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ESR study of adducts of diisopropylphosphoryl radicals with $C_{60}\{C[P(O)(OEt)_2]_2\}_2$ isomers

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The radical adducts of the $P^{\bullet}(O)(OPr^i)_2$ ($R^{\bullet}$) radicals with $C_{60}\{C[P(O)(OEt)_2]_2\}_2$ fullerene derivatives were studed by ESR spectroscopy. The number of stable regioisomers of phosphorylfullerenyl radicals formed by addition of the phosphoryl radicals to the $C_{60}\{[P(O)(OEt)_2]_2\}_2$ isomers depends on the mutual position of the organophosphorus groups and decreases in the series *trans*-2› > *trans*-3 ≈ *trans*-4 >› *e*. The rate constants for addition of the $R^{\bullet}$ radicals to the *trans*-3 regioisomer ($k = 1.7 \cdot 10^8$ L mol^{-1} s^{-1}) were determined.

Key words: fullerene, ESR, radical reactions, phosphorylated bis(methanofullerenes), radical adducts.

Radical reactions are of great importance for fullerene chemistry.[1] Numerous weakly conjugated double bonds in fullerenes make them capable of adding a large number of atoms and radicals. The radical reactions of fullerenes find increasing application in preparative chemistry. Water-soluble fullerene derivatives are efficient inhibitors of radical processes in biological systems.[2] In this connection investigations on the effect of the structure and number of ligands attached to the fullerene cage, as well as of the fashion of their attachment on the reactivity of fullerene derivatives toward radical reactions are topical.

Radical phosphorylation is the most informative method for studying the structure of the radical adducts of fullerenes.[3—5] Fullerene derivatives thus obtained are characterized by violation of symmetry of the carbon cage and by the appearance of groups of nonequivalent carbon atoms. Due to a broad range of the HFC constants ($a_P \approx 40$—80 G)[1] of the unpaired electron with the phosphorus nucleus in the adducts of phosphoryl radicals with fullerenes or fullerene derivatives it is possible to identify particular isomeric radicals with different fullerene cage geometry, degree of delocalization of the unpaired electron, *etc.*, based on the ESR spectra.

In this work we report on the ESR study of adducts of phosphoryl radicals to the *trans*-2, *trans*-3, *trans*-4, and *e* regioisomers of bis-methanofullerenes $C_{60}\{C[P(O)(OEt)_2]_2\}_2$. Particular interest in these compounds is due to two reasons. These are the possibility of using these compounds for preparation of water-soluble derivatives suitable for use in biological systems and the lack of information on radical reactions of fullerene derivatives containing two organic groups occupying particular positions with respect to each other.

Experimental

ESR spectra were recorded on a Varian-E12a radiospectrometer. Solutions of the reaction mixtures (at a $C_{60}\{C[P(O)(OEt)_2]_2\}_2$: $Hg[P(O)(OPr^i)_2]$ mole ratio of about 1 : 1.5]) in toluene were placed in quartz ampoules and thoroughly evacuated. The $P^{\bullet}(O)(OPr^i)_2$ radicals were generated by exposing the solutions to the focussed light of a DRSh-1000 high-pressure mercury lamp in the cavity of the ESR spectrometer. The synthesis of the initial compounds was reported earlier.[6]

Results and Discussion

Earlier,[7] it was shown that six regioisomers of fullerenyl radicals are detected upon UV irradiation of toluene solutions of $C_{60}C[P(O)(OEt)_2]_2$ (**1**) and $Hg[P(O)(OPr^i)_2]_2$ (**2**) and that switching off irradiation causes the regio-

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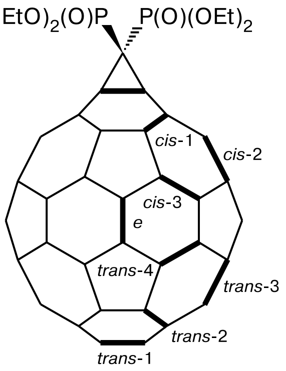

Fig. 1. Notations of isomers for $C_{60}\{C[P(O)(OEt)_2]_2\}_2$.

isomers to completely disappear due to dimerization (characteristic loss channel of fullerenyl radicals).

$$\mathbf{2} \xrightarrow{h\nu} 2\,{}^{\bullet}P(O)(OPr^i)_2\ (R^{\bullet}) + Hg,$$

$$\mathbf{1} + R^{\bullet} \longrightarrow {}^{\bullet}C_{60}C[P(O)(OEt)_2]_2R,$$

$$2\,{}^{\bullet}C_{60}C[P(O)(OEt)_2]_2R \longrightarrow \text{Products.}$$

However, steric shielding, which depends on the mutual arrangement of the organophosphorus groups, puts in the forefront when we deal with the addition of the $R^{\bullet}$ radicals to the fullerene derivatives containing two methano fragments.

In the case of addition of the $R^{\bullet}$ radicals to *trans*-2-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ (Fig. 1; shown is one methano fragment, while the second $C[P(O)(OEt)_2]_2$ substituent is added to the *trans*-2 bond) the ESR spectrum reveals the presence of six regioisomers of the fullerenyl radical (Fig. 2). Their magnetic resonance parameters (a_P is the constant of hyperfine coupling with the P nucleus) are as follows:

Isomer	a_P/G	*g*-Factor	Isomer	a_P/G	*g*-Factor
1	79.5	2.0022	*4*	63.5	2.0024
2	70.4	2.0031	*5*	59.0	2.0026
3	67.6	2.0022	*6*	59.0	2.0028

After switching off UV irradiation the spectral pattern remains unchanged, *i.e.*, all the isomers formed are stable and do not undergo dimerization.

In the *trans*-3-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ isomer (see Fig. 1, the second $C[P(O)(OEt)_2]_2$ substituent is added to the *trans*-3 bond) two organophosphorus groups are somewhat closer to each other. As can be seen in Fig. 3, the ESR spectra of the radical adducts of *trans*-3-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ recorded during irradiation and after switching it off are different. Namely, there are two peaks (asterisked), which disappear after switching off UV irradiation. This indicates the formation of two isomers of fullerenyl radicals, which can undergo dimerization. Exposure of the reaction mixture to visible light ($\lambda > 620$ nm) causes dissociation of the dimers of phosphorylfullerenyl

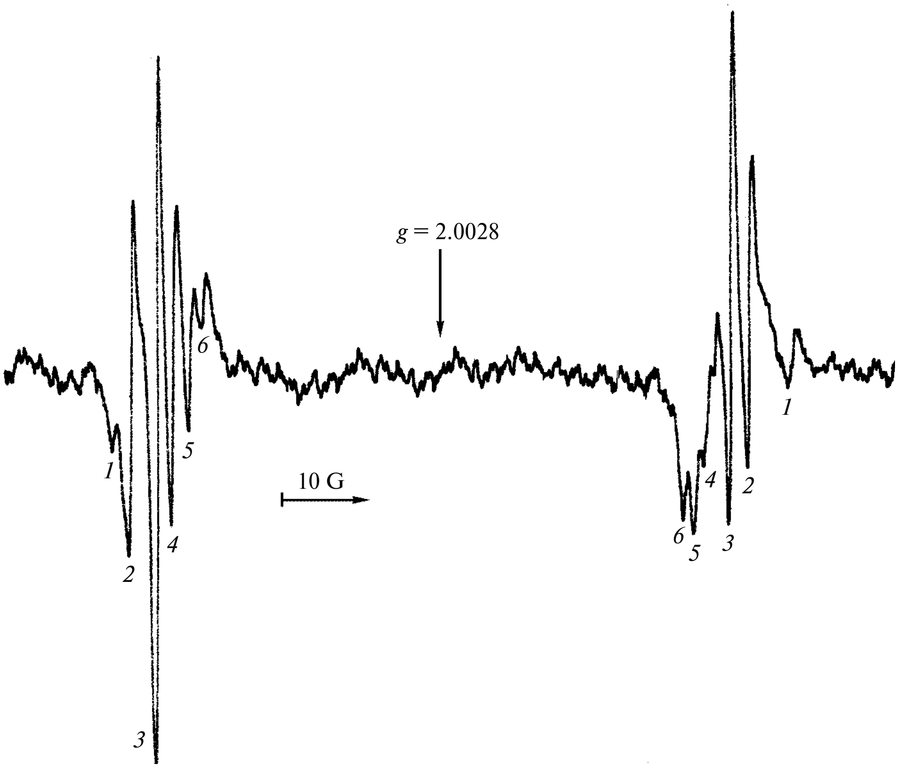

Fig. 2. ESR spectrum of adducts of the $P^{\bullet}(O)(OPr^i)_2$ radicals with *trans*-2-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$.

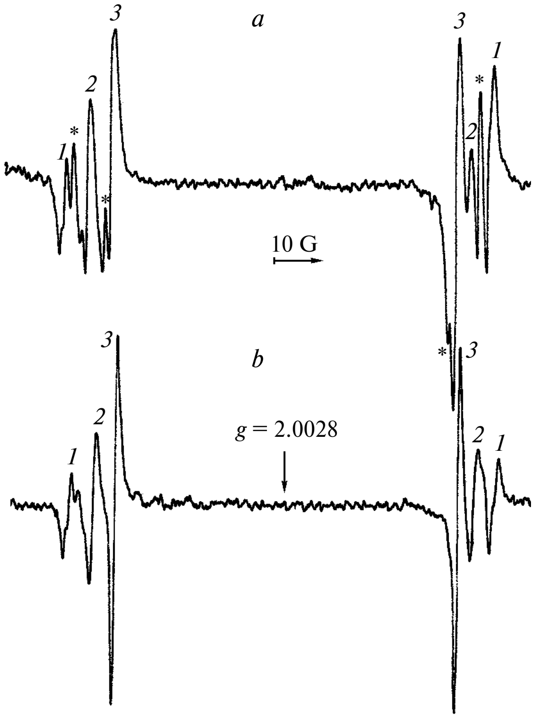

Fig. 3. ESR spectra of adducts of the $P^•(O)(OPr^i)_2$ radicals with *trans*-3-$C_{60}\{P(O)(OEt)_2]_2\}_2$ during (*a*) and after switching off irradiation (*b*).

radicals and the spectral pattern is restored. Irradiation by visible light does not induce decomposition of compound **2** and no new $R^•$ radicals are formed. Three stable isomers characterized by the most intense signals account for 60—70% of the total amount of the radical adducts of *trans*-3-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ and have the following magnetic resonance parameters: a_P = 78.6 G, g = 2.0031 (*1*); a_P = 70.4 G, g = 2.0028 (*2*); and a_P = 63.5 G, g = 2.0025 (*3*).

A similar situation is observed for the radical adducts of the *trans*-4-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ isomer. Six isomers are detected during irradiation while four isomers after switching it off:

Isomer	a_P/G	g-Factor	Isomer	a_P/G	g-Factor
1	83.25	2.0029	*3*	64.0	2.0028
2	67.40	2.0028	*4*	58.25	2.0028

The distributions of the stable and dimerizable radical adducts change significantly in the case of addition of the $R^•$ radicals to the *e*-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ isomer. Irradiation causes the formation of six isomers, of which five can be identified (Fig. 4, *a*) with the following parameters:

Isomer	a_P/G	g-Factor	Isomer	a_P/G	g-Factor
1	82.5	2.0028	*4*	64.0	2.0025
2	76.0	2.0028	*5*	61.4	2.0022
3	70.0	2.0028			

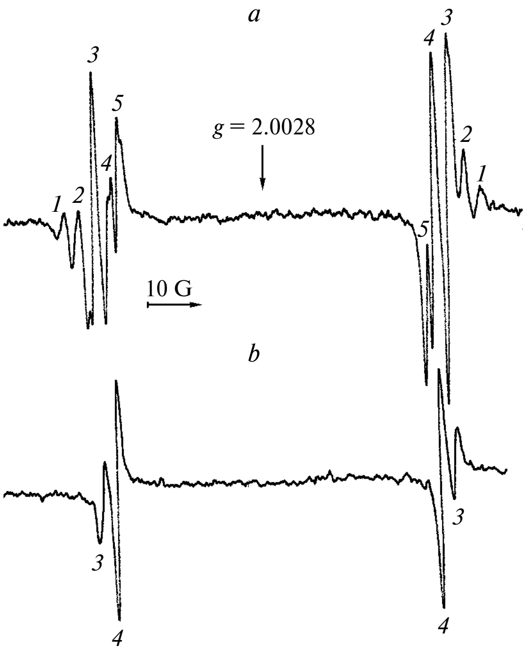

Fig. 4. ESR spectra of adducts of the $P^•(O)(OPr^i)_2$ radicals with *e*-$C_{60}\{[P(O)(OEt)_2]_2\}_2$ during (*a*) and after switching off irradiation (*b*).

After switching off irradiation (Fig. 4, *b*) the intensity of the signal of isomer *4* remains unchanged, while that of the signal of isomer *3* reduces by a factor of 7; other isomers are unstable and the corresponding signals disappear. It seems likely that only isomer *4* is formed by the addition of the $R^•$ radical to the same fullerene hemisphere to which two organophosphorus groups are attached (as a consequence, this isomer cannot undergo dimerization). Isomer *3* is an intermediate case, that is, this fullerenyl radical undergoes dimerization, but the newly formed C—C bond is weak and at room temperature the dimer partially (by ~15%) dissociates into radicals.

Thus, we first studied the radical adducts of the $R^•$ radicals and bis(methanofullerenes) containing four organophosphorus groups. We established that in the case of addition of the $R^•$ radicals to $C_{60}\{C[P(O)(OEt)_2]_2\}_2$ the number of stable regioisomers of the phosphoryl-fullerenyl radicals depends on the level of steric shielding of the fullerene cage and decreases in the series *trans*-2 > *trans*-3 ≈ *trans*-4 > *e*.

To elucidate the reactivity of the fullerene derivatives under study toward the phosphoryl radicals $R^•$, we determined the rate constants for addition of these radicals to the *trans*-3-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ regioisomer

$$C_{60}\{C[P(O)(OEt)_2]_2\}_2 + R^• \xrightarrow{k_1}$$

$$\longrightarrow \underset{\textbf{3a—c}}{{}^•C_{60}\{C[P(O)(OEt)_2]_2\}_2R.} \qquad (1)$$

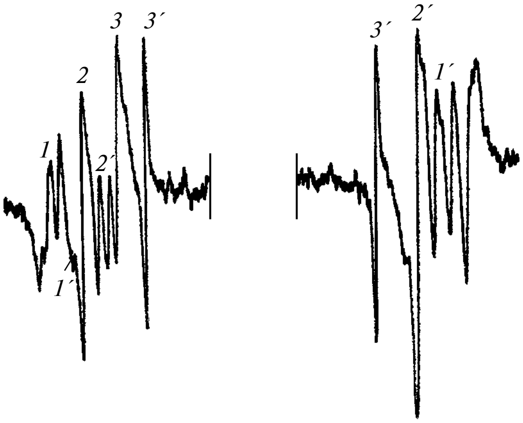

Fig. 5. ESR spectrum of the radicals generated by irradiation of toluene solutions containing $0.79 \cdot 10^{-3}$ mol L^{-1} of *trans*-3-$C_{60}\{C[P(O)OEt)_2]_2\}_2$ (*1—3*) and $0.63 \cdot 10^{-3}$ mol L^{-1} of C_{70} (*1′—3′*). $[Hg[P(O)(OPr^i)_2]_2]_0 = 10^{-2}$ mol L^{-1}.

As a reaction competing with reaction (1), we chose the process

$$C_{70} + R^{\bullet} \xrightarrow{k_2} {}^{\bullet}\underset{\mathbf{4a—c}}{C_{70}R}, \qquad (2)$$

for which the rate constant was determined earlier.[8]

From Fig. 5 it can be seen that the ESR spectrum exhibits simultaneously the signals of radicals **3a—c** (lines *1—3*, *cf.* Fig. 3) and **4a—c** (lines *1′—3′*). We measured the rates of accumulation of radicals **4a—c** (from the changes in the intensity of the line *3′* with time) and radicals **3a—c** (from the changes in the intensities of the lines *1—3* with time). Assuming $k_2 = 2 \cdot 10^8$ L mol^{-1} s^{-1},[8] the rate constants were found to be $k_1 = 1.7 \cdot 10^8$ L mol^{-1} s^{-1} at the initial concentrations $[trans\text{-}3\text{-}C_{60}\{C[P(O)(OEt)_2]_2\}_2]_0 = 0.79 \cdot 10^{-3}$ mol L^{-1} and $[C_{70}]_0 = 0.63 \cdot 10^{-3}$ mol L^{-1}. The rate constant for addition to each carbon atom in *trans*-3-$C_{60}\{C[P(O)(OEt)_2]_2\}_2$ is nearly an order of magnitude higher than the corresponding rate constant for addition to a particular carbon atom in C_{60} (see Ref. 8). Thus, fullerene derivatives containing two methano fragments can be employed as efficient inhibitors of free-radical processes.

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