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The ESR study of the influence of fluorinated alcohols on spin-adducts of phosphoryl radicals with C_{60} and C_{70}: a change of magnetic resonance parameters and exclusive formation of monoadducts

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Complex formation of ${}^{\cdot}C_{60}P(O)(OPr^i)_2$ or three isomers of ${}^{\cdot}C_{70}P(O)(OPr^i)_2$ with fluorinated alcohols CF_3CH_2OH (**1**), $(CF_3)_3COH$ (**2**), and $(CF_3)_2CHOH$ (**3**) results in an increase in the hyperfine splitting constants with the ^{31}P nucleus by approximately 3—4 G. Only monoadducts are formed when alcohols **1**—**3** are added to toluene saturated solutions of $Hg[P(O)(OPr^i)_2]_2$ and C_{60} under photochemical conditions of multi-addition of phosphoryl radicals to C_{60}.

Key words: ESR, radical, phosphoryl; fullerene, complex formation; alcohols.

The capability of fullerenes to add easily free radicals is their characteristic feature caused by the great number of weakly conjugated double bonds in their molecules.[1—4] We have previously studied[5—7] the structure and reactivity of spin-adducts of mono- and polyaddition of dialkoxyphosphoryl radicals ${}^{\cdot}P(O)(OR)_2$ to fullerenes C_{60} and C_{70} and organic derivatives of C_{60}. It has been found that phosphorylfullerenyl radicals (PFR) co-exist in two conformation, the equilibrium between which depends on the temperature. Two isomers different in hyperfine coupling (HFC) constants (~4.0 G) are detected at low temperatures, whereas at high temperatures, the rotation rate increases, and an averaged picture is observed.[8] It could be assumed that the rate of mutual transitions between conformers depends on the temperature and the nature of a solvent. Therefore, in this work, we studied the effect of ethanol and fluorine-containing alcohols CF_3CH_2OH (**1**), $(CF_3)_3COH$ (**2**), and $(CF_3)_2CHOH$ (**3**) capable of interacting with the phosphoryl group[9] on the magnetic resonance parameters of phosphorylfullerenyl radicals.

Experimental

The solutions under study were irradiated with the focused light of a DRSh-1000 high-pressure mercury lamp (1 kW). ESR spectra were recorded on a Varian E-12A spectrometer. Samples were thermostatted using a Unipan electronic regulator.

Results and Discussion

Phosphorylfullerenyl radicals were generated according to the following scheme:

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

$$C_{60} + {}^{\cdot}P(O)(OPr^i)_2 \longrightarrow \underset{\mathbf{4}}{{}^{\cdot}C_{60}P(O)(OPr^i)_2},$$

$$2\ \underset{\mathbf{4}}{{}^{\cdot}C_{60}P(O)(OPr^i)_2} \longrightarrow \underset{\mathbf{5}}{(OPr^i)_2(O)PC_{60}{-}C_{60}P(O)(OPr^i)_2}.$$

The influence of alcohols on the spectral parameters of PFR were studied by two methods. Alcohol **1** (5 vol.%)

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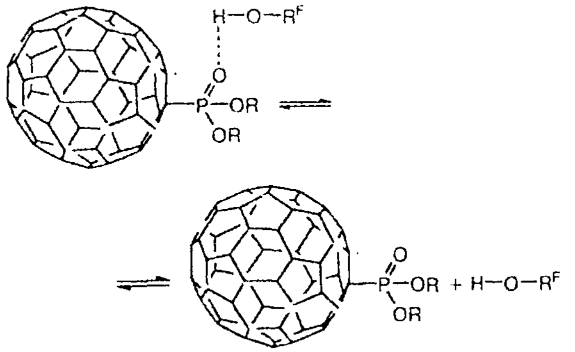
was added to a toluene solution containing ~10% dimer **5**, and the magnetic resonance parameters of radical **4a** that formed were measured under conditions of dimer photodissociation. Another method was the photochemical generation of radical **4a** in a toluene—alcohol solvent (the same toluene : alcohol ratio). In both cases, the results were similar: in the ESR spectrum of radical **4a**, the HFC constant with the phosphorus nucleus (a_P = 66.8 G, g = 2.0022) was 3.3 G higher than that for the spin-adduct of the phosphoryl radical with C_{60} unbound in a complex (a_P = 63.5 G, g = 2.0023).

The HFC constant with the phosphorus nucleus in PFR increases more noticeably when alcohols **2** (radical **6**) or **3** (radical **7**) (a_P = 67.5 G, g = 2.0021) are added. On heating to 420 K, the a_P values for these radicals decreases to 64.6 G. This indicates that on heating the equilibrium between PFR bound into a complex and free is shifted toward the latter.



When the temperature decreases to 190 K, the ESR signals are broadened due to the retarded character of rotation of the phosphoryl group (Fig. 1). At temperatures lower than 210 K in the presence of alcohol **3**, the signals of two isomers with the following parameters are detected: **7a**, a_P = 68.5 G, g = 2.0022; **7b**, a_P = 65.8 G, g = 2.0023. Similar values were obtained for radical **6** in the presence of alcohol **2**. In the case of free PFR, the ESR spectrum in which the ratio of intensities of signals of the two isomers is equal to 1 is observed at a higher temperature (by 20 °C) than that for the radicals bound in a complex. Most likely, the formation of the H atom of the hydroxyl group of alcohol and the phosphoryl group in each conformer results in an increase in the energy barrier of transitions between them.

When the corresponding amount of EtOH is added, the parameters of the ESR spectra of the phosphorylfullerenyl radicals remain unchanged, which is related to the lower proton-donating ability of ethanol.[9]

It is known[6] that the addition of phosphoryl radicals to fullerene C_{70} results in detection of three isomers (**8a—c**) different in HFC constants and g factors: **8a**, a_P = 70.5 G, g = 2.0031; **8b**, a_P = 66.5 G, g = 2.0027; **8c**, a_P = 55.25 G, g = 2.0028. In this case, the addition of alcohols **1—3** favors an increase in the HFC constants with the phosphorus nucleus.

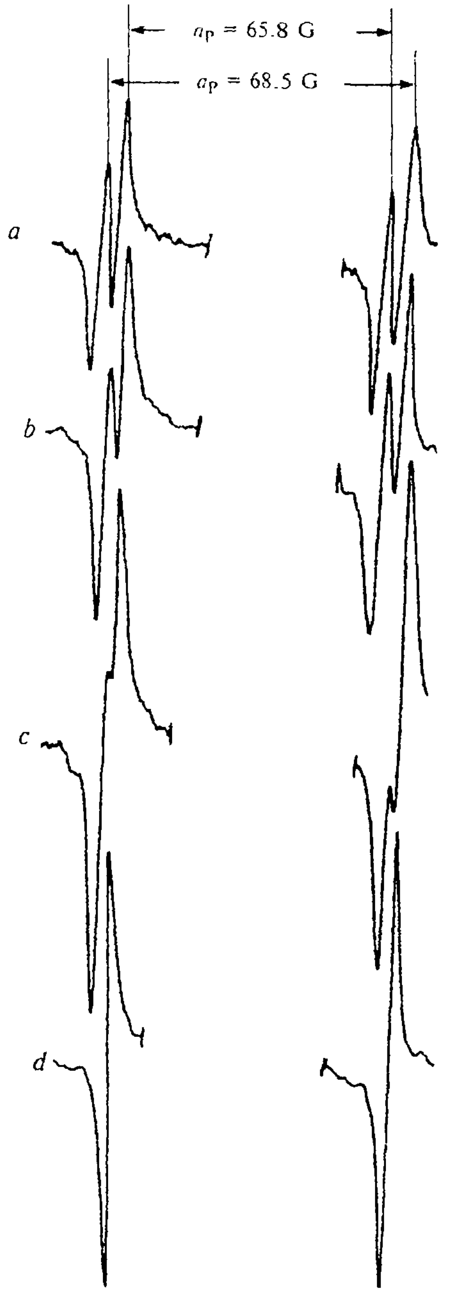


Fig. 1. ESR spectra of radical $^{\cdot}C_{60}P(O)(OPr^i)_2$ in the toluene—3 mixture at 190 K (*a*), 200 K (*b*), 210 K (*c*), and 250 K (*d*).

Alcohol	Isomer	a_P/G	g
1	**8a**	76.25	2.0028
1	**8b**	71.50	2.0023
1	**8c**	58.40	2.0023
2, 3	**8a**	77.90	2.0028
2, 3	**8b**	72.50	2.0023
2, 3	**8c**	59.20	2.0028

It is of interest that the higher the a_P value in isomers of the $^{\cdot}C_{70}P(O)(OPr^i)_2$ radical, the higher the difference between the constants of free fullerenyl radicals and those bound into a complex.

We studied the effect of fluorine-containing alcohols on the parameters of the spin-adducts of C_{60} in a saturated toluene solution of $Hg[P(O)(OPr^i)_2]_2$ under standard conditions of formation of adducts of the multiple addition of the phosphoryl radicals to C_{60}.[10] However, when alcohols **2** or **3** (5 vol.%) are added, even prolonged photolysis (~30 min) results in the formation of the monoadducts only.

It can be assumed that alcohol forms a hydrogen bond directly with the phosphoryl radical and decreases the rate of its addition to fullerene. Since the photochemical generation of spin-adducts is a reversible process, the decrease in the rate of addition of the phosphoryl radicals to C_{60} shifts the equilibrium toward the monoadduct.

Thus, we observed the effect of fluorine-containing alcohols on the magnetic resonance parameters of phosphorylfullerenyl radicals, which can be useful in analysis of ESR spectra of spin-adducts of phosphoryl radicals with fullerene derivatives,[7] especially in the case where the ESR spectra of several isomers are imposed.

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Oxidation of aryl vinyl sulfides in the $Bu^tOOH—Ti(OPr^i)_4—(R,R)$-diethyl tartrate system

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Oxidation of aryl vinyl sulfides into aryl vinyl sulfoxides in the $Bu^tOOH—Ti(OPr^i)_4—$ (R,R)-diethyl tartrate system was studied. The process afforded low optical yields (no more than 5%). A model of the oxidation was proposed that allows interpreting the dependence of the reaction enantioselectivity on the structure of a substrate.

Key words: aryl vinyl sulfides, enantioselective oxidation; Sharpless system; aryl vinyl sulfoxides.

Optically active alkenyl sulfoxides can be obtained by the reaction of (−)-menthyl aryl sulfinates with alkenylmagnesium bromides (the Andersen synthesis),[1–5] the reaction of carbonyl compounds with lithium salts of

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