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Reversible Fullerene Electrochemistry: Correlation with the HOMO-LUMO Energy Difference for C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}

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Abstract: Reversible one-electron oxidations and reductions have been observed by Osteryoung square wave voltammetry (OSWV) for the three higher fullerenes C_{76}, C_{78}, and C_{84} in 1,1,2,2-tetrachloroethane (TCE) containing 0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF_6). Potentials are reported versus the internal ferrocene redox couple. Under these conditions C_{76} displays a reversible oxidation at 0.81 V, an irreversible oxidation at 1.30 V, and two reversible reductions at −0.83 and −1.12 V. The oxidations of C_{78} show evidence of two species, which is consistent with the proposed isomerism for C_{78}. The predominant C_{78} species shows a reversible oxidation at 0.95 V, an irreversible oxidation at 1.43 V, and two reversible reductions at −0.77 and −1.08 V. The minor species displays a reversible oxidation at 0.70 V and an irreversible oxidation at 1.17 V, while the reductions seem to coincide with those of the other isomer. Finally, C_{84} yielded an oxidation at 0.93 V and three reversible reductions at −0.67, −0.96, and −1.27 V. A comparison of the differences in potential of the first reduction and first oxidation, ($E_{ox} - E_{red}$), shows that this difference becomes generally smaller as fullerene size increases, with the exact order being $C_{60} > C_{70} > C_{78}(C_{2v}) > C_{76} > C_{84} > C_{78}(D_3)$. The experimental ($E_{ox} - E_{red}$) differences correlate well with calculated HOMO-LUMO separations for a series of five fullerenes.

Introduction

Since the initial report of the reversible, stepwise, one-electron reductions of C_{60} to the C_{60}^{2-} ion,[1] continued study has culminated in the recent observation of reversibly produced C_{60}^{6-}, C_{70}^{6-}, C_{60}^{+}, and C_{70}^{+}.[2,3] Meanwhile, the higher fullerenes C_{76}, C_{78}, and C_{84}[4] have also begun to be characterized electrochemically. Although there are now several reports about the reversible reductive electrochemistry of these new carbon cages,[5–11] only one report has been made on reversible oxidative electrochemistry.[12] Initial reports on the electrochemistry of metal-encapsulated fullerenes are also beginning to appear.[13–15]

C_{76} has been shown to be a chiral molecule of D_2 symmetry[16] which has very recently been kinetically resolved.[17] The two enantiomers of this molecule should give identical electrochemistry, thus simplifying the interpretation of data collected for this fullerene. Spectroscopic and structural characterization of C_{76} is rapidly appearing in the literature.[18–23] Of the higher

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fullerenes under consideration, C_{78} presents the most vexing isomer problem. As many as three isomers have been reported (C_{2v}, C_{2v}', and chiral D_3), and the number of observed isomers, as well as the isomer ratio, seems to vary according to the exact preparation.[24-26] For example, the pressure of the backing gas of the synthetic carbon arc has been demonstrated to be one of the influencing factors determining which isomers form and in what amounts.[27] Also, a theoretical treatment of the problem has noted that the relative stabilities of the C_{78} isomers are temperature dependent.[28] Finally, C_{84} presents an isomer problem of difficulty intermediate between C_{76} and C_{78}. The two isomers that are known (D_{2d} and chiral D_2)[25,26] appear to be produced in consistent relative ratios (D_2:$D_{2d} \cong 2$:1) in the soots produced by various groups. As with the previous two fullerenes, the chiral isomer of C_{84} has been kinetically resolved,[17] and likewise, characterization is well underway.[29-34] The presence of multiple isomers of C_{78} and C_{84} could be expected to lead to multiplicities in the observed electrochemistry owing to differences in the electronic structure of the different isomers.

Here we report further on the electrochemical oxidations and reductions of the higher fullerenes in solution, providing a full data set of ($E_{ox} - E_{red}$) for C_{76}, C_{78}, and C_{84} for the first time. Combining these data with those already reported for C_{60} and C_{70} yields a full series of data on the size of the "electrochemical gap" between the first oxidation and first reduction of each fullerene and fullerene isomer. The trend observed is related to the theoretically calculated electronic structures of these species in terms of their HOMO-LUMO separations,[35-41] and the present experimental electrochemistry is discussed in relationship to calculated results.

Experimental Section

Fullerene Isolations. C_{76}, C_{78}, and C_{84} were isolated by HPLC, using two Waters model 510 pumps with a Waters U6K injector and a Waters 996 Photodiode Array as a detector. System control and data acquisition were coordinated using Waters Millennium software. Starting with an extract enriched in higher fullerenes (15–20%) dissolved in 100% toluene, the fullerenes were separated on a BuckyClutcher column (10 × 250 mm) (Regis, Morton Grove, IL) using a 60/40 hexane/toluene mobile phase at 2 mL/min, with 0.35-mL injections every 5 min. This yielded four fractions, enriched in C_{60}, C_{70}, C_{76}/C_{78} (50%, with the main impurity being C_{70}), and C_{84} (80%, main impurity C_{76}/C_{78}), respectively. The C_{60} and C_{70} fractions were saved for later use. The C_{84} fraction was concentrated and re-injected using the same parameters to yield a solution of pure C_{84} (98%).

The C_{76}/C_{78} fraction was concentrated and re-injected, using a 50/50 hexane/toluene mobile phase at 3.0 mL/min with 0.4-mL injections every 7 min, to yield a fraction enriched to 85% C_{76}/C_{78}. This mixture was then resolved on the BuckyClutcher column using a 70/30 hexane/toluene mobile phase at 2 mL/min, with 0.2-mL injections every 21 min. The result was three fractions: pure C_{76} (96%), pure C_{78} (93%), and a highly enriched mixture of C_{76} and C_{78}, which was concentrated and re-injected.

All intermediate fractions and final solutions were analyzed using a Nova-pak C_{18} 3.9 × 300 mm column and the above equipment, with a mobile phase of 50/50 methanol/toluene at a flow rate of 2 mL/min. Assuming equal extinction coefficients, the C_{78} fraction contains two isomers in an approximately 5:1 ratio. The similarity of our result to that of Diederich[24] *et al.* suggests that we are also observing a 5:1 C_{2v}:D_3 mixture of isomers.

DCI mass spectra (with methane carrier gas) collected on a MAT 95 high-resolution double-focusing mass spectrometer support the HPLC evidence that the samples are fullerene pure.

Electrochemical Measurements. The electrochemical cell used has been described in detail elsewhere.[2] A glassy carbon working electrode (3 mm in diameter), a platinum wire counter electrode, and a silver wire pseudo reference electrode were employed in all measurements. In addition, ferrocene was added at the end of each experiment as an internal potential standard. The supporting electrolyte ((TBA)PF_6, >99%) was purchased from Fluka, recrystallized twice from an ethanol:water (95:5) solution, and dried in a vacuum oven.

The solvent, 1,1,2,2-tetrachloroethane (TCE), 98%, was purchased from Aldrich, refluxed for 2 days over CaH_2, and dried over P_2O_5 under high vacuum (10^{-5}–10^{-6} mmHg). In every case the electrochemical cell was pumped under high vacuum for at least 2 h while containing the fullerene and electrolyte, before the solvent was vapor transferred through the vacuum line.

A BAS-100W Electrochemical Analyzer, interfaced with a Hewlett-Packard ColorPro plotter, was used for all of the voltammetric studies.

The fullerene solutions were between 0.3 and 0.2 mM. Cyclic voltammograms were recorded at 100 mV/s and the OSWV were obtained using a sweep width of 25 mV, a frequency of 15 Hz, and a step size of 4 mV. All measurements were performed at room temperature.

Results and Discussion

The CV's of C_{76} and C_{78} are shown in Figure 1 and the corresponding OSWV's of C_{76}, C_{78}, and C_{84} are presented in Figure 2. From Figure 1, it can be seen that the features of the first two reversible reductions and the first reversible oxidation of C_{76} and C_{78} are clearly observed. For C_{84} the results were less definitive due to a low current intensity and limited sample. In fact, none of the voltammetric responses in Figure 1 have large currents, mainly due to very low concentrations of these solutions. Nevertheless, it was possible to detect reasonable

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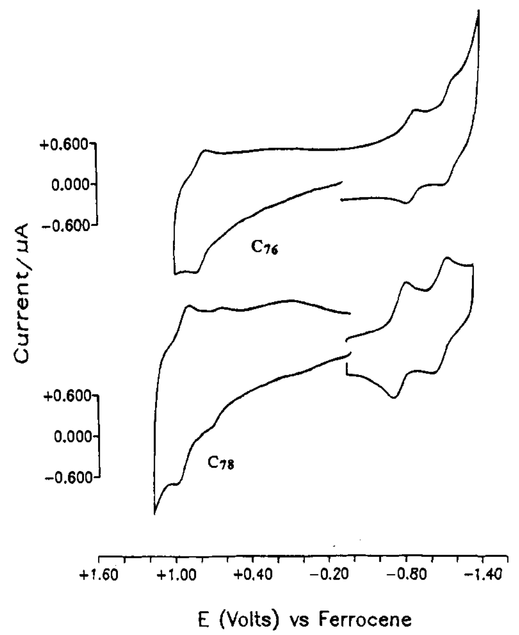

Figure 1. 1. Cyclic voltammograms for (a) C_{76} and (b) C_{78} in 0.1 M ((TBA)PF_6) TCE, recorded at a scan rate of 100 mV/s.

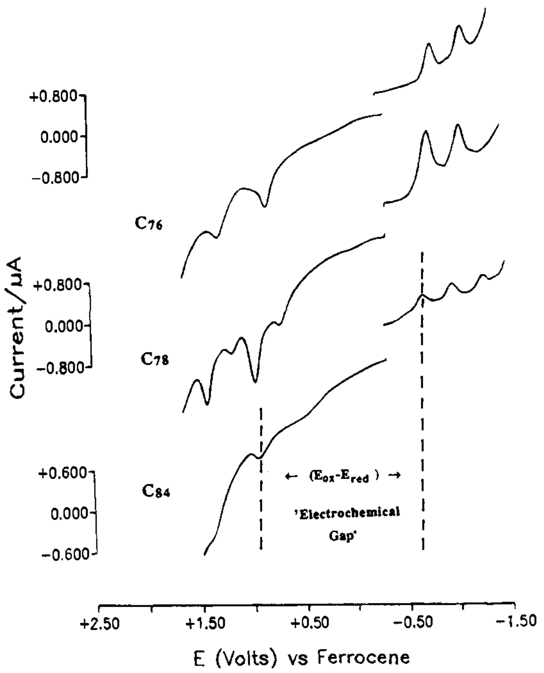

Figure 2. OSWV for (a) C_{76}, (b) C_{78}, and (c) C_{84} recorded at 60 mV/s.

currents for all three fullerenes, including C_{84}, using OSWV, as displayed in Figure 2. Additional oxidations are also evident in the OSWV of C_{78}, with four being clearly observed in the figure. It is also clear that under these conditions OSWV resolves two reductions for C_{76} and C_{78} and three in the case of C_{84}. Where possible, reversibility was established on the basis of ΔE_{PP} values, which ranged between 60 and 100 mV (Table 1). It was not possible to quantitate anodic and cathodic currents due to the relatively small currents that were observed in the CV's. The half-wave potentials reported in Table 1 were determined from the OSWV measurements. For comparison, corresponding values for C_{60} and C_{70} are also contained in Table 1, with all the data being obtained under identical conditions.[3]

There have been several reports of reversible reduction processes occurring for these higher fullerenes in several different solvents.[5-8,11] However, only chemically irreversible processes have been observed at potentials more anodic than 700 mV *vs* the ferrocene/ferricenium couple (Fc/Fc$^+$). It should also be noted that the results reported in refs 7 and 8 are in contradiction with those published earlier by Li *et al.* for C_{76}, who found an easy and reversible oxidation at −46 mV *vs* Ag/AgCl.[12] To our knowledge, this discrepancy has not been resolved in the open literature. Although it was possible to establish the electrochemical quasireversibility and chemical reversibility of the first oxidations of C_{76} and C_{78}, it was not possible to do so here for C_{84} due to the small currents observed. All of the reduction processes were also chemically reversible and electrochemically quasireversible. The second oxidation processes for C_{76} and C_{78} were chemically irreversible under these conditions, similar to the behavior already reported for C_{70}.[3]

Table 1. Half-Wave Potentials, Peak-to-Peak Potential Differences, and ($E_{ox} - E_{red}$) for the Fullerenes in This Study, in TCE (0.1 M TBA(PF_6)) Using Ferrocene as an Internal Potential Reference and a Glassy Carbon Working Electrode

	$E_{1/2}$ *vs* Fc/Fc$^+$ and (ΔE_{PP}), in Volts					
	+2/+1	+1/0	0/−1	−1/−2	−2/−3	$E_{1/0} - E_{0/-1}$
C_{60}[a]	–	1.26	−1.06	–	–	2.32
C_{70}[a]	1.75	1.20	−1.02	–	–	2.22
C_{76}	1.30	0.81(0.07)	−0.83(0.08)	−1.12(0.07)	–	1.64
C_{78}[b]	1.43	0.95(0.07)	−0.77(0.10)	−1.08(0.09)	–	1.72
C_{78}[c]	1.17	0.70(0.06)	−0.77(0.10)	−1.08(0.09)	–	1.47
C_{84}	–	0.93	−0.67(0.07)	−0.96(0.08)	−1.27(0.07)	1.60

[a] The ΔE_{PP} for oxidations and reductions of C_{60} and C_{70} have already been reported to be around 0.08 V under these conditions.[3] [b] Major isomer. [c] Minor isomer.

Most interestingly, each of the anodic waves for C_{78} seems to be accompanied by a smaller, cathodically-shifted wave (Figure 2) for a total of four anodic processes. The potential separation between the small and the large wave for each pair is 0.25 V for the first oxidation and 0.26 V for the second. Comparing the current intensities of the large and small waves in both of these "double-waves" yields a ratio of about 5. This value is in excellent agreement with the reported (C_{2v}/D_3) isomeric ratio for C_{78}, as found experimentally by Diederich *et. al.*[4] The D_3 isomer would thus be easier to oxidize than the corresponding C_{2v} isomer by about 0.25 V. Although such an electronic difference between the two isomers might seem too large upon initial inspection, comparison with calculated HOMO energies shows reasonable agreement with this result.[40] These calculations, using an STO-3G basis set in a HF SCF level of theory, predict a HOMO difference of 0.5 V between these two isomers.[40] Although the calculation overstates the difference between the isomers by twice the observed value when compared with the experimental electrochemical results, it correctly predicts that the lower abundance D_3 isomer should be easier to oxidize. Considering that solvent and counterion effects are present for the electrochemical experiments, but not considered in the calculations, the agreement between experiment and calculation is not unreasonable. Furthermore, the theoretical results are also in agreement with the experimental observations made on the cathodic scan. No extra waves of lower current were observed in the cathodic scan, indicating that the isomers, if present, reduce at comparable potentials under these experimental conditions. The calculations predict that the computed LUMO's have comparable energies for both of these isomers.[40] The largest predicted difference expected would be about 0.1−0.2 V, and such agreement between experimental and theoretical results lends additional credence to the interpretation of the oxidative double-waves.

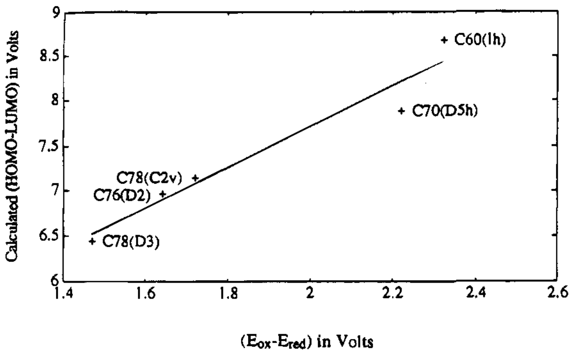

Figure 3. Plot of the calculated HOMO-LUMO energy separations[39-41,43] *vs* the experimentally determined potential differences between the first oxidation and the first reduction ($E_{ox} - E_{red}$) for the fullerenes.

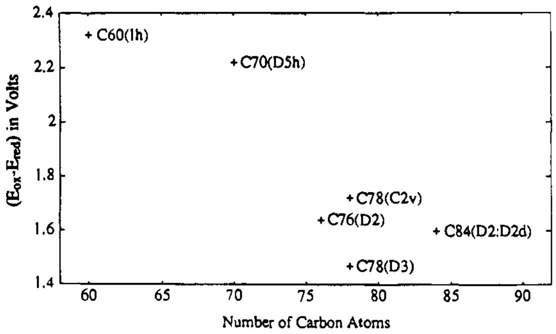

Figure 4. Plot of ($E_{ox} - E_{red}$), *vs* the number of carbon atoms in the fullerene.

Since the correlation between the experimentally determined electrochemical potentials and the calculated HOMO-LUMO energies for C_{78} showed such reasonable agreement, the potential difference between the first oxidation and the first reduction was plotted *vs* the available calculated HOMO-LUMO energy separation for all the fullerenes.[39-41] Figure 3 demonstrates that the electrochemically determined potential differences correlate very well with the calculated HOMO-LUMO separations for the series of C_{60}, C_{70}, C_{76}, and $C_{78}(C_{2v}/D_3)$.

In TCE it was not possible to resolve separate reductions or oxidations for the C_{84} isomers in the present study, although it is known that D_2 and D_{2d} symmetry isomers of this fullerene are formed in a 2:1 ratio. Previously, cathodic electrochemistry of these isomers in benzonitrile and *o*-dichlorobenzene showed signs of only slight separation of waves for the isomers; however, distinctly different reduction processes have been detected in pyridine and in DMF/toluene mixtures.[5-8,11] Therefore, it appears there is a pronounced solvent effect in the voltammetric resolution of the isomeric species for C_{84}. An entry for C_{84} is absent from Figure 3 because an appropriate STO-3G calculation is not available, although the data in Table 1 and the correlation in Figure 3 together predict an STO-3G HOMO-LUMO energy difference of 6.8 V for both isomers of this fullerene. Calculations performed using TBMD and MNDO methods,[42] although not numerically comparable to the STO-3G results, have yielded values for the HOMO-LUMO energy differences of both the D_2 and D_{2d} isomers, indicating that this gap is approximately the same for both isomers. These results are consistent with the observation of single peaks for both the reversible oxidation and reduction of C_{84} observed in Figure 2.

One final relationship considered is that between ($E_{ox} - E_{red}$) and the number of carbon atoms in the fullerene. This plot is shown as Figure 4. As the number of carbon atoms in the molecule increases, one predicts that the HOMO-LUMO gap would decrease, eventually leading to the band structure of graphite. Indeed, Figure 4 demonstrates this general trend, although the relationship is not strictly linear.

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[43] The theoretically determined energies in au were used to calculate theoretical electrochemical potentials in volts for Figure 3 using the following relationships: $\Delta G/n = -F(E_{ox} - E_{red})$, $\Delta G/n = \Delta E_{HOMO-LUMO}N_A$ where $\Delta G/n$ is the HOMO-LUMO free energy difference per mole of fullerene, F is the Faraday constant, ($E_{ox} - E_{red}$) is the difference in potential between the first oxidation and first reduction, $\Delta E_{HOMO-LUMO}$ is the calculated HOMO-LUMO energy difference, and N_A is Avogadro's number.