diethyl sulfide (1:1.3:10). The competition reaction of sulfide and olefin, therefore, resulted in a somewhat low efficiency of epoxidation.

Registry No. TPP, 917-23-7; Fe(TPFP), 36965-71-6; Fe^{IV}(=O)(TPFP), 137364-06-8; Et_2S, 352-93-2; Et_2SO, 70-29-1; Et_2SD_{∞}, 597-35-3; O_2, 7782-44-7; cyclooctene, 931-88-4; norbornene, 498-66-8; *cis*-2-heptene, 6443-92-1; *trans*-2-heptene, 14686-13-6; *cis*-stilbene, 645-49-8; styrene, 100-42-5; cyclooctene oxide, 286-62-4; norbornene oxide, 278-74-0; *cis*-2-heptene oxide, 56052-93-8; *trans*-2-heptene oxide, 56740-07-9; (tetrakis(*p*-anisyl)porphyrinato)iron(III) chloride, 36995-20-7; (tetraphenylporphyrinato)iron(III) chloride, 16456-81-8.

Multiple, Reversible Chlorination of C_{60}

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It is of interest to us to explore the potential for oxidative chlorination of fullerenes, a class of compounds where rules of addition have only begun to be developed. We hope to learn how chlorination affects the chemistry of fullerene clusters and to explore substitution reactions on these systems. Fluorinated fullerenes have been reported recently.[1] In this communication we report initial results on reactions of C_{60} with Cl_2 under conditions where multiple addition produces species containing 12–15 Cl/C_{60}. Chlorine is extracted from these products by thermal, chemical, and electrochemical means, with regeneration of C_{60} in 50–80% isolated yield.

Solid C_{60},[2] exposed to liquid chlorine at its normal boiling point in the absence of light, is converted to chlorinated products which are slightly soluble in the liquid. Quantitative conversions are achieved in about 1 day by passing liquid chlorine continuously over 30–150 mg of C_{60} on a glass filter. The extract is collected and reddish-brown noncrystalline solids are isolated by evaporation of chlorine and drying under vacuum.

Mass spectra have been used to characterize alkylated[6] and fluorinated[1] derivatives of C_{60}. Mass spectra of chlorinated C_{60} showed C_{60} and Cl_2, but ions from $C_{60}Cl_x$ molecules were not detected. However, combustion analyses, IR spectra (ν C–Cl, 850 cm^{-1}, br), and carbon and chlorine binding energies from XPS spectra (Cl 2p 201.2 eV; C 1s 286.1 eV with fwhm of 3.0 eV) are consistent with the presence of species with C–Cl interactions.

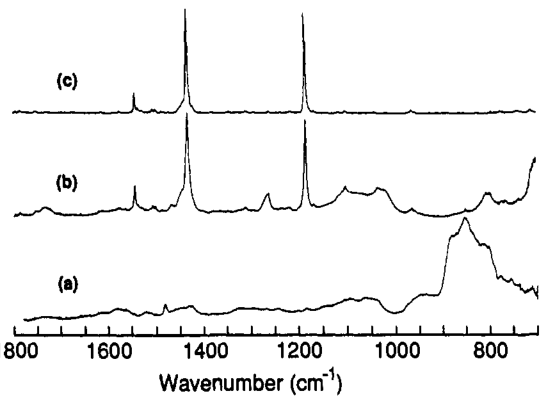

Figure 1. IR spectra: (a) $C_{60}Cl_{12.0}$, deposited on KBr from C_6H_6, at ambient temperature; (b) $C_{60}Cl_{12.0}$, after heating 1 h under vacuum at 200 °C; (c) authentic C_{60}.

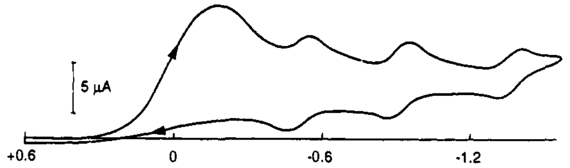

Figure 2. Cyclic voltammogram (Pt button; sweep rate 500 mV/s; Ag/AgCl reference electrode) of 0.5 mM $C_{60}Cl_{11.6}$ in dried CH_2Cl_2 with 0.1 M *n*-Bu_4NBF_4 (recrystallized from acetone and ether; dried under vacuum at 125 °C). Reduction of Cl_2 under these conditions occurs near +0.5 V.

In the absence of detailed information from mass spectra, we sought other means of determining whether chlorination yields products structurally related to C_{60}. When $C_{60}Cl_{12.0}$[7] was warmed under vacuum in an IR spectrometer, the characteristic four-band pattern of C_{60}[8] began to appear as the temperature reached 200 °C (Figure 1), and by 350 °C only C_{60} was detected. On a synthesis scale, $C_{60}Cl_{12.0}$, heated under vacuum to 550 °C, released 80% of the chlorine as Cl_2, leaving a residue which was purified by passage through alumina using toluene as eluent. The eluted product, characterized as C_{60}, was isolated in 50% yield. Reversible addition of phenylthiyl radicals to C_{60} has been reported.[6b]

Triphenylphosphine has been used to dehalogenate polychlorinated aromatics.[9] When toluene solutions of reddish-brown $C_{60}Cl_{12.0}$ and PPh_3 were combined, the color rapidly changed to reddish. After purification, C_{60} was obtained in 80% yield.

Cyclic voltammetry of $C_{60}Cl_{11.6}$ in dichloromethane (Figure 2) on either glassy carbon or Pt working electrodes showed a broad irreversible wave near –0.2 V (vs Ag/AgCl) and three reversible waves characteristic of authentic C_{60}.[3b,10] Controlled potential reduction on the cathodic side of the broad wave (at –0.45 V vs Ag wire) consumed electricity (10.6 F/mol) equivalent to that required for conversion of 91% of the Cl in $C_{60}Cl_{11.6}$ to Cl^-. C_{60} was produced in the electrochemical cell and was isolated in 54% yield.

Information obtained on reactivity of C_{60} with metal complexes[11] and other studies[12] suggest that unsaturation in C_{60} can

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(2) Mixed fullerenes were made by evaporating carbon electrodes in an atmosphere of helium.[3] Products were separated by chromatography on alumina using hexanes eluent[4] with exclusion of light and air.[5] Chromatographed C_{60} in benzene was passed through alumina to yield C_{60} which after drying under vacuum contained small amounts of aliphatic hydrocarbon impurities detected by IR (Found: C, 98.68; H, <0.4). Chlorination produced $C_{60}Cl_{13.1}$ (Found: C, 60.96; H, <0.3; Cl, 39.4). Similar chlorinated compositions were generated from C_{60} from which hydrocarbon impurities had been removed at 400 °C.[1a]

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(7) The fractional quantity of Cl emphasizes that this is not a formula but a representation of the average composition derived from elemental analysis.

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have isolated double bond character. Elemental chlorine adds to olefinic hydrocarbons by polar, nonradical, or radical pathways, and both types of addition can occur in a single system.[13] Several experiments indicate participation of radical species in chlorinations of C_{60}. An ESR absorption with $g = 2.0027$ ($\Delta H = 15$ G) was observed for the solid product of a typical reaction of C_{60} with liquid chlorine as well as for a dilute solution of C_{60} and Cl_2 in *tert*-butylbenzene at −50 °C ($\Delta H = 11$ G). The ESR absorption of the solid was lost when it was dissolved in benzene at ambient temperature. Detection of these radicals does not rule out polar additions of Cl_2 to C_{60} or to its partially chlorinated derivatives.

Broad featureless spectral data obtained on chlorinated C_{60} are symptomatic of mixed species. In the Raman spectrum, the complete absence of sharp strong features from 1500 to 200 cm^{-1} suggests that chlorination, under the conditions reported, extensively alters the normal mode structure of C_{60}, probably because, on average, large numbers of chlorine atoms are present in molecules of low symmetry.[14] The ^{13}C NMR spectrum of chlorinated C_{60} (500 MHz, C_6D_6 or $CDCl_3$) is a broad featureless peak centered near 147 ppm which does not distinguish between chlorinated and non-chlorinated carbons.

Electrochemical data may provide insight into the chemical properties of $C_{60}Cl_{11.6}$. Its multielectron reduction at positive potentials (Figure 2) is more characteristic of compounds with highly electron withdrawing groups such as CCl_3NO_2 or $CCl(NO_2)_3$[16] than of hydrocarbons with active chlorine in allylic and benzylic positions, which are typically reduced near −2 V.[17] The ease of electrochemical reduction is consistent with rapid chemical reduction found with PPh_3 and may be related to the relatively facile reductive dechlorination above 200 °C.

In conclusion we report that C_{60} treated with liquid chlorine near −35 °C is quantitatively converted to multiply chlorinated products whose structural identities are masked because they are mixtures of compounds of low symmetry. We have shown by chemical and electrochemical means that C_{60} can be regenerated in good yield (50–80%) from its chlorinated products. We thus deduce that the integrity of the 60-carbon framework is largely maintained under the reported conditions of chlorination and dechlorination. The multielectron reduction process which takes place at relatively positive potentials sets this system apart from normal chlorinated hydrocarbons.

Note Added in Proof. In liquid bromine at ambient temperature over 6 days, C_{60} is converted to yellowish microcrystals which contain about 28 bromine atoms/C60. The simplicity of the Raman spectrum (intense lines at 132, 178, 538, and 840 cm^{-1}) is consistent with a molecule of high symmetry. Structural studies are in progress.

Acknowledgment. We thank B. A. Parkinson for initial electrochemical experiments; T. Berzins for quantitative analyses of Cl_2; E. W. Matthews for UV–vis spectra; F. J. Kitson, W. J. Simonsick, J. Lazar, and C. N. McEwen for MS data; G. S. Reddy for NMR spectra; R. J. Young, Jr., for technical assistance; and T. Fukunaga, T. V. Rajanbabu, J. I. Brauman, and F. Davidson for discussions.

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Additions and Corrections

Triangulanes: Stereoisomerism and General Method of Synthesis [*J. Am. Chem. Soc.* **1990**, *112*, 7702]. Nikolai S. Zefirov,* Serge I. Kozhushkov, T. S. Kuznetsova, O. V. Kokoreva, K. A. Lukin, B. I. Ugrak, and Serge S. Tratch

Page 7703, right column: Line 1 should be deleted. Line 6 of paragraph 2 should read 4-tuples (1,2,3,4) and (2,3,4,5).

Page 7704, left column: In line 8 of paragraph 2, N should be N_2. In footnote 17a, line 4, 2^{n-B} should be replaced by 2^{n-3}. Page 7704, right column: In footnote 22, line 7, $2.2^{(n-4)/2}$ should be replaced by $2 \times 2^{(n-4)/2}$.

Page 7705, left column: In line 7, **6a**,**b**; **6c**,**d**; **6e**,**h** should be **6a**,**b**; **6c**,**d**; **6e**,**f**; and **6g**,**h**. In line 11, **6h** → **8a** should be **6a** → **8a**. In paragraph 3, lines 9 and 10, N_4 and N_2 should be N_4' and N_2', respectively.

General Parameterized SCF Model for Free Energies of Solvation in Aqueous Solution [*J. Am. Chem. Soc.* **1991**, *113*, 8305]. Christopher J. Cramer* and Donald G. Truhlar*

Page 8308: In eq 13, r_{M+1} should be $(r_{M+1} - 0.5T_{M+1})^{-1}$. In eq 14, r_k should be $\rho_k + 0.5T_1$.

Page 8309: In eq 17, $kk\phi$ should be kk'. In Table IV, the experimental values for F^-, Cl^-, Br^-, and I^- should all be 2 kcal/mol more negative. The final experimental value in Table V is incorrect for the structure listed; no experimental value is available for N-protonated acetamide.

Page 8310: In Table VI, in the heading on the second column of numbers, G_S^0 should be G_{CD}^0.

Page 8311: In the supplementary material, 1-butanol should be *t*-butanol.

Molecular Orbital Theory Calculations of Aqueous Solvation Effects on Chemical Equilibria [*J. Am. Chem. Soc.* **1991**, *113*, 8552]. Christopher J. Cramer* and Donald G. Truhlar*

Page 8552: In ref 7a, p 5129 should be p S129.

Page 8553: In Table I, rows 10–13 should read −3.3, −7.7; 12.2, 6.9; 4.7, 1.6; 10.8, 9.8 instead of 9.6, 11.3; ..., 28.8.