J. Am. Chem. Soc. **1994,** *116,* 1359–1363

Redox Properties of Organofullerenes

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Received August 31, 1993[⊗]

Abstract: A comparative study using cyclic, differential pulse, and Osteryoung square wave voltammetry is presented on organofullerenes derivatized with oxygen-, carbon-, and silicon-containing groups. Electron affinities of the organofullerenes increase with increasing electronegativities of the attached atoms. $C_{60}O$ is a stronger electron acceptor than C_{60}, although its electroreductions are CV irreversible. In the carbon-derivatized C_{60}, hybridization of the attached carbon atoms and electron-withdrawing groups also affect their reduction potentials. As previously described for C_{60}, no CV reversible electrooxidation waves were observed for all organofullerenes studied. Electron-donating groups, such as alkyl and silyl, significantly lower the oxidation potentials of the organofullerenes. The AM1 molecular orbital calculations were performed on C_{60} and selected organofullerenes. The first and second reduction potentials correlate well with the LUMO energy levels, while the third reduction potentials correlate better with the LUMO+1 energy levels. The peak oxidation potentials also show a good linear correlation with the HOMO energy levels.

Buckminsterfullerene, C_{60}, is an electronegative molecule which accepts up to six electrons in solution.[1] Wudl et al. proposed that C_{60} can be derivatized with organic groups while retaining its unique electronic properties.[2] These C_{60} derivatives, so-called fulleroids, exhibited reversible electroreductions with small negative potential shifts relative to C_{60}.[2,3] On the other hand, Fagan et al. studied the electrochemistry of the metal derivatives of C_{60} and found that the electronegativity of C_{60} was greatly reduced by the electron donation of the metals.[4] To design new organofullerenes for applications to material science[5] and biochemistry,[6] one should know how the organic groups on the C_{60} affect its redox properties. Although a variety of organofullerenes have been published from different laboratories, there is little information on their electrochemical properties.[7-10] We describe here the relationship between the structures and redox properties on the basis of a comparative electrochemical study of various organofullerenes **1–10**. These compounds are singly substituted with oxygen-, carbon-, and silicon-containing organic groups which construct three- or five-membered rings on the C_{60}. The AM1 molecular orbital calculations have been carried out on selected organofullerenes to examine the linear correlations of the redox potentials with MO energy levels.

Experimental Section

A C_{60}/C_{70} mixture was prepared according to the graphite-arc vaporization method.[11] Pure C_{60} was obtained using the reported procedure.[12] Toluene and 1,2-dichlorobenzene were distilled from sodium under argon and reduced pressure, respectively. Organofullerenes **2**,[3d] **5**,[7] **6**,[8] **7**,[8] **8**,[2] **9**,[9] and **10**[10] were prepared according to literature procedures. Tetra-*n*-butylammonium hexafluorophosphate was recrystallized three times from EtOH and dried in a vacuum oven at 100 °C overnight. Ferrocene was sublimed. UV–vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were taken with a Perkin-Elmer 1600 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on either a JEOL JNM-EX270 or Bruker AC400D spectrometer; all

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[⊗] Abstract published in *Advance ACS Abstracts.* January 15, 1994.

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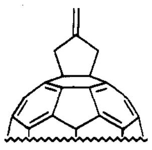

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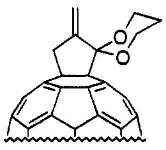

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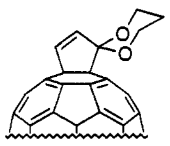

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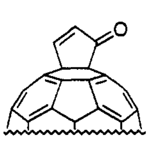

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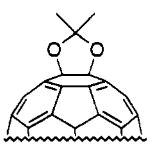

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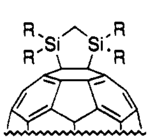

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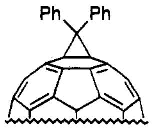
7 (R = Mes)



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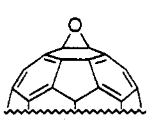

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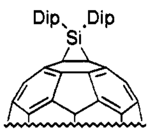

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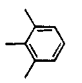

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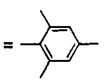

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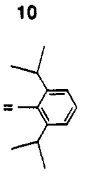

samples were internally calibrated with TMS. FAB mass spectra were recorded on a Shimadzu/Kratos Concept-1S or JEOL SX-102 spectrometer. Elemental analyses were obtained at the Institute for Molecular Science. HPLC was performed with a Shimadzu LC-8A preparative system.

Trimethylenemethane (TMM) Adduct (1). A solution of C_{60} (100 mg, 0.139 mmol) in dry toluene (150 mL) was treated with tetrakis(triphenylphosphine)palladium (160 mg, 0.139 mmol) and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate[13] (258 mg, 1.39 mmol) under argon at room temperature. The solution became dark green due to the formation of $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$[14a] and was heated to reflux for 48 h. The solvent was evaporated, and the residue was purified by flash chromatography (silica gel, hexane/toluene, 10:1) to give a mixture of unreacted C_{60} and TMM adducts. The mixture was separated by HPLC (conditions: C_{18} reversed phase, 5 μm, 250 × 20 mm; flow rate, 10 mL/min; pressure, 54 kgf/cm²; eluant, 55:45 toluene/methanol; detection, at 320 nm; 5-mL injection loop), affording $(TMM)_2C_{60}$ (34 mg, 30%), 1 (35 mg, 33%), and unreacted C_{60} (27 mg, 27%) (retention times: 11.8, 14.0, and 17.0 min, respectively). A CS_2 solution of 1 was poured into pentane, and the mixture was centrifuged. The resulting precipitate was washed with pentane, centrifuged, and dried in a vacuum oven at 100 °C: ^1H NMR (CS_2, $CDCl_3$) δ 5.61 (quintet, J = 1.65 Hz, 2H), 4.29 (t, J = 1.65 Hz, 4H); ^{13}C NMR (CS_2, CD_2Cl_2) δ 156.46, 147.19, 146.06, 145.92, 145.55, 145.44, 145.18, 145.11, 144.40, 143.79, 142.95, 142.40, 142.07, 141.86, 141.66, 139.95, 137.30, 135.39, 69.24, 48.70; FAB MS m/z 777–774 (M^+), 724–720 (C_{60}); FT-IR (KBr) 2954 (w), 2920 (w), 1462 (w), 1426 (m), 1184 (w), 897 (m), 768 (m), 738 (w), 714 (w), 594 (w), 574 (m), 554 (w), 526 (s), 505 (w), 478 (w) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 212, 256, 300, 335, 404 (sh), 432, 637, 669, 691, 702. Anal. Calcd for $C_{64}H_6\cdot(C_5H_{12})_{0.6}$: C, 98.38; H, 1.62. Found: C, 98.47; H, 1.80.

Cyclopentenone Ketal Derivative (3). A toluene solution (100 mL) of C_{60} (50 mg, 0.069 mmol) and cyclopropenone 1,3-propanediyl ketal[15] (7.8 mg, 0.069 mmol) was heated to reflux overnight. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, toluene) to afford 3 (24 mg, 42%) and unreacted C_{60} (18 mg, 36%). Further purification was achieved by precipitation as described above: ^1H NMR (CS_2, $CDCl_3$) δ 7.61 (d, J = 5.94 Hz, 1H), 7.33 (d, J = 5.96 Hz, 1H), 4.55 (m, 2H), 4.35 (m, 2H), 2.45 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (CS_2, $CDCl_3$) δ 154.72, 153.64, 147.16, 147.02, 146.18, 146.09, 146.00, 145.92, 145.84, 145.81, 145.76, 145.35, 145.16, 145.02, 144.51, 144.19, 142.88, 142.56, 142.46, 142.31, 142.26, 142.02, 141.93, 141.72, 141.60, 141.41, 140.10, 139.35, 139.27, 136.66, 134.97, 128.23, 115.15, 78.14, 74.37, 63.30, 26.01; FAB MS m/z 835–832 (M^+), 724–720 (C_{60}); FT-IR (KBr) 2958 (w), 2863 (w), 1635 (w), 1511 (m), 1462 (w), 1427 (m), 1374 (w), 1341 (w), 1282 (w), 1241 (w), 1197 (w), 1176 (m), 1149 (m), 1134 (m), 1107 (s), 1089 (m), 1068 (m), 1013 (s), 919 (w), 800 (w), 765 (w), 747 (w), 599 (w), 576 (w), 563 (w), 554 (w), 545 (w), 527 (s), 506 (w), 484 (w) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 212, 256, 316, 324, 428, 638, 660, 690, 702. Anal. Calcd for $C_{66}H_8O_2\cdot(C_5H_{12})_{0.8}$: C, 94.41; H, 1.99. Found: C, 94.19; H, 1.80.

Cyclopentenone Derivative (4). A chlorobenzene solution (50 mL) of 3 (20 mg, 0.024 mmol) was heated at 110 °C for 2 h in the presence of p-toluenesulfonic acid monohydrate (3 mg, 0.016 mmol) and a few drops of water. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chroamtography (silica gel, toluene) to afford 4 (13 mg, 70%). Further purification was achieved by precipitation: ^1H NMR (CS_2, $CDCl_3$) δ 9.02 (d, J = 5.60 Hz, 1H), 7.36 (d, J = 5.61 Hz, 1H); ^{13}C NMR (CS_2, $CDCl_3$) δ 200.97, 167.23, 153.63, 151.03, 147.47, 147.26, 147.00, 146.42, 146.31, 146.07, 146.02, 145.71, 145.64, 145.46, 145.34, 145.30, 144.54, 144.14, 143.04, 142.71, 142.63, 142.33, 142.04, 141.96, 141.87, 141.74, 140.52, 140.43, 136.62, 135.19, 133.43, 128.30, 76.00, 74.23; FAB MS m/z 776–774 (M^+), 724–720 (C_{60}); FT-IR (KBr) 1724 (s), 1589 (w), 1513 (m), 1426 (w), 1177 (m), 1155 (w), 1109 (w), 1092 (w), 849 (w), 815 (w), 763 (w), 746 (w), 680 (w), 653 (w), 641 (w), 574 (w), 554 (w), 539 (w), 526 (s), 478 (w) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 210, 254, 300 (sh), 330 (sh), 430, 632, 664, 686, 698. Anal. Calcd for $C_{63}H_2O\cdot(C_5H_{12})_{0.8}$: C, 96.67; H, 1.40. Found: C, 96.63; H, 1.20.

Electrochemical Measurements. Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and Osteryoung square wave voltammetry (OSWV) were recorded on a BAS-100B/W electrochemical analyzer. A three-electrode configuration was used throughout. All measurements were performed at ambient temperature under an argon atmosphere in a 0.1 M 1,2-dichlorobenzene solution of $(n\text{-}Bu)_4NPF_6$. The concentrations of organofullerenes ranged from 10^{-4} to 10^{-3} M. IR compensation was employed throughout. A platinum working electrode (1-mm diameter) was polished with 0.05-μm alumina before measurements. A platinum wire was used as the counter electrode. The reference electrode was an Ag/0.01 M $AgNO_3$ electrode filled with 0.1 M $(n\text{-}Bu)_4NClO_4$ in CH_3CN. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc$^+$) as the internal standard.

AM1 Molecular Orbital Calculations. All calculations were carried out using the GAUSSIAN 92 program[16] on an IBM RS/6000 workstation. Geometries of C_{60} and organofullerenes 1, 4, 5, and 7–10 were fully optimized at the Hartree–Fock (HF) level using the semiempirical AM1 method.[17]

Results and Discussion

Synthesis of New Organofullerenes. Compounds 1, 3, and 4 were prepared by adaptation of well-established synthetic methods[13,15] to C_{60} (Scheme 1). We have been investigating the possibility of using transition metal catalysts and reagents for the functionalization of C_{60}. It is already known that low-valent transition metals, such as Pd(0) and Pt(0), react with C_{60} to form stable complexes, $(\eta^2\text{-}C_{60})M(PPh_3)_2$ (M = Pd, Pt), whose X-ray structures have been determined.[14] This may imply that C_{60} itself deactivates the M(0) catalysts. However, Lerke et al. indicated that a "catalytic" amount of dissociated $M(PPh_3)_2$ species could exist in the solution of $(\eta^2\text{-}C_{60})M(PPh_3)_2$.[4a] Encouraged by this observation, we tried the addition of trimethylenemethane (TMM)[13] to C_{60} using 1 equiv of $(Ph_3P)_4Pd$ and a 10-fold excess of silyl acetate **11**. This worked well and afforded

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Scheme 1

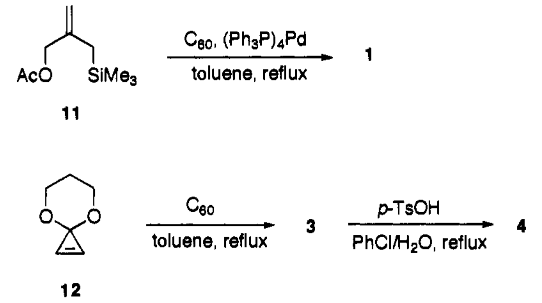

Table 1. Half-Wave Potentials[a] of C_{60} and Organofullerenes by Cyclic Voltammetry

compd	*E*1	*E*2	*E*3
C_{60}	-1.13	-1.50	-1.95
1	-1.23	-1.58	-2.11
2	-1.23	-1.60	-2.14
3	-1.21	-1.57	-2.11
4	-1.14	-1.52	-2.02
5	-1.13	-1.50	-1.99
6	-1.28	-1.66	-2.16
7	-1.29	-1.67	-2.18
8	-1.18	-1.56	-2.03
9	-1.08[b]	-1.48[b]	-1.93[b]
10	-1.26	-1.63	-2.18

[a] V vs ferrocene/ferrocenium couple. $(n\text{-Bu})_4NPF_6$ (0.1 M) in 1,2-dichlorobenzene. Scan rate = 20 mV/s. [b] Irreversible. Values obtained by DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.

$(TMM)C_{60}$ (**1**, 33%) and $(TMM)_2C_{60}$ (30%). A control experiment showed that C_{60} does not react with silyl acetate **11** in refluxing toluene without adding Pd(0). The ^{13}C NMR spectrum of **1** supports the expected C_{2v} structure, in which the addition took place at the bond between the two hexagons. The addition of cyclopropenone ketal **12**[15] to C_{60} gave **3** in 66% yield based on reacted C_{60}. The 1,3-dioxane of **3** was cleaved under acidic conditions to form **4** in 70%. The C_s structures of **3** and **4** were confirmed by ^{13}C NMR.

Electroreduction and Electrooxidation. Reduction potentials of C_{60} and organofullerenes **1–10** are listed in Table 1. All compound except $C_{60}O$ showed three or four reversible electroreductions by CV under our conditions (Figure 1).[18] We used 1,2-dichlorobenzene throughout the measurements because the solubility of both polar and nonpolar organofullerenes is relatively high in this solvent. A 100-mV negative shift relative to C_{60} was observed for **1**. When **1** is substituted with a ketal, compound **2** becomes slightly less electronegative,[19] Compound **3** has a cyclopentene structure and is more electronegative than **2**. This is reasonable because a sp^2 carbon is usually more electronegative than a sp^3 carbon. The conversion of the ketal **3** to the corresponding ketone dramatically changes the reduction potentials, affording a rather electronegative organofullerene **4**.[20] The first and second reduction potentials of dioxolane **5** eventually become equal to those of C_{60}. Unlike most organofullerenes, $C_{60}O$ does not behave reversibly in the CV.[21] However, its DPV and OSWV indicate that the first reduction peak shifts *positive* by 50 mV relative to C_{60} (Figure 2). It is impressive that silicon derivatives **6**, **7**, and **10** are even more electropositive than their carbon analogs **1** and (diphenylmethano)fullerene **8**. When xylene derivative **6** is compared to mesitylene derivative **7**, the latter is slightly more electropositive than the former due to the additional four methyls as electron-donating groups. Figure 3 shows the comparative DPV of oxygen-, carbon-, and silicon-containing organofullerenes. One can easily recognize that the reduction potentials depend on the electronegativities of the attached atoms.[22]

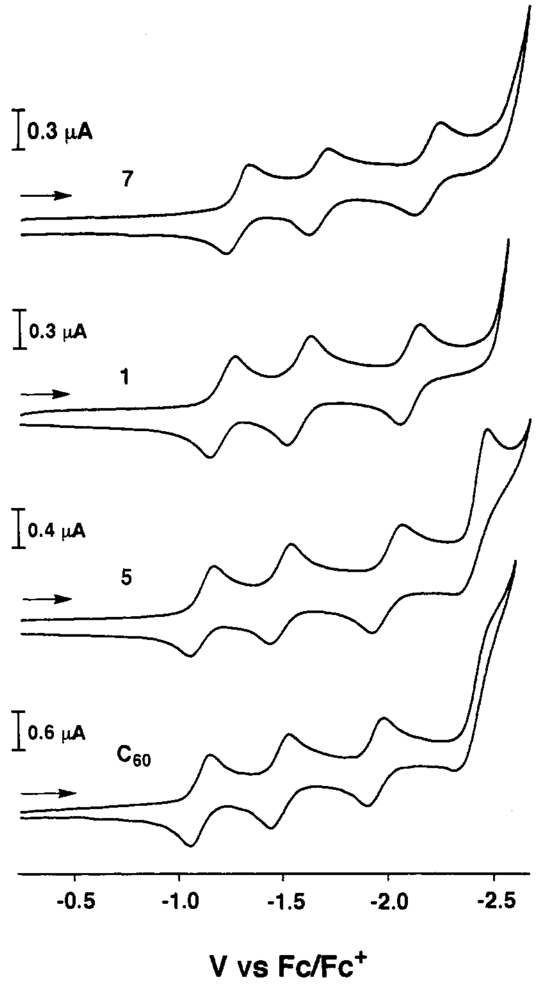

Figure 1. Cyclic voltammograms of C_{60} and **5**, **1**, and **7** at 20 mV/s in 1,2-dichlorobenzene containing 0.1 M $(n\text{-Bu})_4NPF_6$.

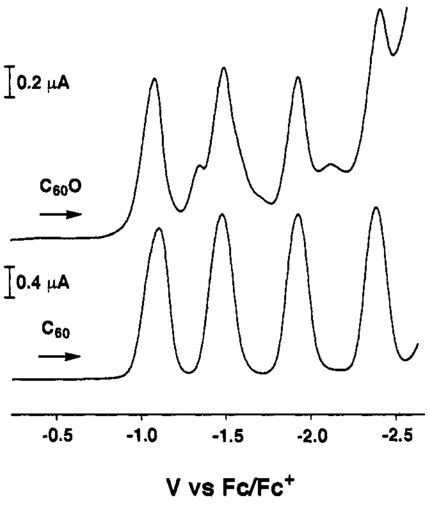

Figure 2. Osteryoung square wave voltammograms of C_{60} and $C_{60}O$ (**9**): square wave amplitude, 25 mV; frequency, 15 Hz; step *E*, 4 mV.

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(18) Also see the supplementary material.

(19) We are not able to explain this shift because oxygen is inductively electron withdrawing.

(20) Since a ketone derivative of **2** is a highly insoluble material, we were not able to obtain a well-defined CV. However, the DPV gave two meaningful peaks, *E*1 and *E*2 (-1.19 and -1.55 V, respectively).

(21) Professor Smith and collaborators had the same observation, suggesting that the epoxide opens up immediately when the molecule accepts an electron. Smith, A. B., III. Private communication.

(22) Electronegativities by Sanderson: Si, 2.138; C, 2.746; O, 3.654; F, 4.000. Sanderson, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 2259–2261.

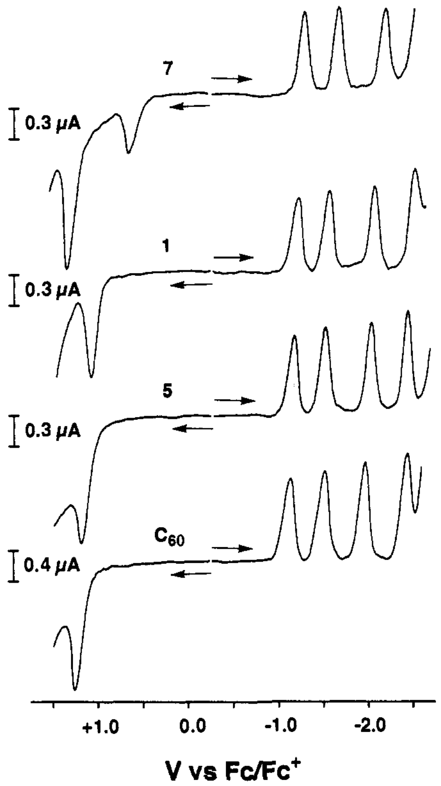

Figure 3. Differential pulse voltammograms of C_{60} and **5**, **1**, and **7**: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.

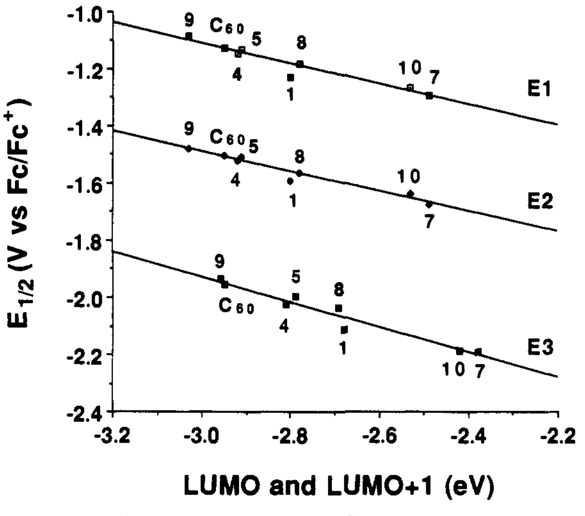

Figure 4. Plots of $E1$ and $E2$ vs the LUMO energy levels and $E3$ vs the LUMO+1 energy levels.

Similarly as described previously for C_{60},[1c] no CV reversible electrooxidation waves were observed for all organofullerenes studied in the present work. Peak potentials by DPV (Figure 3) indicate that the derivatization of C_{60} facilitates the electrooxidation processes (C_{60}, 1.26; **1**, 1.03; **4**, 1.12; **5**, 1.17; **7**, 0.60 and 1.22; **8**, 1.07; **9**, 1.22; **10**, 0.65 and 1.21 V vs Fc/Fc$^+$ couple). Electron-donating groups, such as alkyl and silyl, significantly lower the oxidation potential of C_{60}. Interestingly, silicon-containing organofullerenes show the second electrooxidations. This is in agreement with the calculations which indicate that almost one electron goes to the C_{60} from the silicon group (charges on the C_{60}: **1**, −0.19; **5**, +0.18; **7**, −0.99; **8**, −0.19; **9**, +0.12; **10**, −1.06).

Correlations between Redox Potentials and MO Energy Levels. As shown in Figure 4, the first and second reduction potentials of C_{60} and organofullerenes exhibit remarkable linear relationships with their LUMO energy levels obtained by the AM1 molecular orbital calculation. The third reduction potentials correlate better with the LUMO+1 energy levels than with the LUMO energy levels, indicating that the energy gaps between the LUMO and LUMO+1 should be taken into account to explain the electroreductions of the organofullerenes. The oxidation potentials also display a good linear relationship with the calculated HOMO energy levels as seen in Figure 5. The HOMO and LUMO energy levels should relate to the gas-phase ionization potentials and electron affinities, respectively. Therefore, the linear correlations in solution suggest that the free-energy changes on the redox reactions of C_{60} and organofullerenes are similarly influenced by solvation and ion pairing. This is probably due to relatively weak solvent–solute and solute–solute interactions;[1g] because 1,2-dichlorobenzene is a nonpolar solvent with a small dipole moment ($\epsilon = 9.93$), it is relatively ineffective at solvating both cations and anions. The low charge densities on large anions of C_{60} and its derivatives lead to relatively small electrostatic interactions with the solvent molecules and the supporting electrolyte cations.

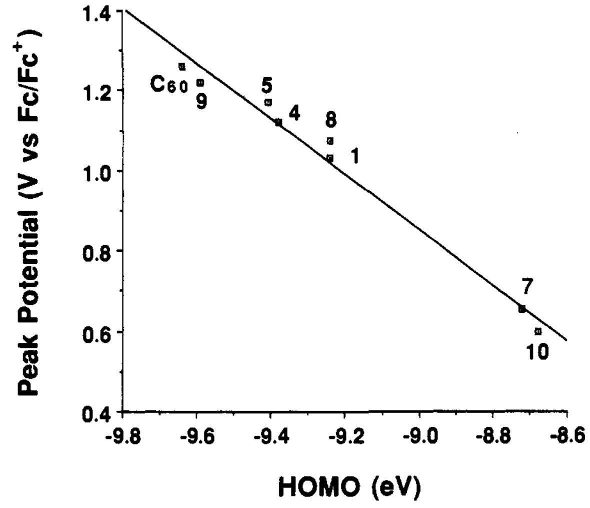

Figure 5. Plot of the peak oxidation potentials by DPV vs the HOMO energy levels.

The linear correlations can be used to estimate the redox potentials of unknown organofullerenes using the calculated HOMO and LUMO energy levels. The calculations predict that electron affinities would increase in the order C_{60} (LUMO, −2.95 eV) < $C_{60}O$ (−3.03 eV) < $C_{60}F_2$ (−3.07 eV) < $C_{60}(CN)_2$ (−3.15 eV). We can estimate the first reduction potentials of $C_{60}F_2$ and $C_{60}(CN)_2$ at −1.07 and −1.05 V (vs Fc/Fc$^+$ couple under the same conditions), respectively.

It should be noted that organofullerenes with the same attached atom (**1** and **8**, **5** and **9**, and **7** and **10**) have similar redox potentials, even though the number of attached atoms is double in the five-membered ring compounds. This may suggest that the inductive effect on the redox potentials is enhanced more with the three-membered rings than with the five-membered rings. In fact, the positive charges induced by oxygen atoms are greater in **5** (+0.18) than in **9** (+0.12), whereas the LUMO energy levels, which correlate with the reduction potentials, are lower in **9** (−3.03 eV) than in **5** (−2.91 eV).

Conclusions

We have shown that, within similar structures, the inductive effect by attached organic groups is the most important factor to determine the redox properties of organofullerenes. This is quite different from planar aromatic compounds in which electrons can be donated or withdrawn by the resonance effect. It was previously thought that the organic groups on the C_{60} sphere decrease its π-conjugation and release its strain energy,[23] affording

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(23) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.

only electropositive derivatives compared to C_{60}. However, our results suggest that even more electronegative fullerene derivatives would be produced by adding strong electron-withdrawing groups. This imples that C_{60} can be functionalized with any redox properties.

Acknowledgment. We thank M. Nagata and A. Suzuki for preparing C_{60} and Dr. S. Yamago for providing compounds **2** and **12**. This work was supported by the Ministry of Education, Science and Culture of Japan (Nos. 05233231 and 05233204).

Supplementary Material Available: Cyclic voltammograms of **2–4**, **6**, and **8–10** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.