The ESR spectra of the spin-adducts of branched perfluorinated σ-radicals with fullerene-60

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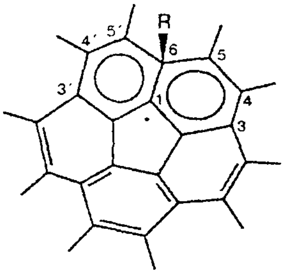
The ESR spectra of the radical adducts of the $^{\bullet}CF{=}CFC(CF_3)_3$ and $^{\bullet}C(O)CF(CF_3)_2$ radicals with C_{60} are characterized by hyperfine interaction with the nucleus of the δ-fluorine atom located above the five-membered cycle in the fullerenyl radical.

Key words: fullerene, ESR, fluorine, radical.

The C_{60} molecule is a superalkene[1] with 30 weakly conjugated double bonds to which free radicals of different chemical nature can be bonded.[2] It has been established[3] that the unpaired electron in the fullerenyl radicals is mainly delocalized in the two six-membered cycles adjacent to the C(1)—C(6)R bond and the spin density is distributed as follows: C(1) ≈ 0.33; C(3), C(3′), C(5), C(5′) ≈ 0.17, and its character is virtually independent of the structure of the attached radical.[2]



The ESR spectra of radical adducts of perfluoroalkyl radicals [$^{\bullet}CF_3$, $^{\bullet}CF_2CF_3$, $^{\bullet}CF_2(CF_2)_5CF_3$, $^{\bullet}CF(CF_3)_2$, and $^{\bullet}C(CF_3)_3$][4,5] with C_{60} have several peculiarities indicating that the rotation of perfluoroalkyl substituents is hindered. The equilibrium position of the perfluoroalkyl fragment with respect to the symmetry axis of the fullerenyl radical depends on the structure of the substituent. For instance, the perfluoroisopropyl group is in an asymmetric position with respect to the symmetry plane: the F atom is above the six-membered cycle, while one trifluoromethyl groups is above a five-membered cycle and one is above a six-membered cycle. The constants of hyperfine interaction (HFI) with the nuclei of the six equivalent δ-F atoms of the trifluoromethyl groups (a_F(6 F) = 2.0 G) are appreciably larger than those for the γ-F atom (a_F(1 F) = 0.83 G).[5] This is associated with the fact that the constant of HFI with the nuclei located above the five-membered cycle is larger than the constant of HFI with the nuclei located above the six-membered cycle, and the observed spectral pattern is associated with a process of fast exchange between the positions of the two trifluoromethyl groups.[6]

In this work, the possible radical functionalization of C_{60} by perfluorinated branched σ-radicals containing C=C and C=O bonds at the radical center has been studied.

Experimental

The solutions under study were irradiated by the filtered (in the 620—680 nm region) or unfiltered light of a DRSh-1000 high-pressure mercury lamp. The ESR spectra were recorded on a Varian T-12A spectrometer.

Results and Discussion

The 3,3-bis(trifluoromethyl)perfluorobut-1-enyl radical (**1a**) was generated by photolysis of the pertinent mercury compound[7] in a saturated solution of C_{60} in 1,2,4-trichlorobenzene in the temperature range from 270 to 430 K.

$$\underset{\mathbf{1}}{Hg[CF{=}CFC(CF_3)_3]_2} \longrightarrow Hg + 2\ \underset{\mathbf{1a}}{^{\bullet}CF{=}CFC(CF_3)_3}$$

$$C_{60} + {}^{\bullet}CF{=}CFC(CF_3)_3 \longrightarrow \underset{\mathbf{1b}}{^{\bullet}C_{60}{-}CF{=}CFC(CF_3)_3}$$

The ESR spectrum of radical **1b** (at 270 K) is a doublet with HFI constant a_F = 0.35 G and g = 2.0031 (Fig. 1, spectrum *1*). It can be assumed that, by analogy with other adducts of fluoroorganic radicals with fullerene, the constant of HFI with the nucleus of the δ-F atom located above the five-membered cycle will be larger than the constant of HFI with the nucleus of the γ-F atom, and thus the HFI constant of 0.35 G should

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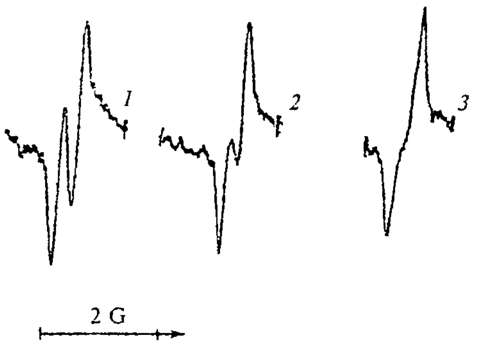
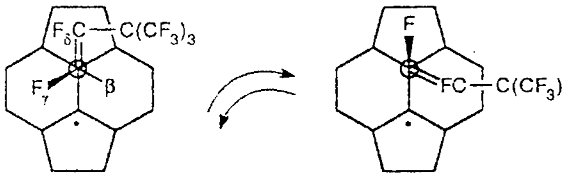


Fig. 1. ESR spectra of radical **1b** at 270 (*1*), 400 (*2*), and 440 K (*3*).

just belong to the δ-F atom. Heating the sample to 460 K results in line broadening (see Fig. 1, spectrum *2*), which is likely due to an increase in the rate of exchange between the different conformations (*cf.* Ref. 3). Thus, there is an increase in the fraction of conformation *B*, in which the constant of HFI with the nucleus of the δ-F atom is smaller than that in conformation *A* but larger than the constant of HFI with the nucleus of the γ-F atom. In this case, the line broadening could be associated either with the formation of a doublet of doublets or a triplet; however, one fails to reach the limiting case for either conformation even at 500 K.



A *B*

The assumption that the observed splitting of the doublet in radical **1b** is associated with the interaction of the unpaired electron with the nucleus of the δ-F atom is confirmed by the data obtained for the adduct of the perfluoroisobutyryl radical with C_{60} that is formed in the case of UV irradiation of $(CF_3)_2CFC(O)C(O)C(O)CF(CF_3)_2$ (**2**) in a saturated solution of C_{60} in 1,2,4-trichlorobenzene:

$$2 \xrightarrow{h\nu} 2\,(CF_3)_2CFC^{\bullet}(O) + CO,$$

$$(CF_3)_2CFC^{\bullet}(O) \longrightarrow CO + {}^{\bullet}CF(CF_3)_2,$$

$$C_{60} + {}^{\bullet}C(O)CF(CF_3)_2 \longrightarrow \underset{\mathbf{2a}}{{}^{\bullet}C_{60}C(O)CF(CF_3)_2},$$

$$C_{60} + (CF_3)_2C^{\bullet}F \longrightarrow \underset{\mathbf{2b}}{{}^{\bullet}C_{60}CF(CF_3)_2}.$$

The ESR spectrum (Fig. 2, spectrum *1*) is a superposition of the signals of fullerenyl radicals **2a** and **2b**. In this case the intensity of the signal of adduct **2a** (a doublet with a_F = 0.2 G and g = 2.003) changes from that of the signal of adduct **2b** (see Fig. 2, spectrum *2*) as temperature changes. This is associated with the fact that the perfluoroisopropyl radical is formed as a result of thermal decomposition of the corresponding acyl radical. For this reason, adduct **2a** is never formed in the thermal generation of radicals from triketone (see Fig. 2, spectrum *3*).

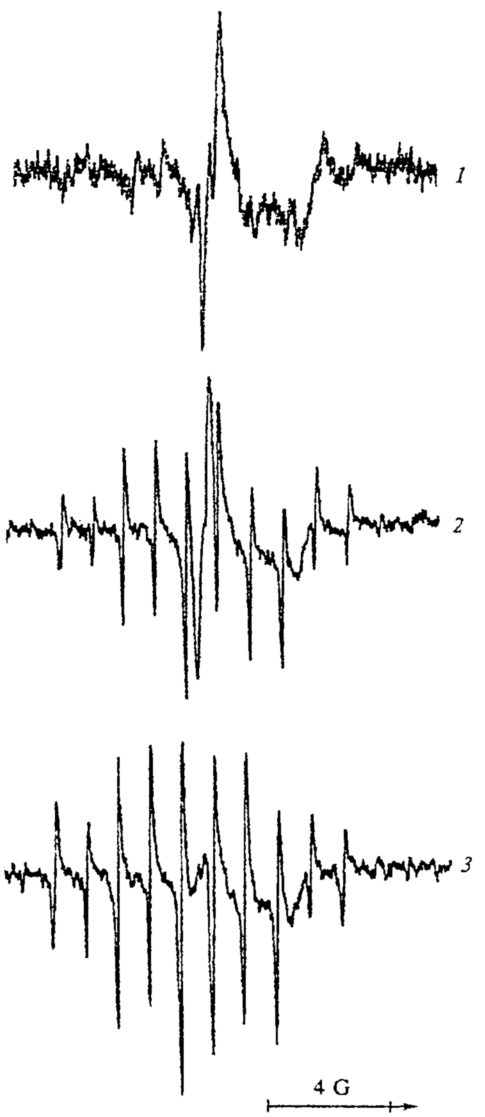


Fig. 2. ESR spectra of radicals: **2a** and **2b** at 380 K with UV irradiation (*1*); **2a** and **2b** with UV irradiation at 500 K (*2*); and **2b** at 500 K (*3*).

In the case of irradiation of the asymmetric triketone[8] $(CF_3)_2CFC(O)C(O)C(O)CF_2CF_3$ (**3**) in the temperature range from 400 to 490 K under conditions analogous to those described above, the ESR signals of the ${}^{\bullet}C_{60}CF(CF_3)_2$ and ${}^{\bullet}C_{60}CF_2CF_3$ radical adducts and a poorly resolved singlet are recorded; the latter could be a result of the overlap of the spectra of acyl radicals $^{\cdot}C_{60}C(O)CF(CF_3)_2$ and $^{\cdot}C_{60}C(O)CF_2CF_3$.

Thus, fullerene instead of thermally unstable nitroso compounds[9] can be used as a radical trap for studying the thermolysis and photolysis of fluoroorganic compounds

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Reaction of 1-chloro-2-phenylethane-2,2-dithiol with divalent metal (Cu, Hg, Pb, Fe, Co, and Ni) salts

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Reactions of 1-chloro-2-phenylethane-2,2-dithiol with lead(II) acetate and mercury(II) chloride lead to 1-chloro-2-phenylethane-2,2-dithiolates of lead and mercury. The reactions with copper(II) chloride, iron(II) sulfate hydrate, cobalt (II) chloride hydrate, and nickel(II) acetate give metal-containing compounds $C_{16}H_{18}S_4M$. The ^1H NMR, IR, and ESR spectra of the obtained compounds were recorded; their specific dark electroconductivities and activation energies of dark conductivity were determined, and their film-forming ability was studied.

Key words: *gem*-dithiols, metallic derivatives; specific dark electroconductivity, organic semiconductors.

Metallic derivatives of 1-halo-2-organylethane-2,2-dithiols [R—C(SH)$_2$—CH$_2$Cl, R = Me, Ph, 5-chlorothienyl][1] have not yet been described. We studied the interaction of 1-chloro-2-phenylethane-2,2-dithiol (**1**) with salts of divalent metals (Cu, Hg, Pb, Fe, Co, Ni).

Dithiol **1** reacts with either lead(II) acetate or mercury(II) chloride in methanol to form 1-chloro-2-phenylethane-2,2-dithiolates of lead (**2b**) or mercury (**2a**):

$$\underset{\text{HS}\ \ \text{SH}}{\text{Ph—C—CH}_2\text{Cl}} + MX_2 \longrightarrow \underset{\underset{\text{M}}{\text{S}\ \ \text{S}}}{\text{Ph—C—CH}_2\text{Cl}} + 2\,HX$$

1 **2a, b**

M = Hg (**2a**); Pb (**2b**)

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