycles, pumped to 10^{-5}–10^{-6} mmHg while frozen with liquid nitrogen, and vapor-transferred directly into the electrochemical cell. All voltammograms were recorded using a BAS-100W electrochemical analyzer interfaced with a Hewlett-Packard HP ColorPro plotter. A conventional three-electrode configuration was used, with a 3-mm-diameter glassy carbon as the working electrode, a platinum wire as a counter electrode, and a silver wire as a pseudo reference electrode. All potentials were referenced to the redox couple for internal ferrocene, Fc/Fc$^+$.

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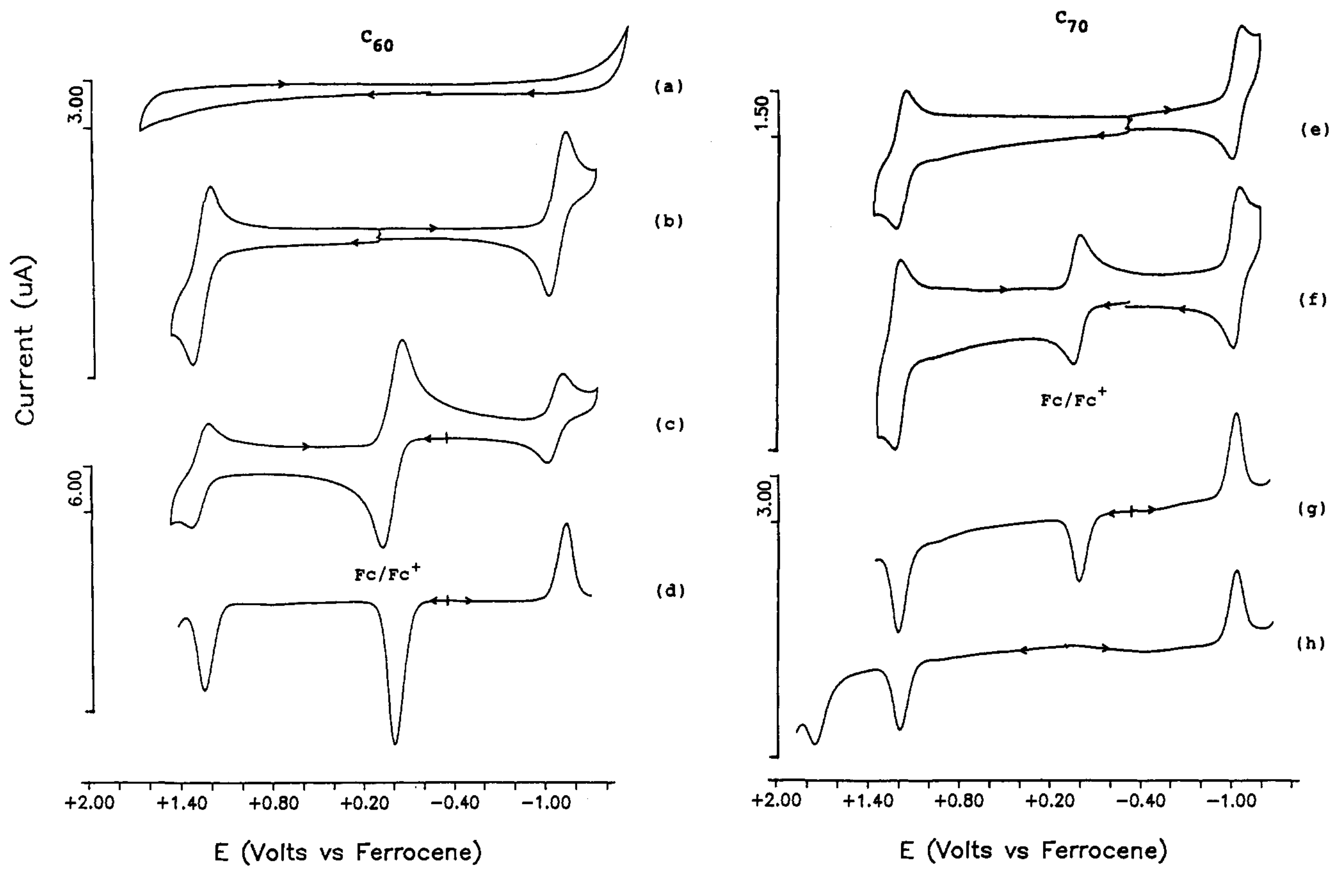

Figure 1. CV and OSVW scans for C_{60} and C_{70} in 0.1 M $(TBA)PF_6$/TCE at room temperature. CVs were run at a scan rate of 100 mV/s, while OSWVs were run at 60 mV/s. (a) CV of background solvent–electrolyte system. (b) CV with C_{60}, no ferrocene added. The cathodic and anodic cyclic scans were performed separately. (c) Same as b after addition of ferrocene. (d) OSWV of the solution in c. Cathodic and anodic scans were performed separately. (e) CV of C_{70} without added ferrocene. Cathodic and anodic cyclic scans were performed separately. (f) Same as e after addition of ferrocene. (g) OSWV of the solution in f. Cathodic and anodic scans were performed separately. (h) OSWV of the solution as in e, without ferrocene added, scanned to more positive potential to show the second oxidation wave for C_{70}.

rate between 10 and 100 mV/s. The ratios determined (i_a/i_c) were all equal to 1 within experimental error (1 ± 0.1). Therefore, the cation radicals generated electrochemically are relatively long-lived on the voltammetric time scale at room temperature. The lifetime of the radicals can be estimated to be ≥0.5 min.

Most interestingly, scanning the potential more positive than that of the first reversible oxidation for C_{70} resulted in the observation of a second, one-electron oxidation of C_{70}, $C_{70}^{\bullet +} \rightarrow C_{70}^{2+}$, at a potential of +1.75 V, see the OSWV in Figure 1h. It is interesting to note that the potential difference between the first and the second anodic waves is 550 mV, close to the values previously reported for the separations between consecutive cathodic waves of C_{60} and C_{70}.[4] This second wave does not appear to be chemically reversible, as judged by preliminary cyclic voltammetric studies. Attempts to observe the second oxidation wave for C_{60} have not been successful. This is not unexpected since the second oxidation for C_{70} was observed at the very limit of the available potential window. Since the second oxidation of C_{60} should be even more positively shifted, it is not surprising that it is not observed at all.

We are currently using this solvent–electrolyte system to generate the cation radicals of both C_{60} and C_{70} to be studied by UV–vis and ESR spectroscopic techniques.

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