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Addition of Alkylthio and Alkoxy Radicals to C_{60} Studied by ESR[†]

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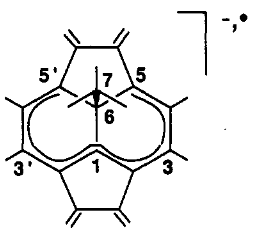
After a relatively slow beginning the chemistry of C_{60} is developing at a very fast pace. A very recent and excellent review on the subject is already outdated.[1] Much of the chemistry of C_{60} can be rationalized in terms of its high electron affinity and by the presence of 30 weakly conjugated double bonds. Accordingly, the molecule behaves as an electron-deficient spherical polyolefin to which nucleophiles[2] and radicals[3] can add very readily and multiply. Although the uncontrolled reactions lead necessarily to complex mixtures of products which are difficult to separate, the initially formed monoadducts of certain carbon nucleophiles and carbon-centered radicals have been well characterized.[2c,3c] Specifically, in the case of the *tert*-butyl carbanion and radical, the negative charge and the unpaired electron in the monoadduct are largely restricted to the two fused six-membered rings bearing the substituent at one of their points of fusion. Each half of the resulting structure can be compared with a cyclohexadienyl carbanion or radical and can be represented by canonic resonance forms that place the charge or the unpaired electron at carbons 1, 3,3′, and 5,5′. It has also been shown that in both the *tert*-butyl carbanion and the *tert*-butyl radical the rotation about the bond connecting the *tert*-butyl group to the C_{60} surface is hindered by a potential function having minima for the staggered and maxima for the eclipsed conformations with barriers of 8–9 kcal/mol in analogy with substituted ethanes.[2c,4,5] In the radical monoadducts, the rotation of less symmetric alkyl groups is also hindered by similar barriers so that the alkyl groups adopt preferred conformations relative to the C_{60} framework.[4]



Much less is known about the addition of heteroatom-centered carbanions and radicals to C_{60}. So far, only the addition of a few silicon- and phosphorus-centered radicals has been reported.[3e,6] We wish to present now an electron-spin resonance study (ESR) of the addition of several sulfur- and oxygen-centered radicals to C_{60} that are known to add readily to olefinic double bonds.[7]

Experimental Section

Saturated solutions (~0.002 M) of pure C_{60} in benzene or *tert*-butylbenzene containing from 1 to 20 equiv of alkyl disulfides or bis(alkylthio)mercury compounds (RSHgSR) were prepared free of oxygen using microsyringe techniques either by the use of previously degassed solvents and reagents in a nitrogen-flushed glovebox or by careful degassing on a vacuum line. The sample containing CF_3OOCF_3 was prepared on a vacuum line by volumetric metering of the gas into a quartz tube equipped with a Teflon stopcock. The samples contained in 4- or 5-mm o.d. quartz tubes were irradiated in the microwave cavity of the ESR spectrometer equipped with standard quartz inserts for variable-temperature work with the focused light of a 500-W Cermax Xenon Illuminator or a 500-W high-pressure mercury lamp. The light was filtered through a 5-cm path of either circulating distilled water or circulating aqueous Kasha filter (240 g/L of $NiSO_4·6H_2O$, 45 g/L $CoSO_4·7H_2O$).[8] The temperatures read by the variable-temperature apparatus were corrected for heating caused by irradiation. ESR spectra were obtained using Varian E4 or Bruker ESP-300 spectrometers. Because of the narrow widths of the spectral lines, very low microwave powers (<200 μW) and magnetic field modulations (e.g., 80 mG) were used.

Results and Discussion

Irradiation of a saturated benzene or *tert*-butylbenzene solution of C_{60} containing 1–20 equiv of methyl disulfide, CH_3SSCH_3, at 295 K yielded a binomial quartet spectrum appropriate for a hyperfine interaction (0.38 G) due to three equivalent protons (Figure 1A).[9] When the light was not filtered through the Kasha filter (to remove most of the visible and infrared radiation) a single absorption was also observed at a slightly higher magnetic field. Its characteristic *g*-factor of 2.001 35 identifies the species giving rise to this absorption as the excited triplet state of C_{60}.[10,11] Both signals decreased in intensity at higher temperatures and decayed immediately when the light was extinguished. The behavior of the quartet spectrum

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(9) The splitting is slightly temperature dependent and is given by $a = 0.309 + (2.6 \times 10^{-4})T$ in the temperature range 250–350 K.

(10) Closs, G. L.; Gautam, P.; Zhang, D.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 5228.

(11) The narrow line width, unusual for a triplet state, is caused by very rapid averaging of the spin–spin dipolar interaction by a fast dynamic Jahn–Teller effect (pseudorotation).

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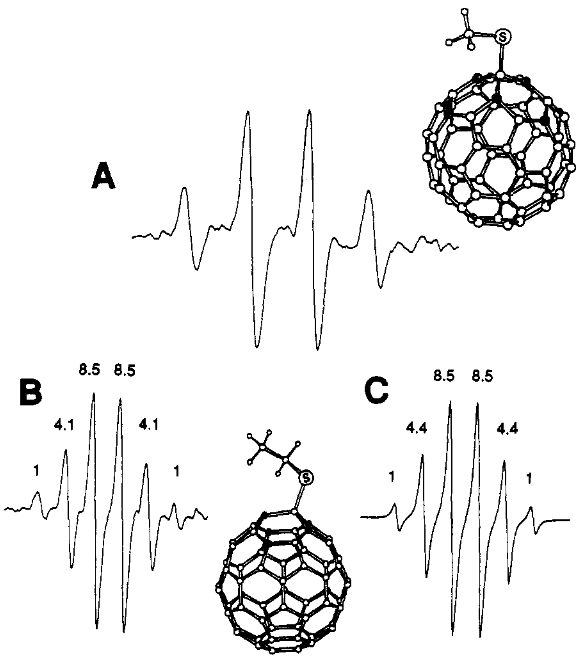


Figure 1. ESR spectra of $CH_3SC_{60}^{\bullet}$ (A) and $CH_3CH_2SC_{60}^{\bullet}$ (B) in *tert*-butylbenzene at 295 K together with a computer simulation of the latter (C). The relative intensities of the hyperfine components of the experimental and calculated spectra are also shown. The major spin bearing carbons are shown in black in the molecular models.

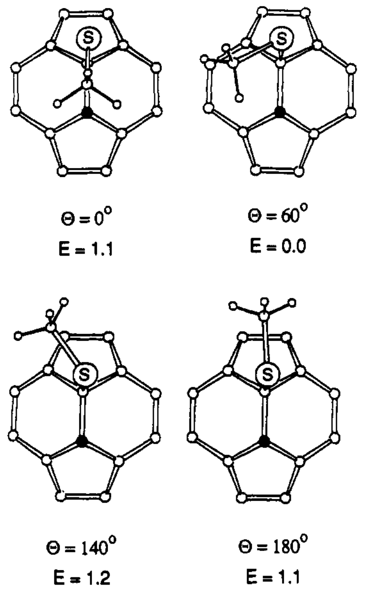
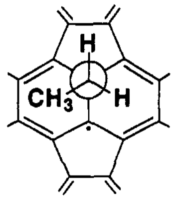


Figure 2. The structure of the local minima obtained by molecular mechanics calculations on $CH_3SC_{60}^{\bullet}$ with the angles of rotation of the CH_3S group and the relative energies in kcal/mol. The remainder of the molecule was deleted for clarity.

is very similar to that of monoalkyl radical adducts $RC_{60}^{\bullet}$: both have similarly small proton hyperfine splittings and very narrow line widths, and they power saturate very readily. Since the *g*-factor of 2.002 40 of the quartet spectrum is significantly higher than the values observed for monoalkyl radical adducts, which do not deviate from 2.002 21 ± 0.000 03, we confidently assign this spectrum to the $CH_3SC_{60}^{\bullet}$ radical resulting from addition of a methylthiyl radical to C_{60} with an unpaired spin distribution analogous to that of $RC_{60}^{\bullet}$ adducts. A positive *g*-factor shift is expected for radicals with spin density on sulfur because of its relatively large spin–orbit coupling. The assignment is supported by the observation of the identical spectrum in an analogous experiment in which bis(methylthio)mercury, $CH_3SHgSCH_3$, was used instead of the disulfide as the source of methylthio radicals. Unlike the spectra of $RC_{60}^{\bullet}$ radicals, which typically become more intense at higher temperatures owing to the dissociation of RC_{60}–$C_{60}R$ dimers present in solution,[3d] the spectrum of $CH_3SC_{60}^{\bullet}$, as well as those of its $RSC_{60}^{\bullet}$ higher analogs described below, rapidly decreased in intensity above room temperature. This difference in behavior might be associated with the reversal of the alkylthio radical addition due to a weaker fullerene–sulfur bond rather than with the failure of the corresponding RSC_{60}–$C_{60}SR$ dimers, which should be formed in these photochemical reactions by analogy with their alkyl analogs, to dissociate.

The hyperfine interaction of the δ protons[12] in $CH_3SC_{60}^{\bullet}$ (0.38 G) is substantially larger than those of γ protons and even γ fluorines in $CH_3C_{60}^{\bullet}$ (0.03 G) and $CF_3C_{60}^{\bullet}$ (0.13 G)[13] radical adducts, even though the latter nuclei are separated by one less bond from the α carbons on the C_{60} surface bearing the unpaired electron (carbons 1, 5, and 5′). The comparison is not entirely appropriate, however, in that the small magnitude of the proton and fluorine couplings in $CH_3C_{60}^{\bullet}$ and $CF_3C_{60}^{\bullet}$ is determined by a change in sign of the γ proton and fluorine couplings with the rotation about the C6–C7 bond, leading to a small average value in the limit of fast rotation.[4,13] A more appropriate comparison is with the methyl protons of $CH_3CH_2C_{60}^{\bullet}$ ($a(CH_3) = 0.12$ G) and the CF_3 fluorines of $CF_3CF_2C_{60}^{\bullet}$ ($a(CF_3) = 2.36$ G)[13] whose splittings are also substantially bigger than the γ splittings in $CH_3C_{60}^{\bullet}$ and $CF_3C_{60}^{\bullet}$. While a detailed understanding will require substantial theoretical work, it is likely that the magnitude of these long-range couplings involves a balance between through-space and through-bond contributions.

In the ethyl radical adduct, $CH_3CH_2C_{60}^{\bullet}$, a barrier to internal rotation of the ethyl group of 6–7 kcal/mol has been estimated.[4] It has also been established unambiguously that the ethyl group adopts the asymmetrical equilibrium conformation shown below in which the terminal methyl group prefers the position directly above one of the fused six-membered rings rather than that above the five-membered ring on the C_{60} surface directly below.



This conformational preference was nicely confirmed by our molecular mechanics calculations.[14] It seemed appropriate, therefore, to carry out the same calculations on $CH_3SC_{60}^{\bullet}$. The four local minima obtained are shown in Figure 2 together with their relative energies in kcal/mol.

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(12) Attached to the δ carbon relative to the primary spin-bearing carbons on C_{60} (carbons 1 and 5,5′) referred to as α.

(13) Krusic, P. J.; Fagan, P. J.; Wasserman, E., submitted for publication.

(14) Molecular mechanics calculations were carried out by allowing the entire $CH_3CH_2C_{60}^{\bullet}$ or $CH_3SC_{60}^{\bullet}$ structures to relax to local minima using the MMX force field as implemented by the program PC-Model (Serena Software, Bloomington, IN).

Table I. Isotropic Hyperfine Splittings (G) in $RSC_{60}^{\bullet}$ and $ROC_{60}^{\bullet}$ Radicals[a,b]

substituent	$a(CH_3)$	$a(CH_2)$	$a(CH)$
CH_3S	$3H_\delta = 0.38$		
CH_3CH_2S	$3H_\epsilon = 0.29$	$2H_\delta = 0.31$	
$(CH_3)_2CHS$	$6H_\epsilon = 0.22$		$1H_\delta = 0.22$
$CH_3CH_2CH_2S$		$2H_\delta = 0.35$[f] $2H_\epsilon = 0.18$[f]	
$(CH_3)_2CHCH_2S$		$2H_\delta = 0.40$	$1H_\epsilon = 0.21$
$(CH_3)_3CS$	$9H_\epsilon = 0.25$		
$(CH_3)_3CO$[c,d]	$9H_\epsilon = 0.35$		
$Ph(CH_3)_2CO$[c,d]	$6H_\epsilon = 0.22$ $3H = 0.17$ (Ph)		
CF_3O[c,e]	$3F_\delta = 3.14$		

[a] All alkylthio radicals were generated by photolysis of alkyl disulfides and of the corresponding bis(alkylthio) mercury compounds in benzene or *tert*-butylbenzene. Best S/N ratios were obtained in *tert*-butylbenzene in the temperature range −20 to +20 °C. [b] The *g*-factors of the alkylthiyl adducts were in the range 2.002 34–2.002 40. [c] Generated by photolysis of the corresponding peroxide in benzene. [d] $g = 2.002\ 33$. [e] $g = 2.002\ 29$. [f] Tentative assignment.

At this level of approximation there is thus a clear preference for an asymmetric conformation for this radical, entirely analogous to that of the ethyl adduct, with the methyl group bonded to sulfur directly above one of the two fused six-membered rings.

The photolysis of other alkyl disulfides and bis(alkylthio)mercury compounds in the presence of C_{60} afforded the spectra of several homologous radical adducts (Table I). The relative intensities of the six-line multiplet for the ethylthio adduct, $CH_3CH_2SC_{60}^{\bullet}$ (Figure 1B), departed somewhat from the binomial intensities appropriate for five equivalent protons. Computer simulations of the spectrum indicated a slight inequivalence between the CH_3 and the CH_2 protons (0.29 and 0.31 G, respectively, Figure 1C). As in the case of the $RC_{60}^{\bullet}$ analogs, appreciable hyperfine interactions are observed for protons attached to δ and even ϵ carbons in this homologous series (Table I).

In a few cases evidence was obtained for the cleavage of carbon–sulfur bonds, particularly if the light was not filtered through the Ni/Co sulfate solution. With benzyl disulfide only the spectrum of the benzyl radical adduct was obtained with parameters identical with published values.[3c] This adduct was also obtained when certain disulfides (e.g., phenyl disulfide) were photolyzed in C_{60}/toluene solutions, indicating hydrogen abstraction from the solvent by thio radicals. With *tert*-butyl disulfide, cleavage of C–S and S–S bonds took place as evidenced by the observation of thio, $(CH_3)_3CSC_{60}^{\bullet}$, as well as alkyl, $(CH_3)_3CC_{60}^{\bullet}$, adducts. Recognition of the two spectra was facilitated by the different *g*-factors and splittings (0.25 and 0.17 G, respectively) and by the narrowness of the spectral lines. Only the latter radical was observed at elevated temperatures. The behavior of phenyl disulfide is less well understood. However, when the irradiation was carried out at sufficiently high temperatures (>360 K) and with a large excess (100:1) of PhSSPh, the radical adduct $C_6H_5C_{60}^{\bullet}$ was observed since the identical spectrum, appropriate for two equivalent protons (ortho?), was obtained by photolysis of diphenylmercury under analogous conditions ($a_{2H} = 0.22$ G, $g = 2.002\ 22$). The observation of the very same spectrum in C_6D_6 solutions rules out the solvent as a source of phenyl radicals. Further support to this assignment is offered by the single line spectrum, with the same *g*-factor, observed when solutions of $C_6D_5SSC_6D_5$ are photolyzed under the same conditions. The radical $C_6D_5C_{60}^{\bullet}$ is expected to have a splitting too small to resolve since the 0.22 G splitting will be reduced by a factor of 6.5, corresponding to the H/D gyromagnetic ratio.

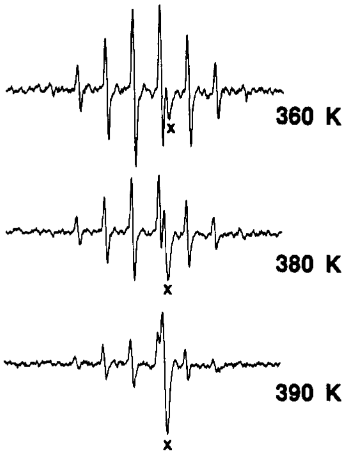

Figure 3. ESR spectra of $(CH_3)_3COC_{60}^{\bullet}$ obtained by photolysis of di-*tert*-butyl peroxide in *tert*-butylbenzene saturated with C_{60} showing the growth of the methyl radical adduct (marked with an X) as the temperature increases.

Alkoxy radicals can also add to C_{60} (Table I). The spectrum of the *tert*-butoxy adduct was obtained by photolysis of a saturated benzene solution of C_{60} containing ~20 equiv of di-*tert*-butyl peroxide (*t*-BuOOBu-*t*) at 360 K (Figure 3). The splitting for the nine equivalent ϵ protons (0.35 G) is actually larger than that of the nine equivalent δ protons of the *tert*-butyl adduct (0.17 G).[3c] A second signal is also present (Figure 3, marked with an x) which increases with temperature. The small quartet structure (ca. 0.03 G) that can be discerned at higher resolution and the characteristically low *g*-factor (2.00 218) unmistakably identify the species as due to the addition of a methyl radical, produced by β scission of a *tert*-butoxy radical, to C_{60}.[4] A similar result, yielding the $Me_2PhCOC_{60}^{\bullet}$ as well as the $MeC_{60}^{\bullet}$ adducts, was obtained when cumyl peroxide, $Me_2PhCOOCPhMe_2$, was irradiated in the presence of C_{60} in benzene. The methyl radical results now from the β scission of the $Me_2PhCO^{\bullet}$ radical. The analysis of the composite spectrum at 280 K was facilitated by the different *g*-factor of $Me_2PhCOC_{60}^{\bullet}$ and $MeC_{60}^{\bullet}$ (g = 2.00 233 and 2.00 218, respectively). With the available resolution the spectrum of the former radical resembles a binomial multiplet of 10 lines appropriate for nine equivalent protons (~0.20 G). A very satisfactory computer simulation was obtained, however, by assuming a slight inequivalence between six protons with a splitting of 0.22 G, belonging to the two methyl groups and three protons (presumably the ortho–para protons of the phenyl group) with a splitting of 0.17 G (Table I). The simulation also included a single line, with the appropriate *g*-factor for the methyl adduct, representing 10% of the total intensity. An analogous experiment using CF_3OOCF_3 afforded a 1:3:3:1 quartet with the unusually large splitting of 3.14 G for the three equivalent fluorines, quite distinct from that belonging to the CF_3 radical adduct (0.13 G),[13] which can only be assigned to $CF_3OC_{60}^{\bullet}$.

Instrumental settings strongly discriminating against broader absorptions (see Experimental Section) were used for the monoradical adducts discussed so far because of the very narrow line widths of their spectra. However, if the in situ photolysis was monitored at conditions appropriate for broader absorptions, less sensitive to microwave power saturation, it became apparent from the growth a single broad line of ca. 1.5 G width that, in addition to the radical monoadducts, other more persistent paramagnetic species are formed that build up with the time of photolysis. The integrated intensities of these absorptions far exceeded those of the transient monoadducts. The positive shift of the *g*-factors (2.0024–2.0027) from the free electron value (2.002 32) strongly implicates sulfur involvement. Mass spectral examination of the products of a typical photolysis experiment using phenyl disulfide[15] revealed masses appropriate for $C_{60}(Ph)_x(SPh)_yH_z$ (x, y, z from 1 to 5), indicating that multiple addition of both phenyl and phenylthio radicals takes place on prolonged irradiation. It is reasonable, therefore, to attribute these signals to complex mixtures of relatively stable paramagnetic species arising by multiple radical attack on C_{60} as well as on the RSC_{60}–$C_{60}SR$ dimers.

Multiple radical addition to the RSC_{60}–$C_{60}SR$ dimers can lead to diradicals with an unpaired electron on each C_{60} sphere of the dumbbell molecules. Evidence for such diradicals was provided by the ubiquitous observation of two shoulders on each side of the central absorption in the spectra of *frozen* solutions after prolonged photolysis.[16] We attribute these shoulders to powder spectra of randomly oriented electronic triplet species with a zero-field splitting parameter D of ~12 G.[17] Using as a first approximation $\langle r\rangle^3$ (Å) = $6954g^2/D$ (G), appropriate for two localized spins,[18] the observed D value corresponds to a distance between two unpaired interacting electrons of about 13 Å which is commensurate with the dimensions of such dimers, considering that each C_{60} sphere has an internuclear diameter of ~7 Å.

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(15) Benzene solutions of C_{60} (~0.002 M) and phenyl disulfide (0.040 M) in a 5-mm o.d. quartz tube were irradiated with the unfiltered output of a low-pressure mercury discharge lamp at room temperature for 30–60 min. After photolysis the solutions were concentrated to a tenth of their initial volume on a vacuum line. They were analyzed with a VG-ZAB-E double-focusing mass spectrometer using a xenon gas fast-atom-bombardment gun and a *m*-nitrobenzyl alcohol matrix.

(16) Similar shoulders in the spectra of frozen solutions of alkyl radical adducts of C_{60} were reported in ref 3a.

(17) For a discussion of powder ESR spectra of electronic triplets see: Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

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