ESR spectra of C_{60} in concentrated sulfuric acid

S. P. Solodovnikov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: tuman@ineos.ac.ru

On dissolution of C_{60} in concentrated sulfuric acid, ESR spectra of paramagnetic species, which were identified as dimers $(C_{120}{}^+)$ or oligomers $(nC_{60})^+$, were recorded. The ESR spectra recorded upon the reaction of a toluene solution of C_{60} with sulfuric acid were assigned to the radical cation $C_{60}{}^+$.

Key words: fullerene, ESR; structure.

Study of the ESR spectra of radical anions and radical cations of aromatic hydrocarbons confirmed the conclusion, based on quantum-chemical investigations, about identical distributions of the unpaired electron density in these species.[1]

Previously,[2] we have studied the ESR spectra of the $C_{60}{}^-$ radical anions and compared them with the spectra of aromatic radical anions.

In the present work, we studied the ESR spectra of the radical cations arising in the reaction of C_{60} with concentrated sulfuric acid, which had been used earlier to oxidize aromatic hydrocarbons.[1]

Study of the electrochemical reduction and oxidation of C_{60} showed that these processes are reversible to different extents. Nevertheless, it was established that at a potential of $+1.26$ V (*vs* the ferrocene—ferricenium system), a reversible one-electron oxidation wave is observed, and the lifetime of $C_{60}{}^+$ is not less than 30 s.[3]

Experimental

Oxidation of C_{60} was carried out by two methods. According to the first method, 1 mg of C_{60} was dissolved in 0.5 mL of H_2SO_4. In the second method, a saturated toluene solution of C_{60} was mixed with H_2SO_4 (1 : 10 v/v); this gave ~0.15 mg of C_{60} in 0.5 mL of the solution.

ESR spectra were recorded on a Varian E-12 spectrometer equipped with double resonator. One resonator contained the sample under investigation, while the other one contained a sample with a g-factor equal to 2.0028 used as the reference compound for the g-factor measurement.

Results and Discussion

The ESR spectrum recorded at 77 K for the sample obtained by the first method exhibited triaxial anisotropy of the g-factor, characterized by $g_1 = 2.0041$, $g_2 = 2.0019$, and $g_3 = 2.0001$ (Fig. 1). As the temperature increases, the frequency of rotation of a paramagnetic

species increases, and the line is broadened. Thus, spectrum (*a*) transforms into an asymmetric line. At temperatures above 200 K, the latter transforms into spectrum (*b*), typical of a system with axial symmetry of the g-factor.

At about the vitrification temperature of sulfuric acid (~250 K), the signals corresponding to $g_{\parallel}$ and $g_{\perp}$ are broadened. Upon further increase in the temperature, the line sharply narrows down.

At 330 K, the line width is 0.0175 mT, and at the edges of the central line, satellite signals are recorded. In all probability, they are components of the hyperfine structure caused by splitting at the ^{13}C nuclei (spectra *c* and *d*). The splitting values are $a_1 = 0.175$ mT, $a_2 = 0.100$ mT, and $a_3 = 0.030$ mT, and $g = 2.0026$. Tenfold dilution of the solution under study with sulfuric acid does not change the observed temperature dependence of the ESR spectra.

The ESR spectrum of the sample obtained by the second method recorded at 77 K is shown in Fig. 2. The triaxial anisotropy of the g-factor is characterized by
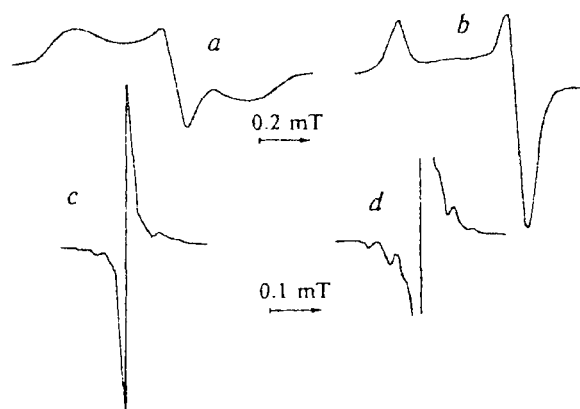

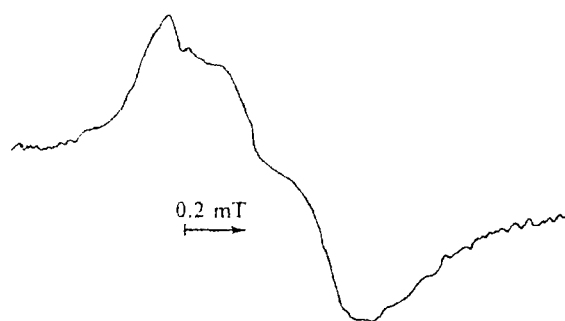**Fig. 1.** ESR spectrum of a solution of C_{60} in concentrated sulfuric acid at various temperatures. K: 77 (*a*), 200 (*b*), 330 (*c*, *d*).

Fig. 2. ESR spectra of C_{60} in a mixture of toluene and sulfuric acid (1 : 10) at 77 K.

Fig. 3. Molecular system of coordinates of C_{120}.

the values $g_1 = 2.0036$, $g_2 = 2.0021$, and $g_3 = 1.9996$. A rough estimate of the inherent line width at 77 K gives a value of ~0.1 mT. At room temperature, the g-factor is 2.0016, and the line width is 0.7 mT.

In this sample, no transition from the triaxial anisotropy to axial symmetry of the g-factor is observed at temperatures above 77 K. The oxidation of toluene under these conditions does not give a recordable amount of paramagnetic species.

The dependence of the ESR spectra on the method of oxidation of C_{60} points to different structures of the reaction products. The characteristic transition from triaxial anisotropy of the g-factor to the axial symmetry in the first sample means that the molecular rotation frequency around one specified axis differs significantly from those around other axes. The different constants of hyperfine coupling with ^{13}C nuclei are caused by the decrease in the symmetry of the paramagnetic species with respect to C_{60}^+.

The results obtained suggest that the oxidation product is a dimer (C_{120}^+) or oligomer $(nC_{60})^+$. In what follows, we assume the dimeric structure of the radical cation. Our conclusions are also consistent with the oligomeric structure.

The frequency of rotation of the dimer in a solid matrix around axis X (Fig. 3) should be much higher than that around axes Y and Z. This rotation should average the positions of the ESR lines corresponding to particular orientations of the Y and Z axes in the magnetic field. Hence, the arrangement of the X axis parallel to the vector of the magnetic field intensity corresponds to the signal $g_1 = g_\parallel$, while averaging of the positions of the g_2 and g_3 signals gives $g_\perp$.

Analysis of spectra c and d shows that the spin density in the detected radical cation is distributed nonuniformly. A formal calculation of the HFS constant expected from the ^{13}C nucleus in the C_{60} radical anion and radical cation, carried out using the HFS parameters of aromatic systems, gives a value of -0.019 mT.[4] This constant might be inaccurate because C_{60} is nonplanar, but it correctly reflects the order of magnitude. The HFS constants observed in spectra c and d are substantially higher.
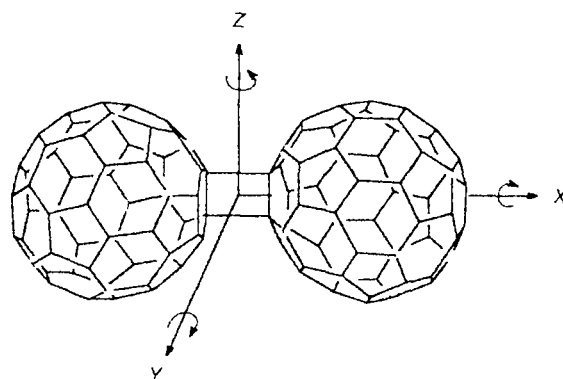
A rough comparison of the total intensities of the satellite lines and the central signal indicates that the corresponding spin density is distributed over approximately 30 carbon atoms, which can be divided into three groups, whose ratio is 1 : 2.5 : 5. Analysis of the ^{13}C NMR spectrum of the C_{120} dimer demonstrated the presence of 16 groups of equivalent atoms, each comprising 4, 8, or 16 atoms.[5] The ratio of these numbers, 1 : 2 : 4, is close to the intensity ratio of the satellite lines.

The distribution of the unpaired electron in one or two fullerene fragments of the dimer can be discussed using the same considerations as had been used in the discussion of the spin density delocalization in the radical anions of bridged diaryl compounds.[6] The location of the 30 ^{13}C carbon nucleus involved in the hyperfine coupling in either one or two fullerene fragments may be judged only from the data on the ESR line width alternation. To observe this effect, the ESR spectra in a wide temperature range should be studied. In this particular case, the alternation might be manifested at elevated temperatures. However, at high temperatures, the paramagnetic species undergo fast decay.

If the positive charge is localized in one fullerene fragment, the energy of Coulomb interaction between the C_{120}^+ radical cation and the HSO_4^- anion is higher than in the case of charge delocalization over the whole molecule; hence, this charge distribution is more favorable. Formation of a contact ion pair between C_{120}^+ and HSO_4^- is possible because of the moderate polarity of H_2SO_4; this can be judged from the Q-factor of the loaded resonator. The delocalization of the unpaired electron between the fragments should have a dynamic nature, associated with migration of the anion from one fragment to the other.

The anisotropy value $g_1 - g_3 = 0.004$ in the radical cations in question is approximately 3 times higher than the corresponding value for the radical anion (C_{60}^-).[2]

The line width in the spectrum of the second sample increases as the temperature is raised, as in the case of the ESR signal of the C_{60}^- radical anion.[2] The decrease in the symmetry of C_{120}^+ with respect to C_{60}^+ violates

apparently the relationship between the oscillating and electronic motions, which is the prerequisite for manifestation of the Jahn—Teller effect. Presumably, the occurrence of this relationship accounts for the short spin—lattice relaxation times in C_{60}^- and C_{60}^+. The width of the C_{120}^+ ESR line at room temperature is of the same order of magnitude as those for radical cations of aromatic hydrocarbons.[1]

The results obtained make it possible to conclude that on dissolution of C_{60} crystals in sulfuric acid, in addition to oxidation of molecules, cation dimerization and oligomerization occur at relatively high local concentrations of C_{60} and probably also on the crystal surface. The reaction of a toluene solution of C_{60} ($4 \cdot 10^{-3}$ mol L^{-1}) with a tenfold excess of sulfuric acid proceeds at such reactant ratios at which the rate of cation oligomerization is insignificant.

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Sulfur ylides
8.* Synthesis of 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione

F. Z. Galin,* S. N. Lakeev, L. F. Chertanova, and G. A. Tolstikov

*Institute of Organic Chemistry, Ufa Research Center of Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: root@chemorg.ufanet.ru*

Intramolecular cyclization of ketostabilized sulfur ylide obtained from β-alanine and 2,3-pyridinedicarboxylic anhydride was studied. The structure of the reaction product, 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione, was established by X-ray diffraction analysis.

Key words: ketostabilized sulfur ylides, intramolecular cyclization, 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione.

In our previous works,[1-6] we described the synthesis and chemical properties of phthalimido-containing ketostabilized sulfur ylides obtained from α-, β, γ-, and δ-amino acids and phthalic anhydride, as well as the influence of substituents in the phthalimide fragment on the regioselectivity of intramolecular cyclization of sulfur ylides obtained from β-alanine and substituted phthalic anhydrides. The intramolecular cyclization results in the formation of compounds with the structure of indolizidine-2,6-dione.[1-6]

In continuation of the study of the intramolecular cyclization observed, we studied the behavior of ketostabilized sulfur ylide (1) obtained from β-alanine and pyridine-2,3-dicarboxylic anhydride. Ylide 1 containing pyridine-2,3-dicarbimide fragment was obtained

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* For Part 7, see Ref. 1.