is interesting to note that although the oxalyl dication is a minimum, the dimer of carbon monoxide, ethylenedione (O=C=C=O), is kinetically and thermodynamically unstable with respect to dissociation into 2 equiv of CO.[18]

It is also interesting to note that $ClCO^+$ is directly formed by the ionization of oxalyl chloride (vide supra). The intermediately formed chlorooxalyl cation **3** loses CO readily. At the 3-21G* level of theory ion, **3** (C_s symmetry employing standard bond lengths for the initial geometry) does not optimize to a minimum but rather dissociates into $ClCO^+$ and CO, verifying the experimental observation.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

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Diamagnetic Polyanions of the C_{60} and C_{70} Fullerenes: Preparation, ^{13}C and ^7Li NMR Spectroscopic Observation, and Alkylation with Methyl Iodide to Polymethylated Fullerenes[1]

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In 1985 it was discovered that vaporization of graphite by laser irradiation produces a remarkably stable C_{60} cluster and to a lesser extent a stable C_{70} cluster as evidenced by mass spectrometry.[2] Kroto, Heath, O'Brien, Curl, and Smalley proposed the structure for the 60-carbon cluster to be a truncated icosahedron composed of 32 faces of which 12 are pentagonal and 20 are hexagonal, a structure analogous to a soccerball and reminiscent of the geodesic domes of Buckminster Fuller. Thus, C_{60} is commonly referred to as "buckminsterfullerene". The structural support for C_{60} as well as the related cluster C_{70} comes from a variety of experimental and theoretical studies.[3-7]

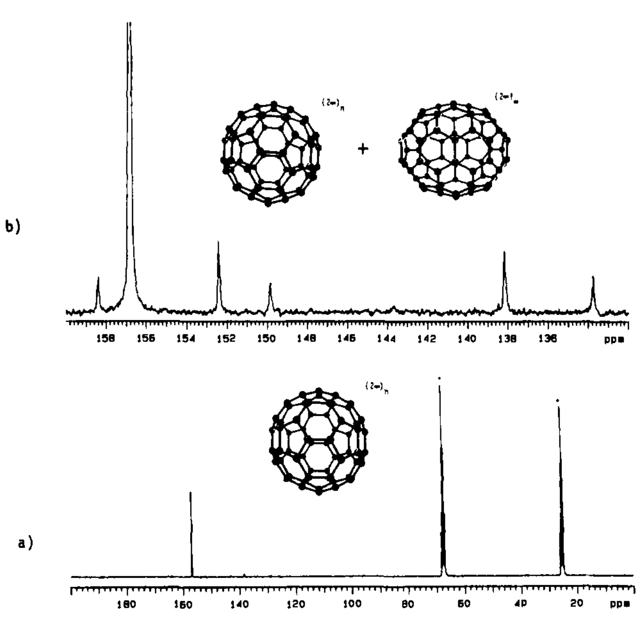

Figure 1. (a) Room temperature 75-MHz ^{13}C NMR spectrum of C_{60} polyanion in THF-d_8 [(*) peaks due to solvent]; (b) 75-MHz ^{13}C NMR spectrum of a mixture of C_{60} and C_{70} polyanions in THF-d_8 at −80 °C.

The fullerenes C_{60} and C_{70} were separated by Kroto[6] via column chromatography and their structures characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of C_{60} in benzene consists of a single line at 142.7 ppm confirming the icosahedral structure **1**. The ^{13}C NMR spectrum for C_{70} in benzene consists of five lines (150.7, 148.1, 147.4, 145.4, and 130.9 ppm in a 1:2:1:2:1 ratio, respectively) confirming a highly symmetrical egg-shaped structure[8] **2** (C_{5h} symmetry).

In view of our interest in cage compounds and persistent organic ions, we undertook a study of the anion(s) and cation(s) of the C_{60} and C_{70} fullerenes. Theory predicts an extremely high electron affinity (facile reduction) for both fullerenes.[4a,k] Initial experimental support for the ease of reduction of C_{60} was the formation of $C_{60}H_{36}$ via a Birch reduction.[9] Further cyclic voltammetry studies[9] indicated that C_{60} undergoes reversible two-electron reduction. More recently, Wudl, Diederich, and co-workers[10a] carried out cyclic voltammetry studies on pure samples of C_{60} and C_{70}, which showed that each fullerene undergoes reversible three-electron reduction (down to −1.5 V vs Ag/AgCl electrode).[10b]

We reduced a mixture of fullerenes C_{60} and C_{70} (in an approximately 85:15 ratio generated by using a carbon arc)[5b,11a] using Li metal (reduction potential of $Li^0 \sim -3.0$ V) in THF-d_8 with the aid of ultrasound.[11b] The fullerenes C_{60} and C_{70} are only slightly soluble in THF; however, the reduced fullerenes are highly soluble and generate a deep red-brown solution after sonication.[12] The ^{13}C NMR spectrum[13] at room temperature (see Figure 1a)

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[12] Initial sonication generates a cloudy green-colored solution. Further vigorous sonication results in a deep red-brown solution.

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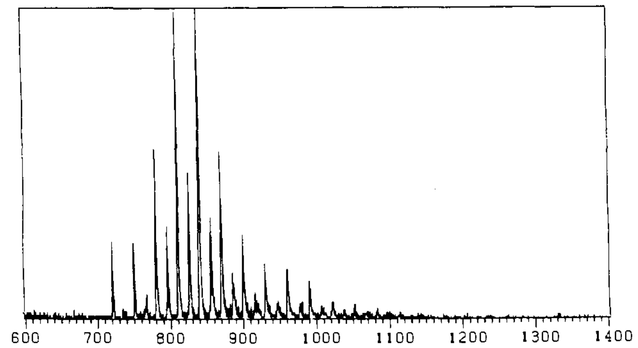

Figure 2. Field-ionization mass spectrum (FIMS) of the mixture of methylated fullerenes.

contains a single resonance at $\delta(^{13}C)$ 156.7 for the reduced C_{60}. This *deshielding* of 14 ppm/carbon atom is remarkable, because generally carbanion carbons are *shielded* compared to their neutral precursors. Such deshielding in the case of C_{60} polyanion may be rationalized by populating the antibonding LUMO.[14] The ^{13}C NMR spectrum which indicates the presence of reduced C_{70} was obtained at −80 °C to improve the signal to noise ratio (see Figure 1b). The five resonances are at 158.3, 152.3, 149.6, 137.9, and 133.7 ppm in a 1:2:1:2:1 ratio, respectively, showing a slight overall deshielding compared to neutral C_{70}.[15] We also reduced chromatographically purified (alumina and hexanes/toluene as eluant) samples of C_{60} to confirm our results. Further, we obtained a ^{7}Li spectrum of the reduced C_{60}/C_{70} solution at −80 °C which showed a fairly sharp resonance at +1.6 ppm (versus 1 M LiCl in THF). The ^{7}Li spectrum at room temperature was extremely broad, indicating a solvent-separated ion pair/contact-ion pair equilibrium in the temperature range studied.[16]

The polyanions generated contain an even number of electrons, judging from the sharp ^{13}C NMR signals, indicating a diamagnetic species.[17] Since a previous cyclic voltammetry study[10a] (vide supra) indicates reversible three-electron reduction for each fullerene, it seems likely under the present conditions that C_{60} and C_{70} each accepted four or more electrons. Theoretical calculations[4a,b,d-g,m] indicate a triply degenerate LUMO for C_{60}, making it possible that a hexaanion of C_{60} could have been generated. A similar situation exists for C_{70}, in which the LUMO and doubly degenerate LUMO^{1+} are closely spaced.[4d] Attempts to determine the exact number of electrons added to fullerenes **1** and **2** by quenching the polyanions with D_2O were unsuccessful. The isolated product mixture when analyzed by field-ionization mass spectrometry (FIMS) displayed only a mixture of C_{60} and C_{70}. Presumably, the deuterated product mixture undergoes rapid oxidation to regenerate the more stable starting fulerenes in both cases.[18]

Alkylation of the C_{60} and C_{70} polyanion mixture with excess methyl iodide, on the other hand, yielded a light brown solid that FIMS (Figure 2) indicates to be a mixture of polymethylated fullerenes (also confirmed by ^{1}H and ^{13}C NMR, $\delta(^{1}H) \approx 0.06$, $\delta(^{13}C) \approx 1.0$). The FIMS analysis show a range of methylated products from one all the way to 24 methyls. There is a preponderance of products with even numbers of methyl groups (with six and eight predominating). The nominal masses of the products with odd numbers of methyl groups correspond to the addition of a methyl group(s) and a hydrogen atom(s). However, the exact mechanism of the observed alkylation is not yet clear but possibly involves electron transfer to methylated fullerenes during quenching. This result represents the first functionalization of C_{60} and C_{70} via alkylative C–C bond formation. We will report complete characterization (NMR, IR, X-ray diffraction) of the methylated products. The achieved methylation of C_{60} and C_{70} fullerenes opens up the possibility of other functionalizations with alkyl halides, as well as other versatile substituents such as trialkylhalosilanes. Direct Barbier type reactions were successfully carried out in the case of chlorotrimethylsilane. We are continuing our studies toward diverse functionalization of fullerenes.

We also carried out oxidation studies on C_{60} and C_{70} using SbF_5 in SO_2ClF solution, a system found highly efficient for the oxidation of polycyclic aromatics to their dications.[19] Green-colored solutions were obtained that gave extremely broad ^{13}C NMR spectra at all temperatures employed (−80 °C to room temperature). Similar spectra were obtained by using SbF_5 and Cl_2 as the oxidant in SO_2ClF solution. It appears that radical cations have been generated and no diamagnetic di- or polycations were formed. This is not surprising since electrochemical studies[9] and FT-ICR experiments[20] indicate a high oxidation potential for C_{60}.

Acknowledgment. Support of the work at USC by the National Science Foundation, the National Institutes of Health, and the Office of Naval Research is gratefully acknowledged. The work at SRI International was supported by the IR & D fund. We thank Professor F. Wudl for a sample of pure C_{70} and together with Professor F. Diederich for a preprint of their work describing the details of the chromatographic separation and cyclic voltammetry of the fullerenes. We also thank Dr. Frank Devlin for carrying out ESR studies.

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(13) The ^{13}C NMR spectra were obtained on a Varian UNITY 300 NMR spectrometer equipped with a variable-temperature broad-band switchable 5-mm probe. The ^{7}Li spectra were obtained on a Varian VXR-200 spectrometer equipped with a variable-temperature broad-band switchable 5-mm probe.

(14) According to ref 4k, C_{60} hexaanion should be more diamagnetic than neutral C_{60}. However, the paramagnetic contribution to the carbon chemical shift is greater in the hexaanion, resulting in net deshielding.

(15) The deshielding is 0.9 ppm/carbon.

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(17) At early stages of sonication (cloudy green-colored solution), no ^{13}C NMR signal could be detected. This solution was ESR active and showed a strong signal at the *g* value close to that of a free electron.

(18) Similarly, Vollhardt et al. found that quenching of the dianion of [3]phenylene with methanol gave an extremely air sensitive solid that upon exposure to even traces of air regenerated the starting [3]phenylene quantitatively. See: Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670.

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The Electronic Structure of K_2^{2-}

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Recently the crystal structures of the alkalides $K^+(C222)K^-$ (I), $Rb^+(C222)Rb^-$ (II) and $Rb^+(18C6)Rb^-$ (III) have been reported.[1] The alkali-metal anions form dimers in I and II and chains in III, in which the anion–anion distances are at least one angstrom shorter than expected from other alkalide structures. These results suggest that, in the crystal, a chemical bond exists between two K^- or Rb^- anions. We report here the results of ab initio electronic structure calculations on K_2^{2-}, which provide insight into a possible mechanism for the anion–anion bonding in these materials. The basis set used for K was constructed from Wachters'[2] 14s9p set by first contracting it to 8s5p and then adding the two p functions recommended by Wachters, followed by three diffuse s functions (α = 0.007 649, 0.003 542, 0.001 640), two diffuse p's (α = 0.005 541, 0.002 019), and two diffuse d's (α = 0.09, 0.01). The quality of the resulting (11s, 9p, 2d) basis was tested by calculating various properties of K, K_2^{0}, and K_2^{1-}.

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