Fullerene Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lfnn19

ESR Studies on C\textsubscript{60}.O\textsubscript{X} and C\textsubscript{60}.HMTTEF

K. K. Singh\textsuperscript{a}, T. Pradeep\textsuperscript{b}, D. E. Morris\textsuperscript{a}, L. Chen\textsuperscript{c} & J. V. Acrivos\textsuperscript{c}

\textsuperscript{a} Morris Research Inc., 1918 University Avenue, Berkeley, CA, 94704, USA
\textsuperscript{b} RSIC, Indian Institute of Technology, Madras, 600036, India
\textsuperscript{c} Department of Chemistry, San Jose State University, San Jose, CA

Published online: 19 Aug 2006.

To cite this article: K. K. Singh, T. Pradeep, D. E. Morris, L. Chen & J. V. Acrivos (1996) ESR Studies on C\textsubscript{60}.O\textsubscript{X} and C\textsubscript{60}.HMTTEF, Fullerene Science and Technology, 4:3, 583-598, DOI: 10.1080/10641229608001572

To link to this article: http://dx.doi.org/10.1080/10641229608001572

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages,
ESR STUDIES ON C\textsubscript{60}.O\textsubscript{x} AND C\textsubscript{60}.HMTTEF

K. K. Singh\#, T. Pradeep\*, D. E. Morris

Morris Research Inc. 1918 University Avenue, Berkeley, CA 94704, USA

*RSIC, Indian Institute of Technology, Madras 600036, India

L. Chen and J. V. Acrivos

Department of Chemistry, San Jose State University, San Jose, CA

Abstract

The electron spin resonance (esr) of C\textsubscript{60}.O\textsubscript{x} and C\textsubscript{60}.HMTTEF (hexamethylentetratellurafulvalene) has been investigated at 9.36 GHz as a function of temperature, T (298 \geq T \geq 4 K). C\textsubscript{60}.O\textsubscript{x} shows an esr absorption of equal 'g' value to that of C\textsubscript{60} exposed to O\textsubscript{2} and light but is more intense. The C\textsubscript{60} in its pure form is in a singlet state. The impurity sites introduced by O\textsubscript{2} produce the esr absorption. The Curie - Weiss plots of inverse esr absorption intensity versus temperature indicate an

\# To whom correspondence should be addressed.
antiferromagnetic $\Theta \approx 50$ for air exposed C$_{60}$ and 90K for C$_{60}$O$_x$. From the esr intensity at room temperature, the calculated number of free spins ($S = 1/2$) is $\approx 1/3$ per mole of C$_{60}$O$_x$. In case of C$_{60}$.HMTTEF, there is a very weak esr absorption at room temperature suggesting that the room temperature form is diamagnetic with very small charge transfer between C$_{60}$ and HMTTEF. This conclusion is consistent with the structure and magnetic susceptibility of this cocrystal. As the temperature is lowered, the equilibrium: $AD \leftrightarrow A^* + D^{**}$ is displaced towards the formation of free radical species, $A^*$ and $D^{**}$.

**Introduction**

C$_{60}$ is in a singlet ground state and should be esr silent. However C$_{60}$ exposed to air and light as well as its charge transfer compounds are esr active. ESR spectra have given useful information, on C$_{60}^{-1,-2,-3}$ anions produced as a result of electron transfer to C$_{60}^{1-10}$ and on C$_{60}$.R adducts$^{11-13}$. We have applied esr to study two new derivatives: C$_{60}$.O$_{22}$ and C$_{60}$.HMTTEF.

**Experimental**

C$_{60}$.O$_x$ was prepared by the procedure described earlier$^{14}$. Samples weighed immediately after reaction in 10$^3$ bar O$_2$ pressure at room temperature showed a weight increase of $\approx 48\%$ giving $x \approx 22 \pm 2$. The material is esr active, and the
results presented here throw interesting light on the nature of this compound. The other new compound studied is C\textsubscript{60}.HMTTEF, a compound reported recently\textsuperscript{15}. This was synthesised using the method reported by Pradeep et al.\textsuperscript{15}. X-ray diffraction measurements were made on samples on a Scintag PAD-V diffractometer using Cu-K\textalpha radiation and an intrinsic Ge solid state detector with 200 eV energy resolution. The diffraction pattern (20 values and intensity) matched with our earlier patterns obtained from single phase C\textsubscript{60}.HMTTEF samples. This was presumed to be a charge transfer complex between C\textsubscript{60} and HMTTEF and esr was expected to throw light on the extent of charge transfer and on the energy states of the system. The results, however, indicate very little charge transfer.

The esr data were obtained using a Bruker esr spectrometer ER200 with a dual cavity, which allows one to obtain absolute intensity measurements. The sample cavity was equipped with an Oxford 900 liquid He Cryostat and the reference cavity contained a known amount of free radical 1,1\'bisdiphenyllene2phenylallyl with \(g = 2.0027\) (ref. 16). The number of spins, \(S\) was determined using the calibration relation:

\[
\text{Unknown}(s) \frac{N_s}{N} = f \left[ \frac{(T,MA)}{S(S+1)} \right] (A_u/A_r) \frac{\Delta B_{\text{ms, unknown}}}{2}
\]

where \(A_u\) and \(A_r\) are the derivative amplitudes of sample and
reference respectively and $\Delta B_{ms}$ is the line width between the points of maximum slope in mT. The accuracy of scan rates $dB/dt \leq 2$ mT/s was better than $\pm 10\%$. $f(T,MA) = MA \times 5.3E11 \times (T/298)$ when Boltzmann statistics are obeyed and the line shapes are Lorentzian. MA is the modulation amplitude and saturation was ruled out using $B1 \leq 10$ mT.

**Results and Discussion**

Figure 1 shows the esr powder absorption derivative $dP/dB$ versus $B_z$ for the C$_{60}$ (air exposed), C$_{60}$.O$_x$ ($x=22$) and C$_{60}$.HMTTEF samples at 298 K together with the esr absorption parameters. As is well known, pure C$_{60}$ has a singlet ground state and esr silent. However, epr signals are observed for C$_{60}$ that has been exposed to oxygen and light. This is shown in figure 1. The behavior of C$_{60}$.O$_x$ is also quite similar to that of C$_{60}$ exposed to O$_2$ and light. Both have the same line shape, line width, absorption intensity and the same g value (Table 1). The number of unpaired spins is estimated to 1/3 per C$_{60}$ molecule. This is much larger than what has hitherto been observed. Furthermore, linear variation of the inverse esr signal intensity with for C$_{60}$.O$_x$ as shown in Fig. 2a implies absence of any activated term suggesting that the signal is coming from ground state and not from an excited state. The observed g value is 1.9975 (below 20 K) is also close to the value observed for C$_{60}$.TDAE$^{12}$ and that for electrochemically produced C$_{60}^{-1}$ (1.9991). Such a similarity in the g values suggests that spins
Fig. 1  ESR powder absorption derivatives $dP/dB$ versus $B_z$ of $C_{60}$ (air exposed), $C_{60}\cdot O_x$ and $C_{60}\cdot HMTTEF$ at 298 K.

Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>g</th>
<th>$\Delta H_{ms}$/mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$ (exposed to $O_2$)</td>
<td>1.9983</td>
<td>0.2</td>
</tr>
<tr>
<td>$C_{60}\cdot O_x$</td>
<td>1.9985</td>
<td>0.2</td>
</tr>
<tr>
<td>$C_{60}\cdot HMTTEF$</td>
<td>0.9986</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Fig. 2(a) Normalized inverse ESR Intensity vs T of C$_{60}$ complexes: C$_{60}$($\diamond$), C$_{60}$.O$_x$ (+) and C$_{60}$.HMTTEF (†).

Fig. 2(b) Ln [I*T] vs 1/T plot of C$_{60}$.HMTTEF. This indicates that there are definitely two temperature regimes. From 298 K to 150 K, $\Delta H^*_{1} = -3.1$ KJ/mole and from 100 K to 11 K, $\Delta H^*_{2} = -128$ J/mole.
are primarily located on C60 having $S = 1/2$ and singlet orbital state as deduced for C60$^-$ anions.

It looks highly probable that the spin resides on the C60 moiety rather than on oxygen in C60O22 for the following reasons:

(i) Whereas C60 and C70 are highly electronegative molecules, with C60 able to undergo up to six reversible reduction steps, no reversible oxidation steps have been observed in the cyclic voltametry of either molecule. C60$^+$ appears very difficult to form.

(ii) The unpaired electron resides on the oxygen site is also ruled out because the $g$ value observed (1.9975) is smaller than that observed for oxygen centered radicals (they have a typical $g$ value of ~2.01). The observed $g$ value indeed matches with that for C60$^{-1}$.

(iii) Lorentzian line shape implies delocalization of the observed electron over a large molecule e.g. C60

(iv) The temperature dependence of the linewidth similar to those of singly ionized fullerene molecule in various diamagnetic organic solvents10.

(v) This still leaves the question of identifying the donor unit (D) open. The donor mechanism has to involve the trapped oxygen and has to leave a epr silent D$^+$ after the transfer of electron to C60.

We are also not sure about any additional changes that have taken place to the solid C60 in addition to the loss of
crystallinity. As is known the residue is no longer soluble in toluene.

The close proximity of the observed $g = 1.9975$ to the pure spin value indicates that the electron is in an orbitally singlet and not in orbitally triplet state. This is the same situation as in $C_{60}^{-1}$. The $g$ value observed in case of $C_{60}^{-1}$ (1.9991-1.9998) is close to the free electron $g$ value of 2.0023. Although it is known that the lowest unoccupied orbital state in neutral $C_{60}$ is triply degenerate, the esr results strongly suggest a lifting of orbital degeneracy and quenching of orbital angular momentum possibly as a result of crystal field effects due to surrounding counter ions or solvent molecules and Jahn Teller effects. The temperature dependence of the spectral line width also points towards the existence of close lying states near the ground state, presumably as a result of the splitting of the triply degenerate ground state of the free molecules.

The esr of both $C_{60}$ (air exposed) and $C_{60.0_{x}} (x = 22)$ materials seem to follow a Curie - Weiss susceptibility temperature dependence in a wide temperature range of 5 K to 300 K. The inverse intensity shows a Curie - Weiss dependence in the observed temperature range (fig. 2a). Extrapolation of the inverse intensity to zero gives an antiferromagnetic Curie - Weiss temperature, $\Theta = -50$ K for air exposed $C_{60}$ and -90 K for $C_{60.0_{x}} (x = 22)$ sample.

Oxygen is known to interact with $C_{60}$ particularly in presence of UV radiation\textsuperscript{17-24}. Solid $O_{2}$ in contact with
multilayer films of C₆₀ on solid substrates showed conversion to CO, CO₂, carbonyl like structures and a carbon residue upon exposure to photon sources of appropriate energy. No reaction of O₂ with C₆₀ was observed without photo excitation. A C₆₀O adduct has been identified by Wood et al. The C₆₀O adduct was enhanced relative to C₆₀ and C₆₀ + OH adduct by one order of magnitude upon UV irradiation of C₆₀ solutions in air. Higher oxides C₆₀Oₙ (n = 2, 3, 4, 5) were also obtained. Of particular interest are surface reaction of C₆₀ with oxygen to form an epoxide at ambient temperature and pressure. Reaction of C₆₀ with oxygen is supported by Raman spectroscopy, which shows an intense peak at 1458 cm⁻¹ upon exposure of C₆₀ films to O₂ (ref.19). Pace et al. have observed an esr signal in chromatographed C₆₀ powder sample that was oxygen dependent. The identity of the radical was not determined by the available data. For C₆₀ in vacuum, the esr signal was constant and the signal intensity did not change upon admitting N₂ gas into the evacuated C₆₀ sample. Admitting O₂ caused an immediate increase in signal by 40%. Heating C₆₀ in air for 24 hr at 250 °C resulted in an increase in spin concentration by two orders of magnitude.

Our sample is different, firstly there is no photon irradiation (except daylight) and secondly there is no possibility that a pressure of 10³ bar can cause any excitation or ionization of oxygen. Furthermore loss of CO and CO₂ would entail a weight loss. In our case, the residue obtained after the
oxygen has been taken out by heating the sample to 200 °C, weighs between 100-105 % (ref. 14) of the original C₆₀ weight. There is no weight loss. The ease with which oxygen can be taken out also rules out any possibility of stable epoxide or ether formation. Also, Raman spectroscopy shows no evidence of any C=O ketone, C-O ether and epoxide bonds.¹⁴

The ease with which oxygen gets inserted in the structure (under O₂ pressure), the ease with which it can be taken out and the lack of evidence for any possible compound suggests that the material is a weak C₆₀·Oₓ adduct. There are adequate number of interstitial positions to accommodate oxygen atoms in the structure. And with the breakdown of the structure, the space availability also becomes more abundant.

C₆₀·HMTTEF

C₆₀·HMTTEF exhibits a very different behavior. It shows a very weak esr absorption intensity near room temperature. The estimated number of spins per C₆₀ molecule is <0.01. Furthermore, the intensity is essentially independent of temperature as was found for the magnetic susceptibility of this compound in the temperature range of 50 - 300K (ref. 25). There is a sharp increase in the signal intensity below 20 K. However no hyperfine splitting is observed down to 5 K indicating absence of any ordering. Table 1 gives their line widths and 'g' values. The absence of charge transfer in C₆₀·HMTTEF is in sharp contrast to several other C₆₀ adducts,
e.g. C\textsubscript{60}.TDAE. Substantial charge transfer and strong ESR spectrum of C\textsubscript{60}.TDAE [TDAE = Tetrakis(dimethylamino)ethylene] has a simple Lorentzian form without hyperfine structure at room temperature\textsuperscript{12}.

The difference between C\textsubscript{60}.HMTTEF and C\textsubscript{60}.TDAE in regard to the extent of charge transfer arises from the difference in structure. The analysis of the high resolution synchrotron X-ray powder diffraction data for C\textsubscript{60}.HMTTEF at room temperature gives a triclinic unit cell with \(a = 9.9297\text{\AA}, \ b = 9.9359\text{\AA}, \ c = 13.1472\text{\AA}, \ \alpha = 106.966^\circ, \ \beta = 95.887^\circ \) and \(\gamma = 118.252^\circ\) in the space group \(P1\) (ref. 25). Steric considerations suggest that there is a nearly close packed layer of C\textsubscript{60} molecules in the ab plane and the HMTTEF molecules are sandwiched between adjacent layers of closed packed C\textsubscript{60} molecules. The inter C\textsubscript{60} distance with the ab plane is very close that found in K\textsubscript{3}C\textsubscript{60}, C\textsubscript{60}.TDAE, C\textsubscript{60}.(BEDT-TTF)\textsubscript{2} and several other C\textsubscript{60} compounds. However, the interplanar spacing of ca 12.5\text{\AA} is much larger than those found in superconducting K\textsubscript{3}C\textsubscript{60} and ferromagnetic C\textsubscript{60}.TDAE, but close that observed in C\textsubscript{60}.(BEDT-TTF)\textsubscript{2}, CH\textsubscript{2}I\textsubscript{2}.C\textsubscript{6}H\textsubscript{6}.C\textsubscript{60} and C\textsubscript{60}I\textsubscript{4} (ref. 25 and reference cited therein). The last three have a similar alternating guest - host layer structure. Thus we have two classes in the C\textsubscript{60} adducts; (i) charge transfer complexes, e.g. C\textsubscript{60}.TDAE or K\textsubscript{3}C\textsubscript{60} and (ii) cocrystals where the C\textsubscript{60} and the organic molecules co-exist without any charge transfer, for example C\textsubscript{60}.HMTTEF, C\textsubscript{60}.(BEDT.TTF)\textsubscript{2} and C\textsubscript{60}.(CH\textsubscript{2}I\textsubscript{2}.C\textsubscript{6}H\textsubscript{6}). This
class of compounds is characterized by larger C60-guest distance as compared to that in (i).

The weak ESR signal indicates that there is very little charge transfer between the C60 molecule and the nearby HMTTEF molecule. Each C60 molecule is in near contact with other C60 molecules in the same a-b plane. The charge transfer amongst the adjacent molecules is also decreased as compared to the solid C60. It is also likely that below 150 K the free rotation of the C60 molecule is frozen as a result of the presence of the sandwiched HMTTEF molecule.

It is not clear as to what changes take place to bring about the enhancement of the ESR signal intensity below 150 K. An increase in intensity of the spectrum with increasing temperature, has been observed in ESR of C60.R adducts [R= CCl3, CBr3, C(CH3), (CH3)2CH] (ref. 13). Temperature dependence of this type has been interpreted as due the formation of its dimer and shift in the dimer (S = 0)/monomer (S=1/2) equilibrium. However, the present case is just the opposite.

In a general way, one can assume a dissociation (or charge transfer) reaction for an initial concentration [A:D] = No >>Ns,

\[ A:D \leftrightarrow A^- + D^+ \] obtains,

\[ K_{eq} = \frac{[A^-][D^+]}{[A:D]} \]

\[ = \frac{(Ns/2)^2}{[No - Ns]} = \exp \frac{-\Delta G}{RT} \]  \hspace{1cm} (2)

where the number of spins are obtained for a Boltzmann distribution \( \chi \propto Ns/T \), the data of fig. 2b then gives
ESR STUDIES ON C₆₀·OX AND C₆₀·HMTTEF

\[ \frac{\partial \ln(I/T)}{\partial 1/T} \equiv -\Delta H^*/2R \]  

The calibration relation (1) together with (3) give \( \Delta H^* = +0.13 \) kJ/mole and \( \Delta S = 90 \pm 8 \) J/k. The dissociation reaction (2) is controlled by the energy gap \( \Delta H^* > 0 \) and \( \Delta S^* \) measures the increase in entropy in going from the diamagnetic complex to free spins which is less than the value for the entropy of formation of free electrons in condensed phases: \( \Delta S^*(e^-_{(am)}) = 154 \pm 20 \) J/K/mole, \( \Delta S^*(e^-_{(YBa_2Cu_3O_7)}) = 261 \pm 15J/K/mole \) (ref. 26), but twice as large as the entropy of formation of ions in condensed phases, e.g., \( \Delta S^* (Cu^{2+}_{(aq)}) = 37 J/K/mole \) (ref. 27).

Conclusions:

The behavior of electron donor - acceptor complexes of C₆₀ depends on whether the fullerene acts as a donor or an acceptor. Since \( C_{60} \) and \( C_{60}\cdot O_x \) behave similarly it appears that the pure fullerene magnetic properties are due to \( C_{60}^{*+} \) spin - spin interactions. In \( C_{60}\cdot HMTTEF \) the nature of the interaction between \( A^{*-} \) and \( D^{*+} \) changes below 150 K. The additional exchange interaction, \( J = -3 \) kJ/mole may arise when rotational motion is frozen.

Acknowledgments:

The work at SJSU was carried out with support from NSF grant DMR 8921163 and 9307387 and, INT 8922483; JVA is most grateful to N. F. Mott, P. P. Edwards and Y. W. Liang while spending a sabbatical leave at the IRC in Superconductivity, Cavendish Laboratory, UK.
References


(Received December 5, 1995)