ESR study of spin-adducts of boron-centered carboranyl radicals with fullerene-60 and fullerene-70*

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Spin-adducts of boron-centered radicals, derivatives of *m*-carboran-12, with fullerenes C_{60} and C_{70} have been studied by ESR spectroscopy. Constants of hyperfine splitting (HFS) of an unpaired electron with ^{10}B and ^{11}B nuclei have been determined from the ESR spectra of $^{\cdot}C_{60}{-}B_{10}H_9C_2H_2$ radicals. Three isomeric spin-adducts were detected with different HFS constants with ^{11}B, and *g*-factors were detected in the reaction of $^{\cdot}B_{10}H_9C_2H_2$ with C_{70}.

Key words: fullerene, boron-centered carboranyl radical, spin-adducts; ESR.

In radical reactions fullerenes behave like polyalkenes, which are capable of adding a large number of free radicals.[1,2] The interaction of fullerenes with radicals containing a free valence localized at the atoms with a magnetic nucleus is of special interest, because this makes it possible to determine the structure of spin-adducts resulting from mono- and polyaddition.[3,4] The problem of the relationship between the nature of an attacking radical and the structure and reactivity of the spin-adducts that these radicals form with fullerene is important in studies of fullerenyl radicals. Earlier we investigated the specific features of the structure and reactivity of the spin-adducts derived from dialkylphosphoryl[5—7] and trimethylaminoboryl radicals and fullerenes.[8] In this study, the addition of boron-centered carboranyl radicals to fullerenes has been investigated by ESR spectroscopy.

Experimental

In the experiments a DRSh-1000 high pressure mercury lamp was used; its filtered and unfiltered light was used for irradiation of the solutions studied, placed in quartz tubes. ESR spectra were recorded on a Varian E-12A spectrometer.

Results and Discussion

Previously it has been shown that photolysis of a di(*m*-carborane-9-yl)mercury solution results in its decomposition to form carboranyl[9] and carboranylmercury radicals.[10]

$$\underset{\mathbf{1}}{Hg[B_{10}H_9C_2H_2\text{-}m]_2} \xrightarrow{h\nu} \underset{\mathbf{2}}{^{\cdot}B_{10}H_9C_2H_2\text{-}m} + {^{\cdot}HgB_{10}H_9C_2H_2\text{-}m}$$

After UV irradiation of a saturated toluene solution of C_{60} and $Hg[B_{10}H_9C_2H_2\text{-}m]_2$ within 30—40 s, the ESR signal of a radical with $g = 2.0023$ and the hyperfine structure corresponding to the carboranylfullerenyl radical was recorded. The HFS constants of an unpaired electron with magnetic isotopes ^{10}B (natural abundance ~20 %, $I = 3$), $a_{^{10}B} = 6.25$ G, and ^{11}B (natural abundance ~80 %, $I = 3/2$), $a_{^{11}B} = 18.25$ G (four lines of equal intensity). The data obtained imply the formation of mono-*B*-carboranylfullerenyl radical in accordance with the following scheme:

$$C_{60} + {^{\cdot}B_{10}H_9C_2H_2\text{-}m} \longrightarrow \underset{\mathbf{3}}{^{\cdot}C_{60}{-}B_{10}H_9C_2H_2\text{-}m}.$$

Radicals **3** dimerize when the UV light is switched off; this is typical of fullerenyl radicals.[3,5]

A more prolonged photolysis of a saturated toluene solution containing C_{60} and an excess of $Hg[B_{10}H_9C_2H_2\text{-}m]_2$, results in multiple addition of carboranyl radicals to fullerene. In this case a stable spin-adduct of multiple addition is recorded in the ESR spectrum for which the spectral lines are 5—10 times broader (depending on duration of irradiation of the sample and relative concentration of the mercury compound). This is a result of superposition of the ESR signals of spin-adducts of multiple addition of carboranyl radicals to C_{60} with various amounts of radicals. Therefore, in the case of boron-centered carboranyl radicals the addition is not concerted, and the allylic structures which are similar to those appearing in multiple addition of benzyl radicals,[2] are not formed because of the carborane large bulk.

Unlike fullerene-70, the structure of fullerene-60 contains five types of inequivalent carbon atoms; therefore, formation of five various spin-adducts of radicals with C_{70} is theoretically possible. However, as a rule,

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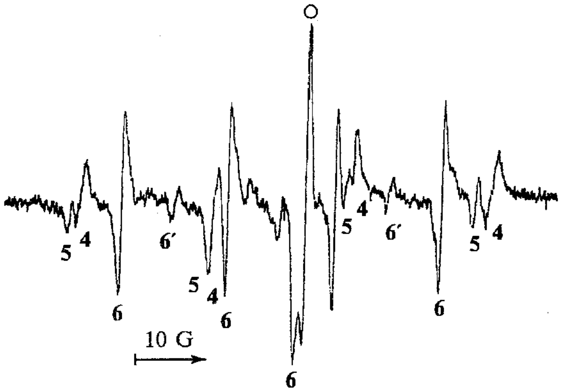

Fig. 1. ESR spectrum of regioisomers of spin-adducts of boron-centered carboranyl radicals with fullerene-70 at 430 K. The figures correspond to the numbers for the radicals given in the text; **6′** — extreme components of the isomer **6** multiplet corresponding to splitting of an unpaired electron with a ^{10}B nucleus; O — a signal resulting from defects in the quartz tube.

the three types of spin-adducts detected are the most energetically profitable.[7,11]

Addition of a boron-centered carboranyl radical to C_{70} affords three isomers characterized by the following HFS constants with the ^{11}B nucleus (Fig. 1): **4**, $a_{^{11}B} = 20.0$ G, $g = 2.0021$; **5**, $a_{^{11}B} = 19.7$ G, $g = 2.0032$; **6**, $a_{^{11}B} = 15.5$ G, $g = 2.0026$. For isomer **6** the HFS constant with the ^{10}B nucleus was determined: $a_{^{10}B} = 5.1$ G. Spin-adducts **4** and **5** decay within less than 1 s after the UV light is switched off, and spin-adduct **6** has a lifetime of more than 10 min. A similar picture was observed for spin-adducts of dialkoxyphosphoryl radicals with C_{70}.[6]

In addition, we performed metallation of dimers of carboranylfullerenyl radicals with complex $Pt(PPh_3)_4$ analogously to platination of dimers of phosphorylfullerenyl radicals.[12]

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

$$\longrightarrow R(PPh_3)_2PtC_{60}{-}C_{60}Pt(PPh_3)_2R$$

7

$$R = B_{10}H_9C_2H_2\text{-}m$$

When platinated dimer **7** is irradiated with visible light, metal-containing carboranylfullerenyl radicals are formed. Unlike metal-containing phosphonylfullerenyl radicals, whose ESR spectra make it possible to identify at least five isomers,[12] ESR spectra for the carboranylfullerenyl radicals do not allow us to make this because of the small difference in the HFS constants with the boron nuclei. In this case we observed only superposition of the signals of isomeric radicals and broadening of the lines.

Thus, we have studied ESR spectra of spin-adducts of boron-centered carboranyl radicals with fullerenes-60 and -70 and the ESR spectra of platinated carboranylfullerenyl radicals. We showed that multiple addition of boron-centered carboranyl radicals to C_{60} was not "concerted". Three types of spin-adducts of *B*-carboranyl radicals to C_{70} have been detected, differing in HFS constants and *g*-factors.

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