ESR study of spin-adducts of dialkoxyphosphoryl radicals with di(*p*-methoxyphenyl)methanofullerene

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The addition of phosphoryl radicals to $C_{60}C(p\text{-}C_6H_4OMe)_2$ was shown (ESR) to result in the formation of at least seven isomers differing in their hyperfine coupling constants (HFC) with the phosphorus nuclei and in their kinetic behavior and thermodynamic stability.

Key words: ESR, diarylmethanofullerene, fullerenyl radical, isomers.

A characteristic feature of fullerenes, owing to the large number of double bonds, is their ability to add free radicals of different chemical nature. Until recently, the addition of free radicals only to fullerenes C_{60} and C_{70} themselves, but not to their derivatives, has been studied.[1–10]

Recently,[11] we studied the interaction of phosphoryl radicals $^{\cdot}P(O)(OPr^i)_2$ with $C_{60}M(PPh_3)_2$ (M = Pd, Pt) by the ESR method and showed that at least five isomers formed; these isomers differed in their hyperfine coupling constants (HFC) (58.5—68 G) and *g*-factors (2.0017—2.0028). The appearance of these isomers is associated with the lowering of symmetry of the C_{60} metal complexes compared to that of the initial fullerene.

An analysis of the ESR spectra of spin-adducts of fullerene derivatives makes it possible to estimate the number of reactive double bonds participating in the reactions of the radical addition. A quantitative description of the reactivity of different positions in a substituted fullerene is difficult because of the kinetic factors; in fact, the intensity of the ESR spectra of the fullerenyl radicals is determined by both the rate of the addition reaction of radicals generated photochemically to the fullerene derivative and the rate of decay (dimerization) of spin-adducts.

In this work, the spin-adducts of phosphoryl radicals with di(*p*-methoxyphenyl)methanofullerene were studied. The structures of diarylmethanofullerenes and η^2-metallocomplexes are topologically similar owing to the presence of a three-membered ring; however, they differ in their geometry since the metal has a square-planar configuration, while the carbon configuration is tetrahedral.[12,13]

Experimental

The solutions under study were irradiated by filtered (620—680 nm) or nonfiltered light of a DRSh-1000 high pressure mercury lamp. The ESR spectra were recorded on a Varian E-12A spectrometer. Compound $C_{60}C(C_6H_4OMe)_2$ was obtained according to the known procedure.[14]

Results and Discussion

Homolytic phosphorylation of $C_{60}C(C_6H_4OMe)_2$ was carried out according to a conventional procedure,[5,6] by photolysis of diphosphorylmercuric compounds in a saturated toluene solution of $C_{60}C(C_6H_4OMe)_2$.

$$Hg[P(O)(OPr^i)_2]_2 \rightarrow 2\ ^{\cdot}P(O)(OPr^i)_2 + Hg$$

$$C_{60}C(C_6H_4OMe)_2 + {}^{\cdot}P(O)(OPr^i)_2 \rightarrow$$
$$\rightarrow (Pr^iO)_2(O)P^{\cdot}C_{60}C(C_6H_4OMe)_2$$

The ESR spectrum (Fig. 1) is a superposition of at least seven different doublets, which originate from the interaction of an unpaired electron with the phosphorus nuclei located in different positions with respect to the three-membered cycle: **1**, a_P = 74.4 G, g = 2.0024; **2**, a_P = 72.0 G, g = 2.0025; **3**, a_P = 68.5 G, g = 2.0023; **4**, a_P = 66.5 G, g = 2.0023; **5**, a_P = 64.8 G, g = 2.0020; **6**, a_P = 62.5 G, g = 2.0022; **7**, a_P = 59.25 G, g = 2.0021.

The picture of the overlapped spectra is almost completely symmetrical, which is evidence for close values of *g*-factors (2.0020—2.0025) of the recorded isomers [*cf.* Ref. 11: g = 2.0017—2.0028 for the radical adducts with $C_{60}Pt(PPh_3)_2$]. There are four main factors, which can cause a change in the hyperfine coupling constant with the phosphorus atom nucleus: a) steric interaction of the phosphoryl group with the substituent, b) a change in the geometry of the carbon polyhedron of $C_{60}C(C_6H_4OMe)_2$ compared to that of C_{60}; in this case flattening of the radical center must result in a stronger delocalization of the unpaired electron and a decrease in the hyperfine coupling constant with the nucleus of the

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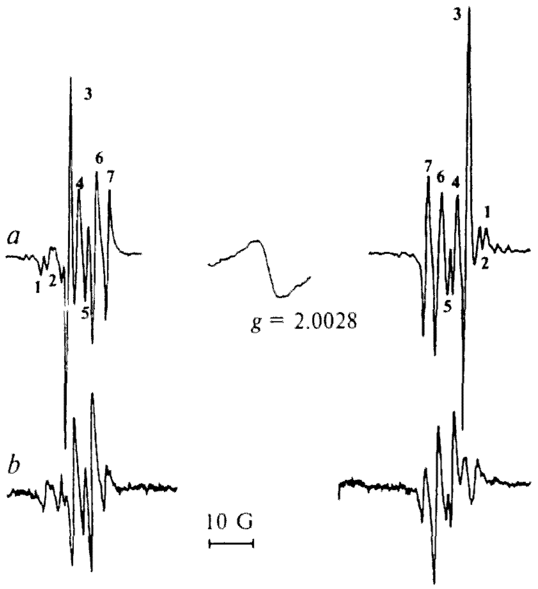
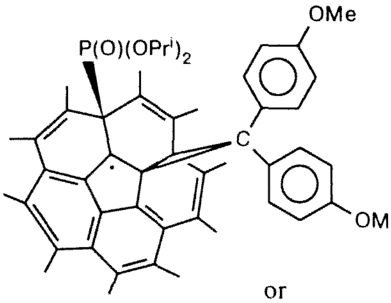
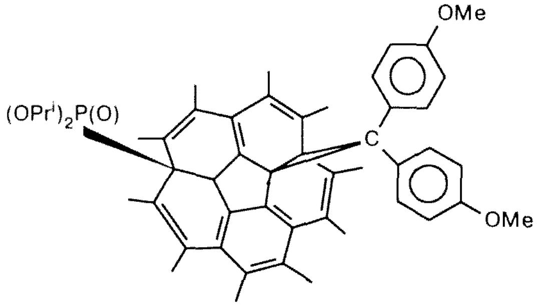


Fig. 1. ESR spectra of the adducts of phosphoryl radicals **1—7** with $C_{60}C(C_6H_4OMe)_2$ at 300 K obtained on irradiation with visible light: *a*, 5 min after photolysis at 300 K; *b*, 45 min after heating at 430 K.

phosphorus atom; it also leads to an increase in the HFC for steeper vertices; c) different positions of the phosphoryl group with respect to the unpaired electron orbital (the conformational isomerism[10]), and d) a decrease in delocalization of the unpaired electron due to the addition of the phosphoryl radical to the double bond neighboring the methylene fragment; in this case, the double bond closest to the radical center is excluded from the delocalization system. The analysis of the values of hyperfine coupling constants with the nucleus of the phosphorus atom is insufficient for determining the position of the attached phosphoryl radical with respect to the methylene group in $C_{60}C(p\text{-}C_6H_4OMe)_2$. Additional data are necessary, in particular, data on the reactivity since the closer to the methylene group the phosphoryl radical is attached, the more shielded will be the fullerenyl radicals. Since dimerization is most characteristic of the fullerenyl radicals, the rate of dimerization and the enthalpy of the radical—dimer equilibrium must depend on the mutual positions of the phosphoryl radical and the substituent. In fact, all radicals except for **3** completely disappear in 1 s when the irradiation is switched off (300 K), whereas the intensity of the spectral lines of **3** decreases only sixfold. Thus, it follows that the enthalpy of the radical—dimer equilibrium for this isomer is lower than that for the others; therefore, a stationary concentration of isomer **3** is observed at 300 K (the value of the enthalpy of the radical—dimer equilibrium for different isomers is an average value since the dimers can have a mixed structure, for instance, radical **3** can dimerize with radicals **4**, **5**, *etc.*). It can be assumed that the phosphoryl group in this isomer is the closest to the shielding substituent:



or



An increase in temperature to 430 K results in dissociation of the dimers of the corresponding isomers and makes possible their recording in the absence of irradiation, an increase in the hyperfine coupling constants with the nucleus of the phosphorus atom, and insignificant changes in the *g*-factors being observed: **2**, a_P = 73.0 G, g = 2.0025; **2a**, a_P = 69.25 G, g = 2.0022; **4**, a_P = 67.0 G, g = 2.0023; **5**, a_P = 65.0 G, g = 2.0022; **6**, a_P = 62.75 G, g = 2.0021; **7**, a_P = 60.1 G, g = 2.0022. These changes in the magnetic-resonance parameters are, evidently, the result of the effect of temperature on the hindered rotation of the phosphoryl group.[10]

It should be noted that the stationary concentration of **3** slowly decreases in 30 min at 300 K, apparently due to the radical decay. The rate of decay increases as the temperature increases, and the rate constant for the decay of **3** (k) is equal to $3.3 \cdot 10^{-3}$ s^{-1} at 430 K. As can be seen from Fig. 2, a decrease in the intensity of the spectrum of **3** is accompanied by a small increase in the amplitude of the peaks of other isomers (**7** and **6**). This increase can be the result of isomerization of **3** into other isomers due to an intermolecular (or possibly of an intramolecular) transfer of the phosphoryl group; the possibility of generation of the phosphoryl radicals in the thermal decay of the diphosphorylmercuric compound should also be taken into account. This problem will also be studied later.

In the irradiation of a sample (at 430 K) with visible light (620—680 nm), which only affects the phosphorylfullerenyl radical dimers, the intensity of signals of the isomers increases differently (Fig. 3). Since the dimers of different isomers have a close extinction, one can assume that the major portion of the dimers in solution is dissociated into radicals under the action of light.

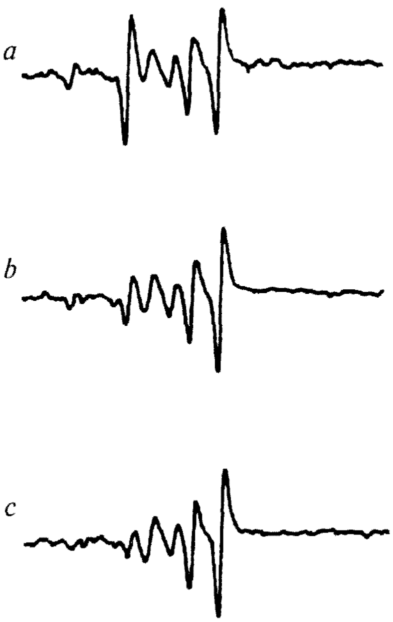


Fig. 2. The low-field multiplet of the adducts of the phosphoryl radicals with $C_{60}C(C_6H_4OMe)_2$ at 430 K: heating for 30 (*a*), 340 (*b*), and 740 s (*c*).

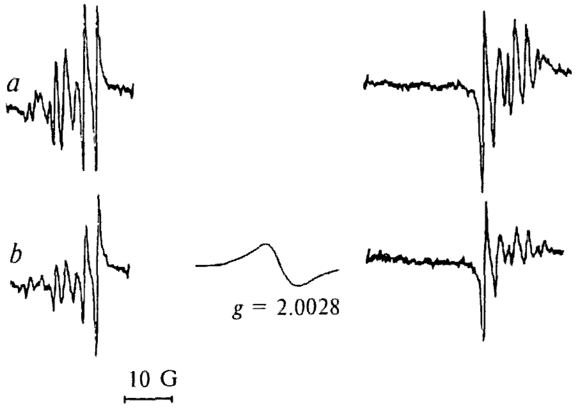


Fig. 3. ESR spectra of the adducts of the phosphoryl radicals with $C_{60}C(C_6H_4OMe)_2$ at 430 K: *a*, obtained on irradiation with visible light; *b*, for a non-irradiated sample.

With this in mind, it is possible to estimate the degree of thermal dissociation of the dimers of different radicals by finding the ratio of the intensity of each isomer in the ESR spectrum on heating to its intensity in the photodissociation. Radicals **4**—**7** appeared to be dissociated at 430 K by 42, 67, 57, and 100%, respectively. The higher the degree of dissociation of the dimer, the lower the energy of its bond and the closer the phosphoryl substituent to the methylene group. It follows from these data that the isomers can be arranged in the following series in accord with the bond strength: **3** < **7** < **5** < **6** < **4**. Prolonged (~40 min) heating of the sample at 430 K results in a decrease in the intensity of the spectrum not only for radical **3**, but also of those for radicals **7** and **5** (see Fig. 1, *b*). It thus follows that the closer the phosphoryl radical is attached to the methylene group, the stronger is the steric strain leading to a decrease in the energy of the $C—P(O)(OPr^i)_2$ bond.

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