Reviews

An ESR study of radical reactions of C_{60} and C_{70}

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The results of ESR spectroscopic studies of radical reactions of fullerenes are presented. Reactivities of radicals of various chemical natures with respect to C_{60} and C_{70}, delocalization of the unpaired electron in monofullerenyl radicals, and their reactivity are considered. The examples of dynamic effects in the ESR spectra of fullerenyl radicals, associated with the hindered rotation of the attached radicals, are presented. Characteristic features of the structures of the spin adducts resulting from polyaddition of free radicals to fullerenes and of fullerenyl radicals containing η^2-bonded metallocomplexes are discussed.

Key words: fullerene; ESR; radicals, structure, reactivity.

Introduction

The elaboration of methods for preparation[1] and chromatographic separation of C_{60}, C_{70}, and other fullerenes[2] has stimulated vigorous development of the chemistry of these compounds. In particular, halogenation,[3] epoxidation,[4] alkylation,[5] formation of organometallic derivatives,[6,7] and other reactions of fullerenes have been studied in detail and described in known papers.[8–10] Radical reactions constitute an important aspect of the chemistry of fullerenes.

The C_{60} molecule is a superalkene,[11] incorporating 30 weakly conjugated double bonds, which can readily add several free radicals. Owing to this ability, fullerene C_{60} has been called a "radical sponge".[12] In an earlier paper,[13] the addition of three or five benzyl radicals to C_{60} was detected by ESR, and the addition of 34 methyl radicals was detected by mass spectrometry.

Fullerenyl radicals as investigation objects have no analogs in organic chemistry. In fact, radicals in which unpaired electrons are delocalized over the surface of a sphere or an ellipsoid have never been studied before. The unusual character of the fullerenyl radicals is also due to the fact that they occupy a sort of intermediate position between planar π-radicals and tetrahedral σ-radicals. Thus, the elucidation of the characteristic features of fullerenyl radicals and their reactivity by ESR spectroscopy and comparison of the results obtained with the results of quantum-chemical studies are of fundamental importance.

In this review we survey the results of studies on the structures and reactivities of fullerenyl radicals obtained by the ESR method.

Structures of radical adducts of C_{60}. Delocalization of an unpaired electron and the reactivity of monofullerenyl radicals $^{\bullet}C_{60}R$

By now, the structures and reactivities of monoadducts of fullerene-60 with alkyl and perfluoroalkyl radicals,

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with oxygen-, sulfur-, phosphorus-, boron-, platinum-, and silicon-centered radicals, and also with hydrogen and fluorine atoms have been studied by ESR. The addition of alkyl radicals to the C_{60} molecule was among the first reactions to be studied;[14] this study made it possible to determine the character of delocalization of unpaired electrons in fullerenyl radicals and their reactivity.

The magnetic resonance parameters of alkylfullerenyl radicals are presented in Table 1. The most intense and information-rich ESR spectra were recorded for the spin-adducts of C_{60} with a *tert*-butyl radical and with its deuterated analog.[14] The $^{\cdot}C_{60}CMe_3$ radical was obtained by UV irradiation (at 323 K) of a saturated solution of C_{60} in benzene containing $BrCMe_3$, whereas the deuterated analog, $^{\cdot}C_{60}C(CD_3)_3$, was prepared by photolysis of di-*tert*-butyl peroxide in a benzene solution containing C_{60} and deuterated isobutane. The ESR spectrum of the $^{\cdot}C_{60}C(CD_3)_3$ radical at high amplification exhibits ten pairs of satellites, which were assigned to the interaction of the unpaired electron with ^{13}C isotopes ($I = 1/2$) (Fig. 1). Their relative intensities and the values of hyperfine coupling (HFC) constants indicate that the radical adduct has C_s symmetry and that the unpaired electron is localized in the two six-membered rings, adjacent to the C—CR bond, as shown in Fig 2.

The isotropic HFC with ^{13}C nuclei characterizes the density of the unpaired electron in the 1s- and 2s-orbitals of carbon atoms and provides no direct information on its density in the 2p-orbital. Based on the assumption that the HFC of the C(1), C(3), C(3′), C(5), and C(5′) atoms are proportional to their spin density in 2p-orbitals, the spin density for the C(1) atom was found to be ~0.33, and those for the C(3), C(3′), C(5), and C(5′) were found to be ~0.17.[14] These results

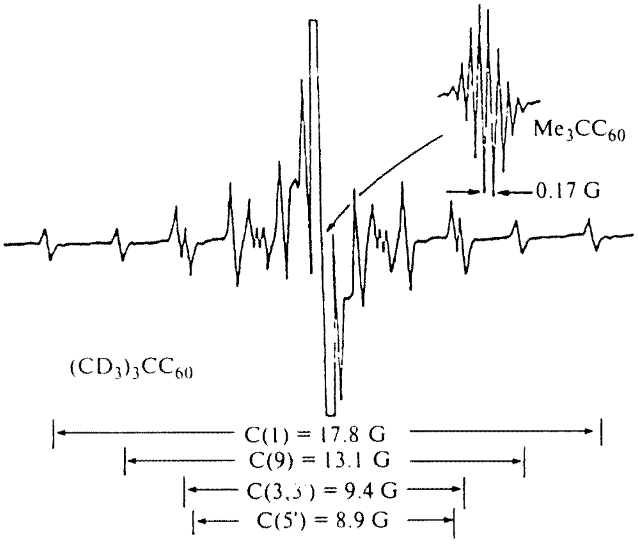


Fig. 1. ESR spectrum of the $^{\cdot}C_{60}C(CD_3)_3$ radical in benzene at 350 K.

Table 1. The HFC constants (*a*) and enthalpies of dimerization (*H*) for $^{\cdot}C_{60}R$ radicals

R	$a_{H(D)}$ /G	$a_{C,P,B,Pt}$ /G	ΔH /kcal mol^{-1}	*T*/K
$MeCH_2$	2 H = 0.28			473
	3 H = 0.13			
$Me^{13}CH_2$		1 C = 15.5		473
Me_2CH	1 H = 0.48		35.5	420—450
	6 H = 0.15			
$PhCH_2$	2 H = 0.42			350
	2 H = 0.19			
$Ph^{13}CH_2$	2 H = 0.42	1 C = 14.9		350
	2 H = 0.19			
$C_6D_5CH_2$	2 H = 0.42			350
CCl_3		1 C = 29.6	17.1	250—310
		1 C = 18.1		
		4 C = 8.8		
$^{13}CCl_3$		1 C = 29.6		310
CBr_3		1 C = 35.3	17.0	300—380
Me_3C	9 H = 0.17	1 C = 17.8	22.0	300—400
		1 C = 13.1		
		2 C = 9.39		
		2 C = 8.86		
		3 C = 5.59		
		2 C = 4.48		
		2 C = 4.02		
		2 C = 3.59		
		4 C = 2.41		
		8 C = 0.84		
Me_3C	3 H = 0.34			225
	6 H = 0.085			
$Me_3{}^{13}C$	9 H = 0.17	1 C = 13.1		370
$^{13}CH_3Me_2C$	9 H = 0.17	1 C = 0.40		370
Me_3Si	3 H = 0.11			320
$(CD_3)_3C$	9 D = 0.028			370
$(MeCH_2)_3C$	3 H = 0.34	1 C = 0.40		370
$(MeCH_2)_3Si$	3 H = 0.34			350
	3 H = 0.17			
1-$C_{10}H_{15}$	3 H = 0.25	1 C = 17.75	21.6	300—400
	6 H = 0.044	1 C = 12.34		
		2 C = 9.30		
		2 C = 8.79		
		3 C = 5.59		
		2 C = 4.48		
		2 C = 4.03		
Ph_3Ge	1 H = 0.04			320
$PO(OMe)_2$	6 H = 0.12	1 P = 64.2		300
$PO(OEt)_2$		1 P = 63.7		300
$PO(OCHMe_2)_2$		1 P = 63.5	13.0	330—430
		1 C = 18.5		
		4 C = 9.0		
		3 C = 7.2		
		2 C = 6.0		
		6 C = 3.6		
PO(OEt)Ph		1 P = 55.3		300
$B_{10}H_9C_2H_2$-*m*		1 ^{10}B = 6.25	10.0	340—430
		1 ^{11}B = 18.25		
BH_2NMe_3		1 ^{10}B = 4.20		
		1 ^{11}B = 12.40		
$Pt(PPh_3)_2CH{=}CPh_2$		1 ^{195}Pt = 52.0		270
		1 P = 3.50		
		1 P = 30.50		
$PO(OCHMe_2)_2$		1 P = 62.10		190
		1 P = 65.00		
PO(OEt)Ph		1 P = 54.20		190
		1 P = 56.70		

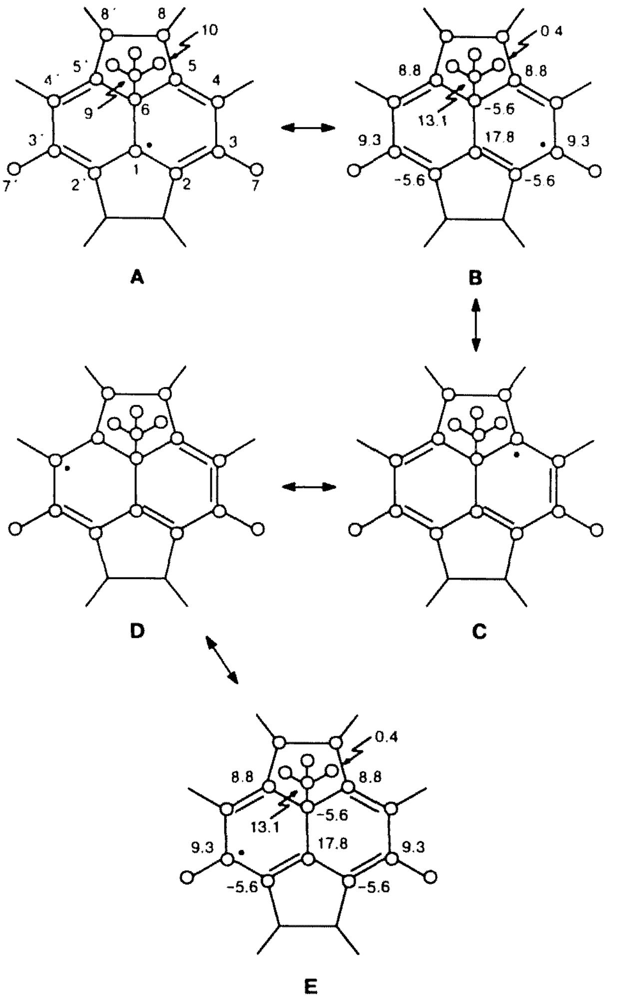


Fig. 2. Five main forms of the $^{\cdot}C_{60}CMe_3$ radical and the splitting (G).

are in good agreement with the splitting due to the ^{13}C nucleus in a methyl radical,[15] in which a constant of 39 G corresponds to an electron located in the 2p-orbital, as well as with the data of semiempirical quantum-chemical calculations.[16] However, in the opinion of other researchers,[14] this analogy is incomplete, since the methyl π-radical is planar, whereas the $^{\cdot}C_{60}-R$ radical is wholly nonplanar. A similar pattern of the HFC of an unpaired electron with ^{13}C nuclei has also been observed for other spin adducts of alkyl radicals with C_{60}.[17]

An important feature of fullerenyl radicals caused by the hindered rotation of the alkyl substituent is clearly manifested in ESR spectra of spin adducts of perfluorinated alkyl radicals.[18] It can be seen from Fig. 3, *a* that the central lines in the triplet exhibited in the spectrum of the $^{\cdot}C_{60}(CF_2)_5CF_3$ radical are broadened. This is due to the fact that the HFC of the unpaired electron with the magnetic nuclei in fullerenyl radicals depends on the positions of the nuclei with respect to the symmetry axis. For example, based on the ESR spectrum of the $CF_3CF_2-C_{60}^{\cdot}$ radical in which the constants of HFC with three equivalent ^{19}F nuclei are larger than those with the two ^{19}F nuclei of the CF_2 group, located closer to the fullerene surface, a symmetrical equilibrium conformation for this radical has been suggested.[18] This conformation is shown in Fig. 3, *b*. The conformational isomerization, during which the nonequivalent atomic groups exchange their positions, accounts for the line broadening. This problem is considered in detail below.

The intensities of the ESR spectra recorded for a series of alkylfullerenyl radicals were found to increase sharply with an increase in the temperature.[17,18] For example, the intensity of the ESR spectrum of $^{\cdot}C_{60}CMe_3$ in benzene increases tenfold as the temperature is raised from 300 to 350 K, and returns to its original value as the temperature decreases. The dependence of the intensity of the signal on the temperature indicates that fullerenyl radicals are in an equilibrium with the corresponding dimers.

$$RC_{60}-C_{60}R \rightleftharpoons 2\ ^{\cdot}C_{60}R$$

The enthalpies for this equilibrium correlate with the size of the radical, which attests that steric factors have a great effect on the bond strengths in the fullerenyl radicals. Based on the experimental data and on the results of calculations performed by molecular

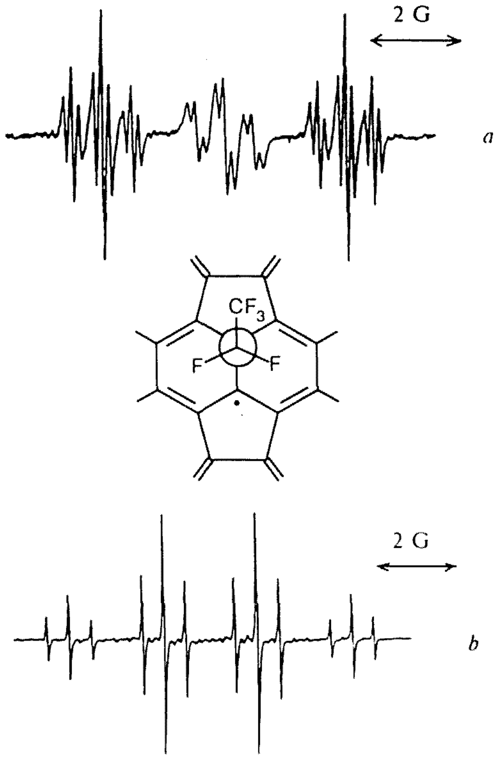


Fig. 3. ESR spectra of the $^{\cdot}C_{60}(CF_2)_5CF_3$ radical at 440 K (*a*); the $^{\cdot}C_{60}CF_2CF_3$ radical at 450 K (*b*).

graphics,[17,18] it has been shown that the dimerization of the fullerenyl radicals occurs according to the "head-to-head" type and involves the C(3) or C(3′) atoms (see Fig. 2). Steric hindrance prevents the dimerization involving C(1), C(5), or C(5′) atoms.

Thus, delocalization of the unpaired electron in alkylfullerenyl radicals does not depend on the structure of the alkyl group.

Let us consider the data on spin adducts of heteroorganic radicals. The spin adducts of phosphoryl radicals with fullerene have been obtained using two procedures for the generation of phosphoryl radicals, namely, the abstraction of a hydrogen atom from a hydrophosphoryl compound with a *tert*-butoxyl radical[19] and photolysis of a diphosphorylmercury compound.[20,21]

$$\mathrm{Hg[P(O)(OR)_2]_2} \longrightarrow 2\ {}^{\cdot}\mathrm{P(O)(OR)_2} + \mathrm{Hg}$$

$$\mathrm{C_{60}} + {}^{\cdot}\mathrm{P(O)(OR)_2} \longrightarrow {}^{\cdot}\mathrm{C_{60}{-}P(O)(OR)_2}$$

$$\mathrm{R = Me,\ Et,\ Pr^i}$$

The spectra of the phosphorylfullerenyl radicals exhibit HFC of the unpaired electron with the ^{31}P and ^{13}C nuclei and with the protons of the methoxy-groups (see Table 1). Note that the constants of the HFC with the C(1), C(3), C(3′), C(5), and C(5′) nuclei in the spectrum of the ${}^{\cdot}C_{60}{-}P(O)(OPr^i)_2$ radicals[22] are fairly close to the similar values for alkylfullerenyl radicals, *i.e.*, the replacement of the alkyl radical attached to C_{60} by a phosphoryl radical scarcely changes the distribution of the density of the unpaired electron.

When the irradiation is discontinued, the phosphorylfullerenyl radicals disappear within fractions of a second. It has been found[22] that they undergo irreversible dimerization, which is indicated by the following facts. (1). The intensity of the stationary ESR signal increases with an increase in the temperature (330—400 K). (2). The steady-state concentration of the radicals is proportional to the square root of the light intensity. (3). The reciprocal of the concentration of radicals, after the light is switched off, depends linearly on time. (4). The irradiation of the sample with visible light (680—600 nm) leads to the dissociation of the dimers of the phosphorylfullerenyl radicals. This can be observed after UV irradiation of $Hg[P(O)(OPr^i)_2]_2$ in a saturated toluene solution of C_{60} for 10—15 min, which results in the accumulation of $RC_{60}{-}C_{60}R$ dimers. The rate of the destruction of the phosphorylfullerenyl radicals does not depend on the solvent used in the series: benzene, toluene, *tert*-butylbenzene. This implies that fullerenyl radicals are incapable of withdrawing hydrogen atoms from the solvent, the dimerization being the only pathway to their destruction. The rate constant of the dimerization of the ${}^{\cdot}C_{60}{-}P(O)(OPr^i)_2$ radical was measured ($k(270\ K) = 1.9 \cdot 10^6$ L (mol s)$^{-1}$) and the enthalpy of the radical—dimer equilibrium was estimated (ΔH = 13.0 kcal mol^{-1});[23] the latter proved lower than those for alkylfullerenyl radicals (see Table 1), apparently due to the larger size of the phosphoryl group. Similar values for the dimerization rate constants have also been obtained for the spin adducts of bulky boron-centered radicals (${}^{\cdot}C_{60}B_{10}H_9C_2H_2$)[24,25] ($k(270\ K) = 10^6$ L (mol s)$^{-1}$) and (${}^{\cdot}C_{60}BH_2NMe_3$)[26,27] ($k(270\ K) = 2.5 \cdot 10^6$ L (mol s)$^{-1}$) with C_{60} (see Table 1). It follows from these data that the rate of dimerization of the fullerenyl radicals is apparently limited by diffusion.

Table 2. The HFC constants (G) for ${}^{\cdot}C_{60}SR$ and ${}^{\cdot}C_{60}OR$ radicals

Radical	a_{Me}	a_{CH_2}	a_{CH}
SH_3	3 H = 0.38		
SCH_2	3 H = 0.29	2 H = 0.31	
$SCHMe_2$	6 H = 0.22		1 H = 0.22
SCH_2CH_2Me		2 H = 0.35	
		2 H = 0.18	
SCH_2CHMe_2		2 H = 0.40	1 H = 0.21
$SCMe_3$	9 H = 0.25		
$OCMe_3$	9 H = 0.35		
$OCMe_2Ph$	6 H = 0.22		
	3 H = 0.17 (Ph)		
OCF_3	3 F = 3.14		

Photolysis of alkyl disulfides and bis(alkylthio)mercury compounds with C_{60} affords various thioalkylfullerenyl radicals (see Table 2).[28] Molecular mechanic calculations of the most favorable conformation of the ${}^{\cdot}C_{60}SMe$ radical have shown that the SMe group is located directly above a six-membered ring. A specific feature of the ESR spectra of alkoxyfullerenyl radicals[28] is that the constants of the HFC with the δ-protons or with the fluorine nuclei are much higher than those for the adducts of alkyl radicals with C_{60} (see Table 2).

Radical adducts of silyl radicals with C_{60} were prepared by the photolysis of di-*tert*-butyl peroxide in the presence of $HSiR_3$.[29] Their ESR data are presented in Table 1. It should be noted that the $-SiR_3$ groups are more free to rotate than their alkyl analogs.

The ESR spectrum of the radical adduct of hydrogen atom with C_{60} is characterized by the constant of the HFC with the proton of ~33 G. This value decreases with an increase in the temperature, according to the equation $a(T) = 94.44 - 0.00488T$ (MHz), which holds in the 320—440 K temperature range. The hydrogen atom was generated by the photolysis of thiophenol, 1,4-cyclohexadiene, or $HSnBu_3$. An interesting peculiarity of the ESR spectrum of ${}^{\cdot}C_{60}H$ is that of low-field component of the doublet has the phase corresponding to emission, while that the high-field component corresponds to absorption (Fig. 4). This spectral pattern is an example of manifestation of chemically induced electron polarization.[31]

Photolysis of a solution of C_{60} in toluene or *tert*-butylbenzene, containing dissolved SF_5Cl, at 260 K yields radical-adducts ${}^{\cdot}C_{60}Cl$ ($g = 2.00268$, $a(^{35}Cl) = 12.42$ G) and ${}^{\cdot}C_{60}F$ ($g = 2.00229$, $a(^{19}F) = 73.03$ G).[29]

Thus, analysis of the ESR spectra of the monoadducts ${}^{\cdot}C_{60}R$ shows that the unpaired electron is mostly delo-

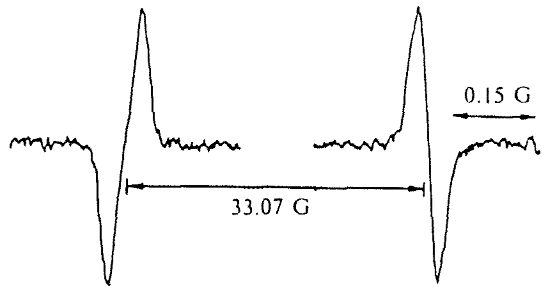


Fig. 4. ESR spectrum of the $^{\cdot}C_{60}H$ radical at 360 K.

calized over the C(1), C(3), C(3′), C(5), and C(5′) atoms. The intensity of the ESR spectra was found to depend on the temperature, that is due to the occurrence of a radical—dimer equilibrium. The rate of dimerization of the fullerenyl radicals is limited by diffusion.

A typical feature of any radical adduct of C_{60} is hindered rotation of the attached radicals, which is clearly manifested in the ESR spectra.

Dynamic effects in the ESR spectra of fullerenyl radicals

As noted above, the ESR spectrum of the $^{\cdot}C_{60}CMe_3$ radical at 340 K is a multiplet corresponding to nine equivalent protons. Upon gradual cooling to 225 K, the spectral pattern changes (Fig. 5), and now it is characterized by coupling of the unpaired electron with two groups of protons, the first of which incorporates six equivalent protons (0.085 G) arranged above six-membered rings, and the second includes three equivalent protons (0.34 G) arranged over a five-membered ring. It was concluded that the rotation of the *tert*-butyl group around the C(6)—C(9) bond (see Fig. 2, *a*) is strongly hindered at low temperatures and that the potential function of the hindered rotation has a minimum for mobile conformations and a maximum for an eclipsed conformation, as in substituted ethanes.[34]

Analysis of the broadening of lines at each temperature yielded the following thermodynamic parameters for the hindered rotation: ΔG = 8.2 kcal mol^{-1}, ΔH = 7.3 kcal mol^{-1}, and ΔS = −2.9 eu. The height of the energy barrier is comparable with the barriers to the hindered rotation of the *tert*-butyl group in substituted ethanes (10 kcal mol^{-1})[35] and in the $Bu^tC_{60}^-$ anion (9.3 kcal mol^{-1}).[36]

The constants of the HFC with γ-H and γ-^{13}C (see Table 1) and the variations observed in the ESR spectra as a function of temperature indicate that there is a high barrier to the internal rotation around the C(6)—C(9) bond in all the alkylfullerenyl radicals.[33] The equilibrium conformation of the alkyl radical with respect to the symmetry axis in a fullerenyl radical varies as a function of the structure of this radical. For example, the isopropyl substituent is arranged symmetrically, its proton being located above a five-membered ring and the two methyl groups being located above six-membered rings; the addition of an ethyl radical leads to an asymmetrical equilibrium conformation in which the methyl group lies above a six-membered ring and the two hydrogen atoms occupy nonequivalent positions (one of them is above a five-membered ring, while the other is above a six-membered ring). Proton exchange between the nonequivalent positions results in the broadening of the central component of the ESR spectrum.[33]

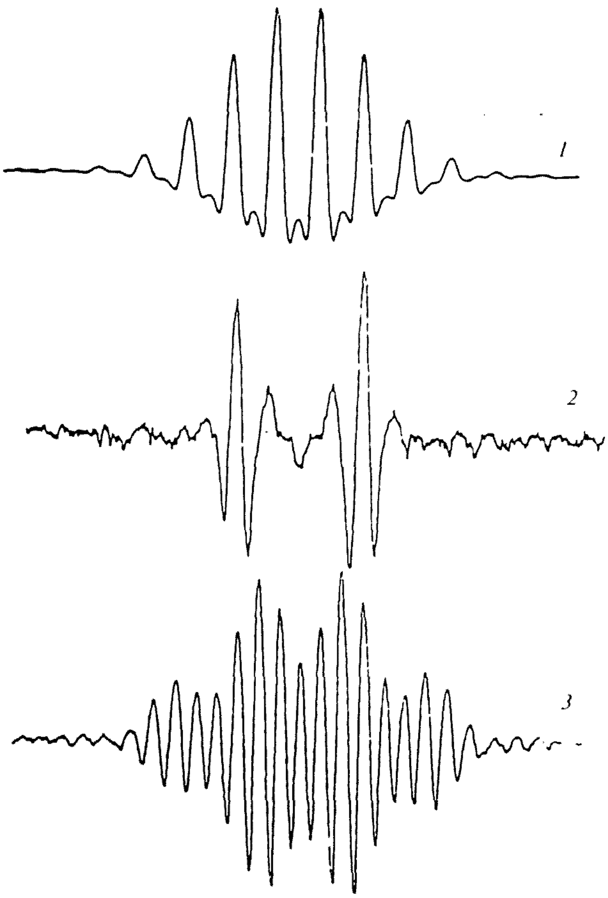


Fig. 5. Second derivatives of the ESR spectra of $^{\cdot}C_{60}CMe_3$ at various temperatures (K): 325 (*1*), 275 (*2*), and 225 (*3*).

In the ESR spectra of phosphonylfullerenyl radicals, unlike those of alkylfullerenyl radicals, "frozen" conformations and exchange between them can be observed. Hence, analysis of ESR spectra recorded at different temperatures makes it possible to obtain kinetic and thermodynamic parameters for the hindered rotation.[37]

When the temperature decreases, the ESR spectral pattern of the $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical markedly changes. It can be seen from Fig. 6, which shows the temperature evolution of the ESR spectrum, that as the temperature decreases from 273 K to 243 K, the components of the doublet due to phosphorus become much broader, and

Fig. 6. ESR spectra of the $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical at various temperatures (K): 300 (*1*), 233 (*2*), and 200 (*3*).

as the temperature decreases further (<243 K), two conformers are "frozen out" (Fig. 6, spectrum *3*); they have the following parameters: **A**, $a_P = 62.1$ G, $g = 2.0022$; **B**, $a_P = 65.0$ G, $g = 2.0020$. The reason for the line broadening is the hindered rotation of the phosphonyl group between the positions characterized by different constants of the HFC of the unpaired electron with the ^{31}P nucleus. From relative intensities of the spectral lines corresponding to radicals **A** and **B**, the equilibrium constants (K) at various temperatures were determined, and the difference (ΔH) between the enthalpies of the two conformers, $\Delta H = 1.8$ kcal mol^{-1}, was found from the dependence of $\ln K$ on T^{-1}.

The spectral and thermodynamic data we obtained make it possible to evaluate the rate constants (k_1 and k_{-1}) for the transition between the two conformations in the 240—270 K temperature range. At 270 K $k_{-1} = 5 \cdot 10^7$ s^{-1}, $k_1 = 4 \cdot 10^6$ s^{-1}. The activation energy for this process: $E_a = 4.8$ kcal mol^{-1} (see Refs. 37 and 38).

The constant of HFC with the phosphorus nucleus in the $^{\cdot}C_{60}P(O)Ph(OEt)$ radical a_P is 55.3 G ($g = 2.0023$). When the temperature decreases, the ESR spectral lines are broadened and two conformers are "frozen out"; they are characterized by the following parameters: $a_P = 56.7$ G, $g = 2.0022$; $a_P = 54.2$ G, $g = 2.0023$. In the case of the $^{\cdot}C_{60}P(O)Ph(OEt)$ radical, the activation energy for the transition between the two conformations is ~0.6 kcal mol^{-1}, and the equilibrium constant at 193 K is 0.3. The "extreme" conformations of the $^{\cdot}C_{60}—P(O)(OMe)_2$ radical have not been observed.[37]

An increase in the g-factor in the conformers is accompanied by a decrease in the constant of HFC with the phosphorus nucleus, which is apparently due to the fact that the orientations of the P=O group with respect to the symmetry axis of phosphorylfullerenyl radicals in the equilibrium conformations are different. If the oxygen atom is arranged above a five-membered ring (closer to the axis of the quasi-2p$_z$-orbital of the unpaired electron), then the higher density of the unpaired electron falls on the oxygen nucleus, which accounts for the positive shift of the g-factor. In another conformation, the oxygen atom can be arranged above a six-membered ring.

Structures of the spin adducts resulting from multiple addition of free radicals to C_{60}

As noted above, fullerenes are capable of adding large numbers of free radicals.[13] It was found that repeated addition of benzyl radicals to the C_{60} fullerene is not chaotic; but it yields stable radicals, whose structures are similar to those of allyl or cyclopentadienyl radicals. Adducts of the repeated addition were identified when benzyl radicals ($^{13}CH_2Ph$) enriched in the ^{13}C isotope by 99% were used. The spectrum consisting of a triplet of doublets [$a(2\ ^{13}C) = 9.7$ G, $a(1\ ^{13}C) = 1.7$ G, $g = 2.00221$] is typical of an allyl-type radical in which the larger HFC constant refers to two ^{13}C nuclei in the benzyl radicals, located at the ends of the allylic system, while the smaller splitting relates to carbon of the benzyl radical located in the middle of the allylic system. The sextet for five equivalent ^{13}C nuclei [$a(5\ ^{13}C) = 3.56$ G] was assigned to a cyclopentadienyl type radical, arising upon the addition of five benzyl radicals to one five-membered ring of C_{60} (Fig. 7). Formation of allylic radicals has also been observed upon the multiple addition of alkyl radicals to C_{60}.[39]

The addition of several phosphoryl radicals to C_{60}[22] at an initial stage of photolysis leads to three types of radical adducts differing in the constants of HFC with the phosphorus nuclei and in their g-factors: **1**, $a_P(1\ P) = 73.5$ G, $g = 2.0019$; **2**, $a_P(1\ P) = 66.75$ G, $g = 2.0023$; **3**, $a_P(1\ P) = 4.25$ G, $a_P(1\ P) = 54.9$ G, $g = 2.0025$. None of these radicals is allylic, which is apparently due to the large size of the phosphoryl group. The magnetic resonance parameters of the multiple addition products **1** and **2** imply that the unpaired electron interacts with only one ^{31}P nucleus, although the radicals contain no less than two phosphoryl groups. Since the unpaired electron is mostly localized in two six-membered rings (see above), the HFS corresponding to far removed ^{31}P nuclei may be not manifested. The additional HFC with the phosphorus atom (4.25 G) in radical **3** is apparently due to a phosphoryl radical attached to the adjacent five-membered ring.[22]

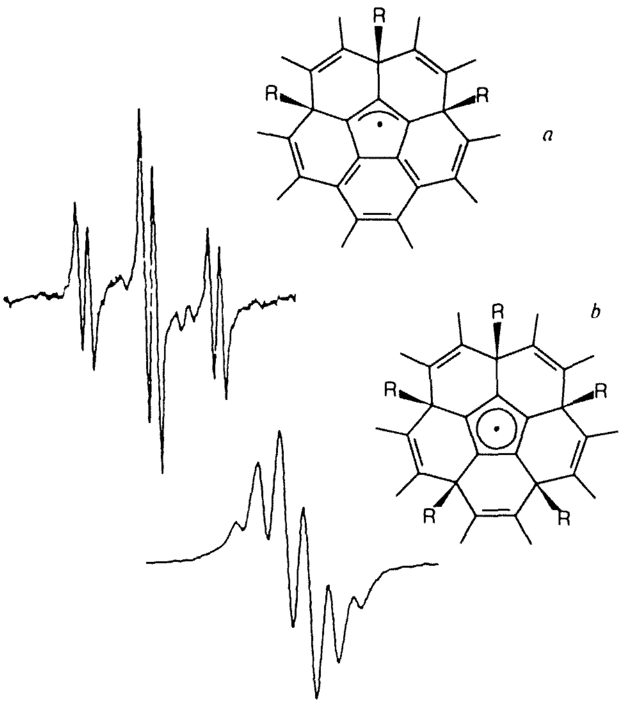


Fig. 7. ESR spectrum of $^{\cdot}C_{60}(CH_2Ph)_n$: *a*, $n = 3$; *b*, $n = 5$.

We detected phosphoryl-containing stable allylic radicals upon simultaneous generation of the phosphoryl radicals $R^1 = P(O)(OPr^i)_2$ and radicals $R^x = C(O)OMe$, Me, CCl_3.[40] Their structure depends on the donor-acceptor properties of the alkyl substituents. When the phosphoryl and methoxycarbonyl radicals are generated simultaneously by a photochemical procedure from the corresponding mercury-containing compounds in a saturated toluene solution of C_{60}, allylic radicals containing phosphoryl groups in the center of the allylic system (a_P = 6.25 G, g = 2.0028) and those containing phosphoryl groups in its terminal positions (a_P (1 P) = 43.0 G, g = 2.0027) are formed synchronously.

$$C_{60} + {^{\cdot}P(O)(OPr^i)_2} + 2\,{^{\cdot}C(O)OMe} \longrightarrow$$

$$\longrightarrow {^{\cdot}C_{60}[C(O)OMe]_2P(O)(OPr^i)_2}$$

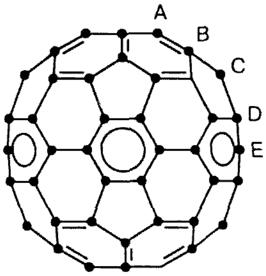
The simultaneous generation of phosphoryl and methyl radicals results in the formation of allylic radicals containing phosphoryl groups only in the center of the allylic system and exhibitng a constant of the HFC with the P nucleus (a_P = 6.75 G).

Unlike the above examples, the simultaneous addition of phosphoryl and electrophilic trichloromethyl radicals yields allylic radicals $^{\cdot}C_{60}[P(O)OPr^i)_2]_2CCl_3$ containing two phosphoryl groups each, the latter being located at the ends of the allylic system. This radical accounts for a constant of HFC with two equivalent ^{31}P nuclei [a_P(2 P) = 41.25 G].

Thus, an active radical does not add to any of the 29 free double bonds of the bis-adduct $C_{60}R_2$; it adds in such a way as to form the thermodynamically most favorable allylic structure. Electrostatic and steric factors are also significant. For example, the allylic radicals are not formed upon the addition of several *tert*-butyl,[39] phosphoryl,[22] boryl,[26] or boron-centered carboranyl radicals,[24] although in these cases, adducts resulting from repeated addition have been detected (they were stable owing to shielding of the carbon atoms that carry the highest density of the unpaired electron).

Adducts resulting from mono- and polyaddition of free radicals to C_{70}

Unlike C_{60} in which all the carbon atoms are equivalent, the ellipsoid C_{70} incorporates five types of nonequivalent atoms: A, B, C, D, and E in a ratio of 10 : 10 : 20 : 20 : 10. Therefore, the addition of free radicals to C_{70} can yield five isomeric radicals $^{\cdot}C_{70}R$, differing both in the parameters of their ESR spectra and in their reactivities. Let us consider the ESR data on the photochemical addition to C_{70} of the following atoms and organic radicals: $^{\cdot}H$, $^{\cdot}F$, $^{\cdot}Me$, $^{\cdot}CMe_3$, $^{\cdot}Et$, $^{\cdot}CF_3$, $^{\cdot}C_2F_5$, $^{\cdot}P(O)(OMe)_2$, $^{\cdot}P(O)(OPr^i)_2$, and $B_{10}H_9C_2H_2$.[24,42–45]



When a benzene solution of C_{70} containing benzophenone and isopropanol is exposed to radiation, hydrogen atoms are generated, which add to C_{70} to give adducts of five different types[42] (Fig. 8), four of which are characterized by a splitting with one hydrogen atom (Table 3), while the fifth adduct is responsible for HFC with three protons, which indicates that several hydrogen atoms added and that an allylic radical formed.[42] Chemically induced electron polarization is manifested in all the spectra. When $^{\cdot}C_{70}H$ is generated by photolysis of a saturated benzene solution containing 1,2-cyclohexadiene, spin adducts of three types are detected.[43]

Adducts resulting from the addition to all five of the nonequivalent carbon atoms have not been observed for any of the radicals studied. In fact, only three $^{\cdot}C_{70}R$ radical adducts are formed in the case where R = $^{\cdot}Me$, $^{\cdot}CMe_3$, $^{\cdot}P(O)(OMe)_2$, $^{\cdot}P(O)(OPr^i)_2$, or $^{\cdot}B_{10}H_9C_2H_2$, while for R = $^{\cdot}Et$, $^{\cdot}CF_3$, or $^{\cdot}C_2F_5$, four radical adducts

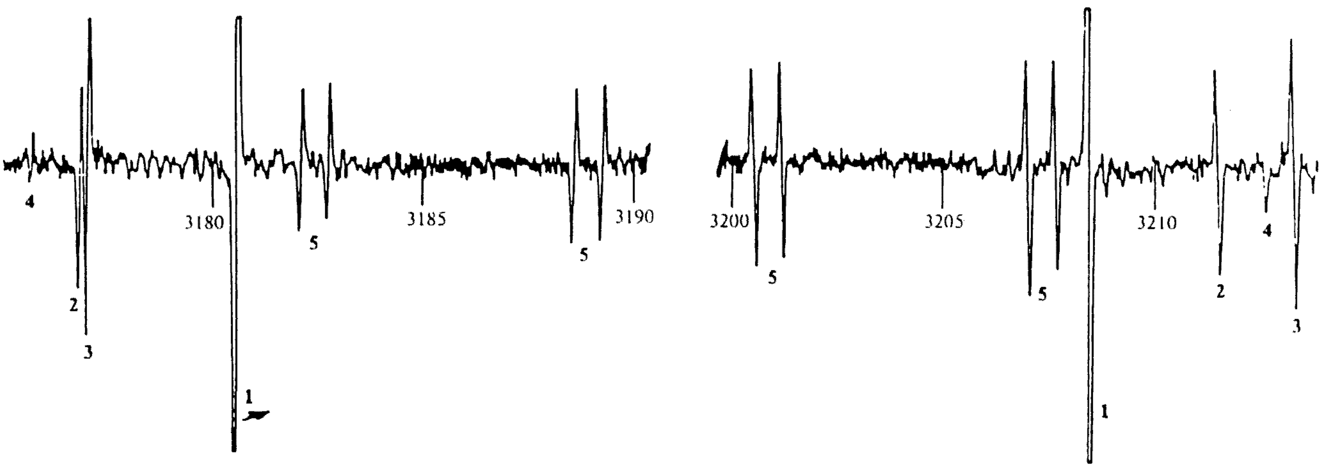


Fig. 8. ESR spectrum of $^{\cdot}C_{70}H$ (isomers **1—4**) and $^{\cdot}C_{70}H_3$ (**5**) in benzene at 295 K.

are observed. The adducts $^{\cdot}C_{70}R$ exhibit three common features, irrespective of the structure of R: (1) the *g*-factors for the spin adducts of each type are different; (2) the constants of HFC with the key atom (*i.e.*, the atom that carries the highest spin density) in the added radical are different, and (3) one of the isomers (that has the lowest HFC constant with the key atom) is stable in the absence of irradiation. Radical adducts of each type were identified by comparing the results of quantum-chemical calculations with experimental data.

By MNDO/PM3 calculations, the relative $\Delta_f H^\circ$ values (kcal mol^{-1}) have been obtained for the five isomers of $^{\cdot}C_{70}R$: 0.0 (**C**), 0.4 (**D**), 1.6 (**A**), 2.5 (**B**), 15.6 (**E**).[43] A calculation of the spin density distribution in the $^{\cdot}C_{70}H$ radical has shown that isomer **D** (**1**), in which the unpaired electron is delocalized to a greater degree than in other isomers and which has no symmetry plane, should be the most stable.

High stability of the $^{\cdot}C_{70}R$ (**D**) adduct is clearly manifested in the ESR spectrum of, for example, $^{\cdot}C_{70}P(O)(OPr^i)_2$.[45] When irradiation is terminated, the concentration of these fullerenyl radicals remains constant over a period of several hours, which indicates that they are unable to dimerize.

Thus, for isomer **1**, the site of the addition was exactly identified (vertex D). The data on the structures of other isomers of the spin adducts derived from C_{70} are less definite. Previously[43] it has been concluded that isomer **4** has the energetically less favorable structure **E** (since the addition is a kinetically controlled reaction). However, based on calculations,[42] structure **A** was assigned to isomer **4**, whereas structures **C** and **B** were attributed to isomers **2** and **3**, respectively.

We studied[46] the characteristic features of the free-radical phosphorylation of C_{70} occurring during prolonged (~0.5 h) photolysis of a saturated toluene solution of C_{70} and $Hg[P(O)(OPr^i)_2]$, where R = Me, Pr^i. The ESR spectrum of the spin adducts $^{\cdot}C_{70}[P(O)(OPr^i)_2]_n$, arising due to multiple addition, is similar to the spectrum of $^{\cdot}C_{60}[P(O)(OPr^i)_2]_n$ radicals. In view of the fact that the large size of diisopropylphosphoryl radicals may be among the reasons preventing the formation of an allylic structure, multiple addition of less bulky radicals, $^{\cdot}P(O)(OMe)_2$, was studied. The latter were also generated by photolysis of the corresponding mercury derivative. After 0.5 h of photolysis, the ESR spectrum of an allyl type radical can be recorded; this radical is responsible for HFC constants with two equivalent phosphorus atoms $a_P(2\ P) = 44.5$ G (a triplet) and with one phosphorus nucleus $a(1\ P) = 5.0$ G. If the photolysis is continued further, two more phosphoryl radicals add. Their HFC constants [$a_P(2\ P) = 48.5$ G, $a_P(1\ P) = 6.0$ G, and $a_P(2\ P) = 3.25$ G] imply that, unlike the addition of five benzyl radicals to C_{60}, which yields a cyclopentadienyl type radical, in the case of $^{\cdot}C_{70}[P(O)(OMe)_2]_5$, the allylic structure is retained, and the additional HFC is due to the fact that two phosphoryl radicals are introduced into the Δ-positions with respect to the terminal carbon atoms of the allylic system.

Calculations of the $^{\cdot}C_{70}H_3$ allylic radical showed[42] that the addition of hydrogen atoms to the $C_3A_1C_{10}$ vertices is the most favorable. A similar structure may occur in the case of phosphoryl radicals.

Metal-containing fullerenyl radicals

The examples of multiple addition of free radicals to fullerenes-60 and 70, yielding in some cases allylic radicals, illustrate the interaction of radicals with mono-, di-, tri-, *etc.* radical derivatives of fullerene. The question arises of whether some regularities can be followed in the addition of free radicals to the fullerene derivatives that are obtained by heterolytic transformations and differ from radical adducts in the type of bonding.

We studied for the first time[48] characteristic features of the ESR spectra of the adducts formed from phos-

Table 3. The HFC constants (*a*) and *g*-factors for $^{\cdot}C_{70}R$ radicals

Radical		$a_{H,C,P,F}$/G	*g*-factor	*T*/K
$^{\cdot}C_{70}H$	**(1)**	1 H = 27.85	2.00251	340
	(2)	1 H = 34.45	2.00271	340
	(3)	1 H = 36.2	2.00213	295
	(4)	1 H = 36.8	2.00274	295
$^{\cdot}C_{70}F$	**(1)**	1 F = 53.54	2.00148	325
	(2)	1 F = 65.25	2.00181	325
	(3)	1 F = 74.21	2.00187	325
	(4)	1 F = 74.46	2.00133	325
$^{\cdot}C_{70}Me$	**(1)**	3 H = 0.24, 1 ^{13}C = 13.5	2.0021	280
	(2)	3 H = 0.0, 1 ^{13}C = 16.7	2.00263	280
	(3)	3 H = 0.21, 1 ^{13}C = 17.5	2.00199	280
$^{\cdot}C_{70}Ph$	**(1)**	2 H-*m* = 0.18	2.00248	290
	(2)	2 H = 0.24	2.00266	290
	(3)	2 H = 0.24	2.00207	290
	(4)	2 H = 0.27	2.00272	290
$^{\cdot}C_{70}CMe_3$	**(1)**	9 H = 0.17, 1 ^{13}C = 14.2	2.00271	300
	(2)	9 H = 0.17, 1 ^{13}C = 11.3	2.00248	300
	(3)	9 H = 0.17, 1 ^{13}C = 13.8	2.00210	300
$^{\cdot}C_{70}CCl_3$	**(1)**	1 ^{13}C = 34.6	2.00425	300
	(2)	1 ^{13}C = 30.5	2.00382	300
	(3)	1 ^{13}C = 26.7	2.00345	300
$^{\cdot}C_{70}CF_3$	**(1)**	3 F = 0.05	2.00251	320
	(2)	3 F = 0.25	2.00271	320
	(3)	3 F = 0.13	2.00218	320
	(4)	3 F = 0.13	2.00283	320
$^{\cdot}C_{70}Et$	**(1)**	1 F = 0.14, 3 F = 1.35	2.00240	450
	(2)	2 F = 0.63, 3 F = 2.13	2.00260	450
	(3)	2 F = 0.18, 3 F = 2.27	2.00197	450
	(4)	2 F = 0.57, 3 F = 2.52	2.00270	450
$^{\cdot}C_{70}PO(OMe)_2$	**(1)**	6 H = 0.12, 1 P = 71.2	2.00277	300
	(2)	6 H = 0.12, 1 P = 66.8	2.00269	300
	(3)	6 H = 0.08, 1 P = 55.9	2.00248	300
$^{\cdot}C_{70}PO(OPr^i)_2$	**(1)**	1 P = 70.5	2.00310	293
	(2)	1 P = 66.5	2.00270	293
	(3)	1 P = 55.25	2.00280	293
$^{\cdot}C_{70}B_{10}H_9C_2H_2$-*m*	**(1)**	1 ^{11}B = 15.5	2.0026	430
	(2)	1 ^{11}B = 19.7	2.0032	430
	(3)	1 ^{11}B = 20.0	2.0021	430

phoryl radicals and η^2-metallocomplexes of fullerene (L_2MC_{60}, where M = Pd, Pt; L = PPh_3).

UV irradiation of a saturated toluene solution of the Pd complex in the presence of an equimolar amount of $Hg[P(O)(OPr^i)_2]_2$ at room temperature in the resonator of an ESR spectrometer leads initially to at least five radicals differing in the constants of HFC of the unpaired electron with ^{31}P nuclei (70—55 G) and in their *g*-factors (2.001—2.003). The parameters of the dominating signal correspond to the $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical. After 3—5 min of irradiation, only the spectrum corresponding to this radical is retained, and the green color typical of solutions of fullerenes coordinated to metals disappears.

The phosphoryl radicals attack the metal complex nonselectively, and the set of signals arising in the ESR spectrum corresponds to the isomeric spin adducts $L_2PdC_{60}P(O)(OPr^i)_2$ and to the demetallated adduct $^{\cdot}C_{60}P(O)(OPr^i)_2$.

$$L_2PdC_{60} + {}^{\cdot}P(O)(OPr^i)_2 \rightarrow [L_2(Pr^iO)_2(O)PPdC_{60}] \rightarrow$$
$$\rightarrow L_2(Pr^iO)_2(O)PPd^{\cdot} + C_{60}, \textit{ etc.}$$

The rate of the addition of phosphoryl radicals to the metal is probably higher than the rate of their addition to a double bond of fullerene.

In order to obtain additional data on the structure of the spin adducts under consideration, we used the Pt-containing complex (magnetic isotope ^{195}Pt with a natural occurrence of 33%). However, the results obtained in this case were similar to those described above. Thus, η^2-complexes of C_{60} with platinum and palladium are unstable with respect to phosphoryl radicals.[48]

We were able to obtain metal-containing phosphorylfullerenyl radicals by an alternative procedure, *i.e.*, by the addition of PtL_2 or PdL_2 to the dimers of phosphorylfullerenyl radicals.[48] An equimolar amount of the complex $Pt(PPh_3)_4$ was added under argon to a toluene solution containing ~10% phosphorylfullerenyl radical dimers (similarly to the preparation of the complex of C_{60} with Pd^0 and Pt^0).[7,47] The reaction occurred very rapidly, and the solution became dark green. When the reaction was completed, the sample was irradiated with visible light (620—680 nm), in order to avoid generation of new phosphoryl radicals and to affect only the dimers of fullerenyl radicals in which the C—C bond energy is relatively low (~10 kcal). The whole process can be represented as follows:

$$RC_{60}{-}C_{60}R + Pt(PPh_3)_4 \longrightarrow R(PPh_3)PtC_{60}{-}C_{60}Pt(PPh_3)R$$

$$R = P(O)(OPr^i)_2$$

$$R(PPh_3)_2PtC_{60}{-}C_{60}Pt(PPh_3)_2R \xrightarrow{h\nu} 2\ {\cdot}C_{60}Pt(PPh_3)_2R$$

a—e

The irradiation of the sample with visible light results in the appearance of new radicals: **a**, $a_P = 58.5$ G, $g = 2.0017$; **b**, $a_P = 63.5$ G, $g = 2.0023$; **c**, $a_P = 64.7$ G, $g = 2.0025$; **d**, $a_P = 65.7$ G, $g = 2.0028$; **e**, $a_P = 68.0$ G, $g = 2.0032$.

Based on these data, it was concluded that the addition of $Pt(PPh_3)_2$ to $RC_{60}{-}C_{60}R$ is not regioselective. The interaction of the unpaired electron with metal atoms located in various positions with respect to the radical center is manifested in the variation of the HFC constants and g-factors.[48]

To identify each isomer, it is necessary to determine the parameters of the fullerenyl radical in which the maximum spin density is known to be concentrated on the carbon atom, located in the β-position with respect to the metal atom. To obtain this fullerenyl radical, we used the compound $(CF_3)_2CF{-}Hg{-}Pt(PPh_3)_2{-}CH{=}CPh_2$, whose photolysis in a saturated toluene solution of C_{60} affords a Pt-centered radical:[49]

$$(CF_3)_2CF{-}Hg{-}Pt(PPh_3)_2{-}CH{=}CPh_2 \xrightarrow{h\nu}$$

$$\longrightarrow (CF_3)_2CF{-}Hg^{\cdot} + {}^{\cdot}Pt(PPh_3)_2{-}CH{=}CPh_2$$

$$C_{60} + {}^{\cdot}Pt(PPh_3)_2{-}CH{=}CPh_2\text{-}cis \longrightarrow$$

$$\longrightarrow {}^{\cdot}C_{60}Pt(PPh_3)_2{-}CH{=}CPh_2\text{-}cis$$

The Pt-containing fullerenyl radical is characterized by the following HFC constants: $a_{Pt^{195}} = 52.0$ G, $a(1\ P) = 30.5$ G, $a(1\ P) = 3.5$ G, and $g = 2.0013$. The constants of HFC with the ^{31}P nuclei are nonequivalent, since the triphenylphosphine ligands are arranged asymmetrically with respect to the symmetry axis of the radical: one PPh_3 group is located above a five-membered ring (the HFC constant is 30.5 G), while the other group is above a six-membered ring. The obtained g-factor value is much lower than those for the adducts of phosphoryl radicals with C_{60} (2.0023); therefore, the metal-containing fullerenyl radical $(Pr^iO)_2(O)P{-}\dot{C}_{60}Pt(PPh_3)_2$, which accounts for $g = 2.0017$ ($a_P = 58.5$ G), may be assumed to be that particular isomer in which the phosphoryl group is located most closely to the metal atom.

Conclusion

Thus, it was shown by ESR spectroscopy that the unpaired electron in the ${}^{\cdot}C_{60}R$ radicals is mostly delocalized over five carbon atoms: C(1), C(3), C(3′), C(5), and C(5′) incorporated in the two six-membered rings adjacent to the C—CR bond.

It was found that the intensity of the ESR spectra depends on the temperature; this is due to the occurrence of the radical—dimer equilibrium.

In relation to phosphoryl-, borocarboranyl-, and borylfullerenyl radicals, it was shown that the rate of dimerization of fullerenyl radicals depends only slightly on the structure of the radicals attached to them and is apparently limited by diffusion.

In the ESR spectra of radical adducts of C_{60}, dynamic effects are manifested, which are associated with the exchange of substituents between positions, nonequivalent with respect to the unpaired electron orbital.

The addition of several free radicals affords stable fullerenyl radicals, whose structures depend on the nature of the radicals added. In the formation of allylic structures, electrostatic and steric factors are significant.

Of the five possible isomers of ${}^{\cdot}C_{70}R$, three isomers are normally formed; one of them (resulting from the addition to vertex D) is stable owing to the substantial delocalization of the unpaired electron.

The interaction of the unpaired electron with the nuclei of metal atoms located in various positions with respect to the radical center is manifested in the values of the HFC constants and of the g-factors.

The rapid development of the radical chemistry of fullerenes brings up new questions. It may be expected that the following timely problems will be solved in the near future:

— the rate of the addition of free radicals to C_{60} and C_{70} will be determined;

— the general regularities of the addition of free radicals to various fullerene derivatives will be identified;

— a procedure will be developed that will make it possible to use the constants of HFC with the magnetic nucleus in the radical attached to fullerene as a "paramagnetic reporter," which carries information not only on the structures of radical adducts but also on the addition of functional groups to fullerene upon heterolytic reactions;

— the possibility will be studied of using fullerenes as thermally stable radical traps, enabling identification of free radicals or atoms at temperatures of up to 470 K based on the magnetic-resonance parameters of fullerenyl radicals;

— fullerenyl radicals derived from higher fullerenes and containing metal atoms inside the fullerene sphere (endohedral metallocomplexes) will be studied;

— stable nitroxyl radicals bound to fullerene will be synthesized (for the investigation of the biological activities of fullerenes);

— preparative methods for the radical functionalization of fullerenes will be developed.

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