ESR study of spin-adducts of phosphoryl radicals with methano[60]fullerenes

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The influence of structurally different methanofragments attached to [60]fullerene on the spectral parameters of the spin-adducts of phosphoryl radicals with these compounds was studied by ESR spectroscopy. The main direction of attack of phosphoryl radicals is the same fullerene hemisphere to which the methanofragment is attached.

Key words: ESR spectroscopy, fullerenyl radical, methanofullerene, phosphoryl, spin-adduct.

Previously,[1—4] we have studied the spin-adducts of phosphoryl radicals with some $C_{60}X$ ($X = M(PPh_3)_2$; M = Pt, Pd; $C(C_6H_4OMe)_2$, *etc.*) derivatives. We recorded the ESR spectra of several isomers differing in the constants of hyperfine coupling (HFC) of the unpaired electron with the nuclei of phosphorus atoms, *g*-factors, and stability. In these isomers, the phosphoryl group is at different distances from the fragment X attached to the fullerene.[1—3] A deformation of the carbon cage, which results in a change in the curvature of the fullerene surface,[4] can be one of the reasons for changes in the constants of HFC with the nucleus of phosphorus atom in the case of fullerene derivatives. Steric interaction between the X fragment and P=O group can also affect the HFC constants of the isomers in which the phosphoryl group is at a distance of two or three bond lengths from X. In addition, such isomers are more stable because of the shielding of the radical center.[4]

The ESR spectra of spin-adducts of phosphoryl radicals with fullerene derivatives contain information on the effect of functional groups on the degree of distortion the carbon cage, regiochemistry of the addition of phosphoryl radicals, as well as on the bonding character and mutual arrangement of the groups attached to fullerene.[5]

In this work, the influence of the structure of methylene fragment in the molecules of methyl(*p*-methoxyphenyl)methano[60]fullerene (**1**) and spiro(2,6-di-*tert*-butyl-2,5-cyclohexadienon)methano[60]fullerene (**2**) on spectral parameters of the spin-adducts of phosphoryl radicals with **1** and **2** was studied by ESR spectroscopy.

Experimental

ESR spectra of specimens placed in degassed quartz ampoules were recorded on a Varian E-12A spectrometer. The specimens were irradiated by the focussed light of a DRSH-1000 lamp. Compound **1** was obtained by thermal decomposition of sodium salt of tosylhydrazone *p*-methoxyacetophenone in toluene in the presence of C_{60} (see Ref. 6). Compound **2** was obtained following the known procedure.[7] The structure of methano[60]fullerene **2** was confirmed by ^1H NMR spectroscopy. The ESR spectrum observed upon reduction of compound **2** with sodium amalgam in THF was analogous to that described previously.[7] Calulations were carried out by the molecular mechanics (MM^+) method.

Results and Discussion

Diisopropylphosphoryl radicals were generated by photolysis of a corresponding mercury compound[8] in saturated toluene solutions of the methylene derivatives of fullerene immediately in the cavity of the ESR spectrometer:

$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} 2\ {}^{\cdot}P(O)(OPr^i)_2 + Hg,$$

$$Z + {}^{\cdot}P(O)(OPr^i)_2 \longrightarrow {}^{\cdot}ZP(O)(OPr^i)_2,$$

$Z =$ **1** or **2**.

The ESR spectrum of the isomers of the spin-adducts of phosphoryl radicals with methano[60]fullerene **1** is a superposition of six doublets. The constants of HFC with the nuclei of phosphorus atoms (a_P) are equal to 60.0 (**1a**), 62.7 (**1b**), 65.0 (**1c**), 67.0 (**1d**), 68.8 (**1e**), and 69.3 G (**1f**), and the *g*-factors for all isomers are close to 2.0017. This suggests the formation of monoadducts, as in the previously described experiments on the addition of phosphoryl radicals to fullerenes derivatives.[1—4]

In order to prevent the formation of the adducts of polyaddition of phosphoryl radicals to methano[60]fullerene **1**, phosphorylation was carried out in the

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presence of perfluoro-*tert*-butyl alcohol ($HOC(CF_3)_3$),[3] whose addition results in an increase in the constants of HFC of the unpaired electron with the nucleus of phosphorus atom by 2—4 G and in a narrowing of the lines in the ESR spectrum of the spin-adducts of phosphoryl radicals with C_{60} derivatives.[9] In fact, as can be seen in Fig. 1, *a*, the number of signals observed in the ESR spectrum recorded upon the photolysis of the reaction mixture in the presence of $HOC(CF_3)_3$ increases and equals nine. The constants of HFC with the nuclei of phosphorus atoms (a_P) are equal to 63.4 (**1a'**), 64.4 (**1b'**), 66.3 (**1c'**), 68.6 (**1d'**), 70.5 (**1e'**), 73.0 (**1f'**), 76.0 (**1g'**), 77.5 (**1h'**), and 78.5 G (**1i'**) (the *g*-factor values for all isomers lie in the range between 2.0017 and 2.0019).

Switching off the irradiation leads to disappearance of the regioisomers of spin-adducts (during 1 s) due to dimerization (*cf.* Ref. 10), except for the **1a'**, **1c'**, and **1f'** isomers for which the intensities of the ESR signals decrease by 76, 96, and 87%, respectively (see Fig. 1, *b*). It is likely that the enthalpy of the radical $\rightleftharpoons$ dimer equilibrium for the spin-adducts decreases because of the steric shielding by the methylene fragment, and the integrated intensity of these signals is ~83% from the total integrated intensity of the spectra of all isomers obtained.

In order to assign the observed signals in the ESR spectrum to possible regioisomers, we calculated the deviations from 360° of the sum of the bond angles at the carbon atoms of the fullerene cage, which are at different distances from the attached methylene group, taking structure **1** (Fig. 2) optimized by the molecular mechanics (MM$^+$) method as an example. The results of calculations are listed in Table 1. We found that the larger the deviation, the greater the curvature of the corresponding cage surface area and the higher the probability of addition of the attacking radical to the double bond at the corresponding carbon atom.

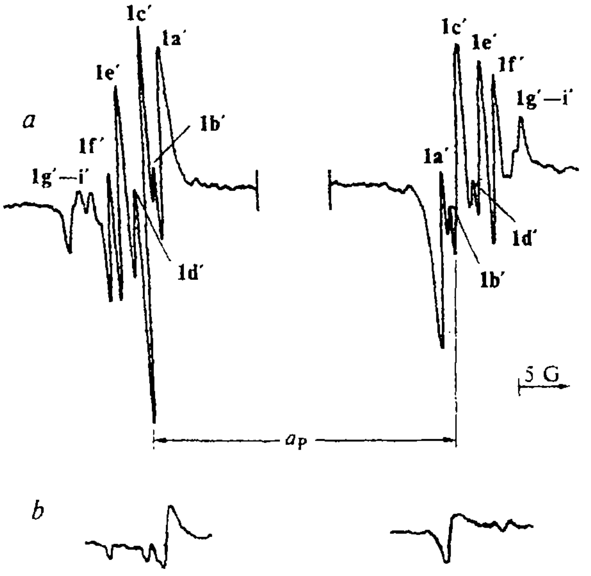
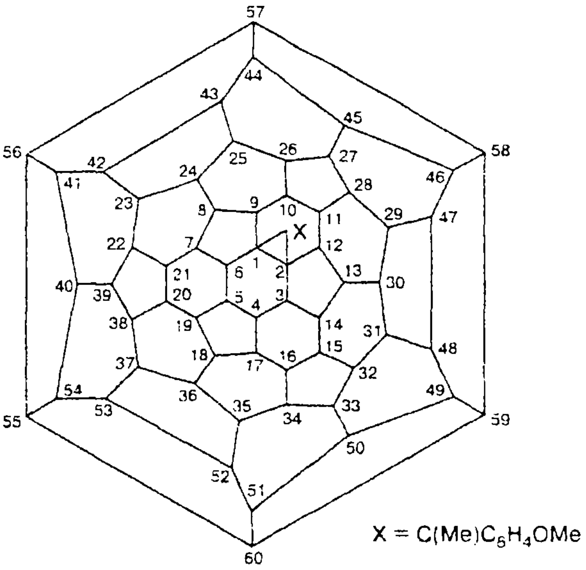


Fig. 1. ESR spectrum of the spin-adducts of addition of phosphoryl radicals to methano[60]fullerene **1** in the presence of $HOC(CF_3)_3$: irradiated (*a*) and non-irradiated (*b*).



X = C(Me)C_6H_4OMe

Fig. 2. Graph of compound **1**.

As follows from the results obtained, the most sterically strained are the surface areas near the carbon atoms that are at a distance of two or three bond lengths from the methylene group (the C(4), C(5), C(10), C(11), C(15), C(21), C(24), and C(30) atoms). However, the addition to the C(4) and C(5) atoms is sterically hindered because of a neighboring bulky phenyl group. The addition to the C(3), C(6), C(7), C(8),

Table 1. Deviations of the sum of the bond angles ($\Delta\varphi_\Sigma$) at carbon atoms of the fullerene cage from 360°

Atom of fullerene cage	$\Delta\varphi_\Sigma$/deg
C(4), C(5), C(10), C(11)	15.339
C(15), C(21), C(24), C(30)	13.527
C(22), C(23), C(31), C(32)	12.313
C(33), C(39), C(42), C(48)	12.107
C(16), C(20), C(25), C(29)	12.097
C(35), C(37), C(44), C(46)	12.051
C(34), C(38), C(43), C(47)	12.043
C(52), C(53), C(57), C(58)	12.025
C(55), C(60)	12.012
C(51), C(54), C(56), C(59)	12.003
C(40), C(41), C(49), C(50)	11.943
C(36), C(45)	11.639
C(18), C(27)	11.533
C(17), C(19), C(26), C(28)	11.427
C(7), C(8), C(13), C(14)	8.851
C(3), C(6), C(9), C(12)	6.766

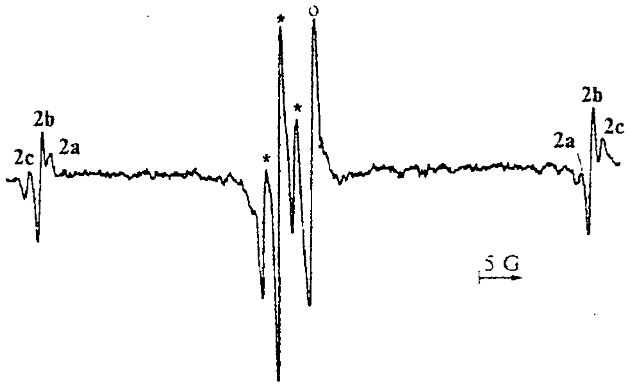


Fig. 3. ESR spectrum of the reaction mixture obtained after irradiation of methano[60]fullerene **2** in the presence of $Hg[P(O)(OPr^i)_2]_2$ in toluene (the components of the signal of fullerenylphenoxyl radical are asterisked; the signal of the carbon-centered fullerenyl radical is shown by an open circle).

C(9), C(12), C(13), and C(14) atoms is less probable since they are less sterically strained.

Thus, the three stable isomers whose signals are observed in the ESR spectrum after switching off the irradiation correspond to spin-adducts with the phosphoryl group attached to the carbon atoms in positions 10, 11, 15, 21, 24, and 30.

Another spectral pattern was observed (Fig. 3) in the case of addition of phosphoryl radicals to methano[60]fullerene **2**. Here, signals of three types of species were recorded, namely, three isomers of monophosphorylfullerenyl radicals with the parameters $a_P = 62.25$ G, $g = 2.0022$ (**2a**); $a_P = 66.0$ G, $g = 2.0020$ (**2b**); and $a_P = 66.0$ G, $g = 2.0023$ (**2c**); phenoxyl radical (a_H(2 H) = 1.9 G, $g = 2.0046$), and fullerenyl radical (singlet, $g = 2.0024$). The formation of species **2a—c** is due to the attack of the phosphoryl radicals on the carbon atoms of the fullerene cage, which are distant from the methylene group.

Photolysis of the reaction mixture results in the photoexcitation of compound **2** and generation of a biradical. Interaction between the phosphoryl radical and fullerenyl biradical results in the formation of stable fullerenylphenoxyl radical; this direction of the attack of the phosphoryl radical may appear to be preferable (Scheme 1).

Thus, studies of the regiochemistry of the addition of phosphoryl radicals to methano[60]fullerenes **1** and **2** showed that the dominating direction of attack of the phosphoryl radicals is the same fullerene hemisphere to which the methanofragment is attached.

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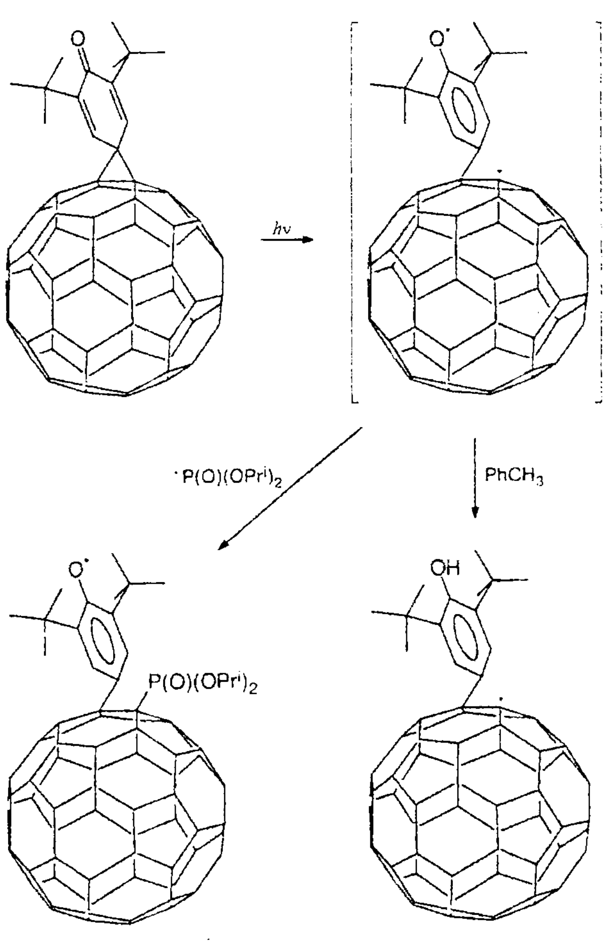
Scheme 1



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