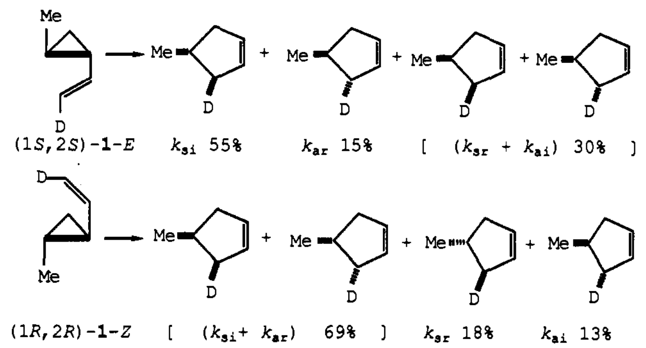

with results reported in 1976[1] for a similar vinylcyclopropane rearrangement based on totally different analytical techniques for quantifying product mixtures (GC, polarimetry) reinforces the fundamental conclusion: the direct "ai" pathway does indeed participate, and the "allowed" alternatives, while more important, are only negligibly advantaged energetically. With no significant energetic preference for concert in evidence, orbital symmetry control of stereochemistry does not seem a serviceable mechanistic rationale. The four stereochemically distinct paths used may involve four distinct diradical transition structures of closely similar energies.

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Electron Spin Resonance Study of the Radical Reactivity of C_{60}[†]

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The discovery that the novel allotropes of carbon, C_{60} and C_{70}, can be produced in chemically significant quantities with relative ease has triggered an intense interest in exploring their chemical reactivity.[1] The esthetic soccerball structure of the C_{60} framework has been confirmed by recent X-ray studies.[2] In a platinum complex, C_{60} behaves as an olefin, affording a classical transition-metal π-olefin complex.[2b] We now report our ESR results, which show (a) that a variety of photochemically generated, reactive, neutral radicals efficiently add to C_{60} to yield remarkably persistent radical adducts and (b) that the photolysis of C_{60} in the presence of donor molecules produces the radical anion of C_{60}. The latter was also generated electrochemically. The integrity of the C_{60} framework in these radical reactions is supported by the reversibility of radical addition in the case of phenylthiyl radicals and by MS analyses of the products. Spectra of frozen solutions of C_{60} radical adducts show the presence of electronic triplet species whose origin is discussed.

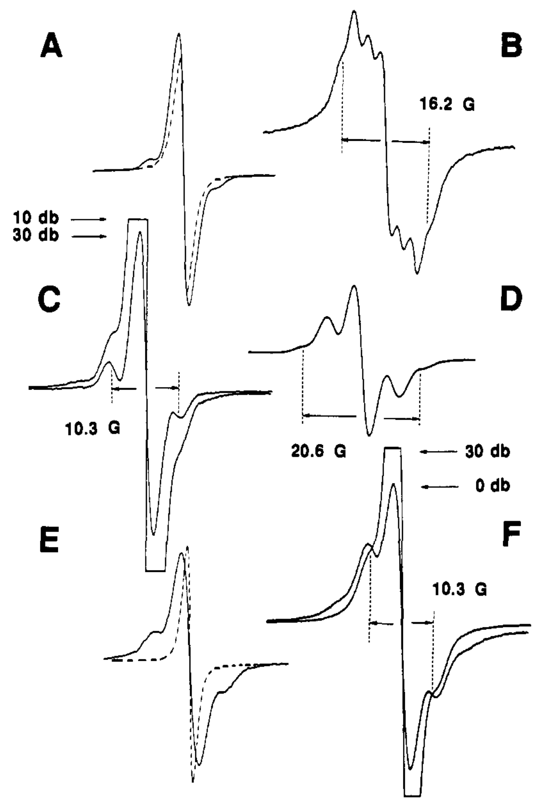

Figure 1. (A) ESR spectra at 220 K (dashed line) and 100 K (solid line) (10 dB) obtained by photolysis of a ca. 0.002 M toluene solution of C_{60} in the presence of di-*tert*-butyl peroxide. (B) ESR spectrum at 220 K obtained as in Figure 1A with [α-^{13}C]toluene as solvent. (C) The spectrum of Figure 1A (100 K) at two microwave power levels (0 dB: ca. 200 mW). (D) The spectrum of Figure 1A at 4.2 K (30 dB). (E) Spectra at 280 K (dashed line) and 100 K (solid line) (25 dB) obtained as in Figure 1A with benzene as solvent. (F) Spectrum of Figure 1E (100 K) at two microwave power levels. All spectra have the same horizontal scale.

Brief UV photolysis in the ESR cavity of a purple toluene solution of C_{60} containing di-*tert*-butyl peroxide[3] produces an intense ESR absorption (Figure 1A) with $g = 2.002\,32$ and $\Delta H = 1.9$ G that does not saturate at the available microwave powers. The absorption grows in intensity as the irradiation continues and decays slowly on shuttering the light at higher temperatures. No ^{13}C satellites could be detected. After photolysis, the clear solution has a light amber color characteristic of all radical adducts of this study. Photolysis of the same solution without C_{60} produces the highly transient spectrum of the benzyl radical.[4] We conclude that $C_6H_5CH_2^{\bullet}$ radicals, produced by H atom abstraction from toluene by photochemically generated *t*-BuO$^{\bullet}$ radicals, readily add to C_{60}. Accordingly, the spectrum obtained in exactly the same manner using 99% [α-^{13}C]toluene clearly shows the effects of the ^{13}C label (Figure 1B). The observation of a spectrum other than the expected doublet appropriate for a hyperfine interaction with one ^{13}C ($I = {}^1/_2$) indicates that *multiple* addition of benzyl radicals took place.

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(1) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (c) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Shriver, K. E.; Seusharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630. (d) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(2) (a) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160.

(3) (a) To a 0.003 M C_{60} toluene solution in a quartz ESR tube was added ca. $^1/_{10}$ volume of di-*tert*-butyl peroxide. (b) The UV light source was a 500-W Cermax xenon illuminator whose output passed through a circulating Kasha solution (240 g/L $NiSO_4{\cdot}6H_2O$ and 45 g/L $CoSO_4{\cdot}7H_2O$). The ESR spectrometer was a Bruker ESP 300 equipped with tracking gaussmeter and digital frequency counter.

(4) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 7155.

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Table I. ESR Parameters for C_{60} Radical Adducts

radical	source	solvent	*T*, K	*g*	ΔH^a
$CH_3^{\bullet}$	$CH_3C(O)OOC(O)CH_3^b$	toluene	230	2.002 29	2.6
$CH_3^{\bullet}$	$Bu_3SnSnBu_3/CH_3Br$	toluene	180	2.002 31	2.8
$CF_3^{\bullet}$	$CF_3C(O)OOC(O)CF_3^c$	toluene	190	2.002 25	2.0
$C_6H_5^{\bullet}$	$C_6H_5C(O)OOC(O)C_6H_5$	benzene	275	2.002 40	1.2
$(CH_3)_3CO^{\bullet}$	$(CH_3)_3COOC(CH_3)_3$	benzene	275	2.002 55	1.5
$C_6H_5CH_2^{\bullet}$	$(CH_3)_3COOC(CH_3)_3$	toluene	190	2.002 32	2.0
$C_6H_5S^{\bullet}$	$C_6H_5SSC_6H_5$	toluene	180	2.002 47	2.2

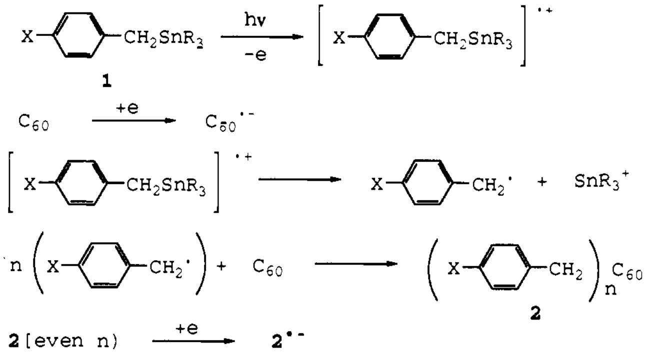
[a] Peak-to-peak line width in gauss. [b] Commercially available as a 25% solution in dimethyl phthalate. [c] In Freon 113. The two immiscible layers were shaken in the ESR tube to extract the peroxide into the benzene layer.

If the solution is frozen at 100 K after photolysis, two shoulders appear in the spectrum with a separation of 10.3 G and relative intensities that depend on the microwave power (parts A and C of Figure 1). At higher powers an additional pair of shoulders can be discerned. The latter become plainly visible at 4 K and are separated by 2 × 10.3 = 20.6 G (Figure 1D). The frozen solutions of all radical adducts of this study show such shoulders, with relative intensities that vary from case to case. We assign these shoulders to triplet species with the very small zero-field splitting parameter *D* of 10.3 G (9.63×10^{-4} cm^{-1}).[5,6] Since the triplet spectrum can be seen prominently at 4 K, the triplets are either ground-state triplets or nearly degenerate with a ground singlet state. Using as a first approximation $\langle r \rangle^3$ (Å) $= 6954g^2/D$ (gauss), appropriate for two localized electrons,[7a] we obtain a distance of 14 Å.[8] Among the explanations we are considering are pairs of C_{60} radical adducts or even two radicals attached to a single C_{60} producing a triplet. Such a triplet might have a very small *D* if the spin distribution is of approximately cubic or spherical symmetry.[7b]

An analogous experiment using benzene instead of toluene gave a very similar, persistent absorption (ΔH = 1.5 G, Figure 1E) that also displays two sets of shoulders on freezing. There are two striking differences; the *g* factor is shifted to the higher value of 2.002 55 and the central line power-saturates very easily (Figure 1F). In benzene, which is more resistant to radical attack, it is the initially formed *t*-BuO$^{\bullet}$ radicals that add to C_{60}, and the positive *g* shift is a consequence of the larger spin–orbit coupling of oxygen relative to that of carbon.

Photolysis of a variety of photochemical radical precursors in toluene or benzene solutions of C_{60} readily yields similar persistent ESR spectra, including the shoulders in spectra of frozen solutions (Table I). We note two interesting results. First, photolysis of phenyl disulfide, an established source of phenylthiyl radicals,[9] also produces the ESR spectra we associate with C_{60} radical adducts (Table I) and the characteristic amber solutions. Their color, however, gradually (ca. 30 min) reverts to the original purple of C_{60}, indicating reversibility of the radical addition.[10] Second, after photolysis or thermolysis (110 °C, sealed tubes) of dibenzoyl peroxide in benzene/C_{60}, FAB mass spectrometric analyses of the products clearly show C_{60} adducts bearing from one to at least 11 phenyl groups.

The ESR spectrum of $C_{60}^{\bullet-}$ is obtained by photolysis of C_{60} solutions containing benzylic trialkyltin derivatives **1** (X = H, OCH_3, CH_3, F, Cl)[11] in toluene/2-MeTHF.[12] The reactions that take place are shown herein in their simplest form. The fast fragmentation of the initially formed tin radical cation ensures that the photochemical electron transfer is irreversible and provides a diamagnetic countercation for $C_{60}^{\bullet-}$.[11] A complication is that adducts **2**$^{\bullet}$(odd *n*) and their radical anions **2**$^{\bullet-}$(even *n*) are also observed.[13]



Intense spectra of $C_{60}^{\bullet-}$, unencumbered by other species, are obtained by exhaustive electrolysis of benzonitrile solutions of $C_{60}/Bu_4N^+BF_4^-$.[14,15] The spectrum at 100 K has *g* = 1.997 57, ΔH = 5.0 G, and no ^{13}C satellites. The line width increases dramatically at higher temperatures (50 G at −40 °C), making the unperturbed $C_{60}^{\bullet-}$ undetectable in liquid solutions. Both the negative *g* shift and the line width behavior are associated with the occupation of the triply degenerate LUMO[16] by one electron.

The radical anion of C_{60} is also produced in the photolysis of toluene/2-MeTHF solutions of C_{60} in the presence of a variety of donor molecules (diethylaniline, tetramethylphenylenediamine, hexamethylbenzene, etc.).[17] Here the electron transfer is highly *reversible* and the spectrum of $C_{60}^{\bullet-}$, with its characteristic low *g* factor, can be observed only on photolysis of *frozen* solutions below 120 K together with the powder spectra of the radical cations derived from the donor molecules.

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(5) (a) Cf.: Wasserman, E.; Snyder, C. C.; Yeager, W. D. *J. Chem. Phys.* **1964**, *41*, 1763. (b) With a *D* parameter of this magnitude, the half-field $\Delta M = \pm 2$ line would be expected to be very weak, and none was observed. Its intensity decreases as the square of *D*.

(6) A triplet ESR spectrum associated with photoexcited C_{60} has been reported. Wasielewski, M. R.; O'Neil, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774.

(7) (a) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Claredon: Oxford, 1970; p 492, (b) p 151.

(8) The distance between diametrically opposite carbons in C_{60} is ca. 7 Å.

(9) Cf.: Krusic, P. J.; Kochi, K. J. *J. Am. Chem. Soc.* **1971**, *93*, 846.

(10) The reversibility was monitored by UV/visible spectrometry in the region 460–640 nm by using an ESR tube to which was fused a 1-mm UV/vis cell. Photolysis was carried out in the ESR cavity (0.06 M PhSSPh in 0.003 M C_{60}/toluene solution) at −60 °C.

(11) (a) Eaton, D. F. *Photogr. Sci. Eng.* **1979**, *23*, 150. (b) Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235. (c) Eaton, D. F. *Pure Appl. Chem.* **1984**, *56*, 1191.

(12) In a typical experiment 20 μL of **1** was added to a quartz ESR tube containing 0.3 mL of a 0.003 M toluene or benzene solution of C_{60} and 0.1 mL of 2-MeTHF. Photolysis was carried out in situ, typically at −80 °C, and the sample was frozen to observe the spectrum of $C_{60}^{\bullet-}$.

(13) The radical anions **2**$^{\bullet-}$ display narrow, single absorptions in solution (*g* = 1.999 89, ΔH = 0.9 G at −90 °C, X = H) and slight g-tensor anisotropy ($g_{\perp}$ = 2.000 80, $g_{\parallel}$ = 1.998 90, X = H). Very similar ESR spectra were obtained for the radical anion of a C_{60}/platinum complex generated electrochemically[14] (with P. J. Fagan).

(14) $C_{60}^{\bullet-}$ was generated by complete one-electron reduction at a potential just beyond the first reduction wave of a 5.5×10^{-4} M solution of C_{60} in benzonitrile/0.1 M $Bu_4N^+BF_4^-$ at 25 °C. Spectra obtained after two- and three-electron reductions are under study.

(15) An ESR study of electrochemically grown salts of $C_{60}^{\bullet-}$ has appeared very recently. Essentially the same *g* factor and line width behavior were observed. Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 2780. Cf. also: Dubois, D.; Kadish, K. M.; Flanagan, S.: Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(16) See, for example: Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459.

(17) Samples were prepared as described in footnote 12 by using comparable amounts of donor molecules.