Brief Communications

ESR study of the photolysis of $C_{60}Cl_6$

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The photolysis of $C_{60}Cl_6$ in the presence of α-phenyl-*N*-*tert*-butylnitron (PBN) as a spin trap was studied by ESR spectroscopy. It was shown that a C—Cl bond undergoes homolytic cleavage to give a stable fullerenyl radical of the cyclopentadienyl type, whose formation was confirmed by quantum-chemical computations.

Key words: ESR spectroscopy, fullerenyl radical, spin trap, photolysis, semiempirical quantum-chemical computations.

Hexachlorofullerene[1] $C_{60}Cl_6$ (**1**) is used as the starting reagent in the synthesis of various C_{60} derivatives by replacing the Cl atoms by functional groups in the presence of catalytic amounts of $FeCl_3$.[2] However, radical reactions involving **1** have not been investigated so far. In the present work, the photolysis of compound **1** in different solvents was studied by ESR spectroscopy. Quantum-chemical computations were performed to determine the most probable structure of the resulting fullerenyl radical.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Reaction solutions were degassed in glass vials and irradiated at room temperature with the use of a DRSh-1000 lamp directly in the resonator of the spectrometer. A band with λ = 366 nm was isolated on a glass color filter. The initial concentration of α-phenyl-*N*-*tert*-butylnitron $[PBN]_0 = 5 \cdot 10^{-1}$—$2 \cdot 10^{-2}$ mol L^{-1} and $[C_{60}Cl_6] = 5 \cdot 10^{-5}$ mol L^{-1}. Compound **1** was synthesized according to the known procedure.[1]

Quantum-chemical computations were performed by the MNDO/PM3 method in the ROHF approximation[3] with the GAMESS program package for Workstation DEC 3000 Alpha AXP-400X.[4]

Results and Discussion

Irradiation of degassed solutions of **1** in benzene or toluene with light (λ_{max} = 366 nm) at T = 293 K gives a stable fullerenyl radical (a singlet with g = 2.0022, Fig. 1, *a*) as a result of elimination of a Cl atom from molecule **1**. In the presence of PBN, the ESR spectrum recorded under the same photolysis conditions (Fig. 1, *b*) shows signals from spin adducts of a Cl atom with PBN:

$$Cl + PhCH{=}N(O)CMe_3 \longrightarrow \underset{\mathbf{2}}{PhCHClN(O^{\cdot})CMe_3}.$$

The constants of hyperfine coupling (HFC) between the lone electron and the magnetic nuclei of N, H, and Cl atoms (a_N = 12.1 G, $a_{\beta\text{-}H}$ = 0.75 G, $a_{^{35}Cl}$ = 6.1 G,

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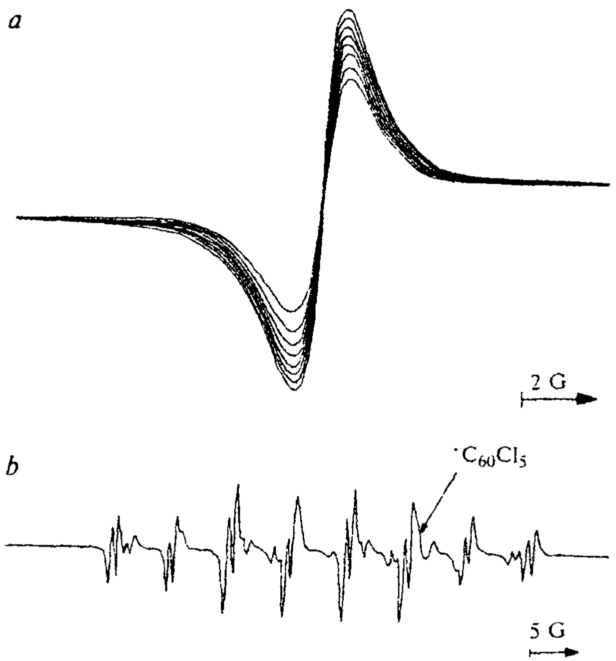

Fig. 1. ESR spectra of (*a*) a $^{\cdot}C_{60}Cl_5$ fullerenyl radical ~30 min after irradiation and (*b*) a spin adduct of the Cl atom with α-phenyl-*N*-*tert*-butylnitron. A signal from $^{\cdot}C_{60}Cl_5$ overlapping a multiplet component from the spin adduct is marked with an arrow.

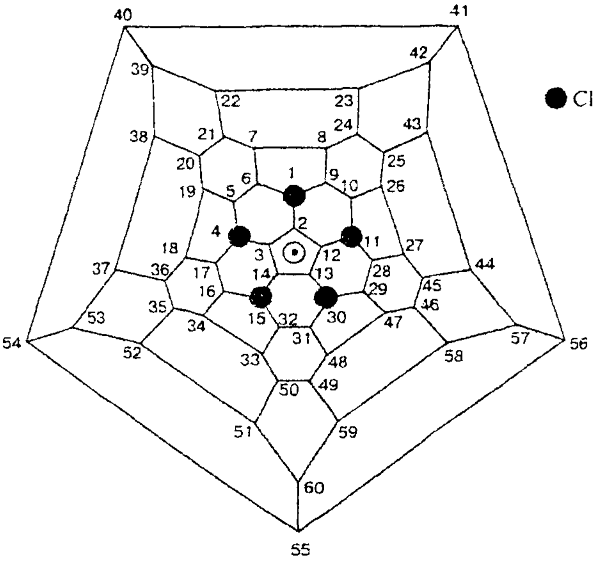

Fig. 2. MNDO/PM3-optimized structure of the $^{\cdot}C_{60}Cl_5$ radical.

and $a_{^{37}Cl}$ = 4.9 G) are very close to those obtained for the known[5,6] radicals **2**. These results suggests that, under our reaction conditions, C—Cl bonds in compound **1** undergo homolytic cleavage.

To find out which of the C—Cl bonds is homolytically broken, we calculated the enthalpies of formation of two possible pentachlorofullerenyl radicals by the MNDO/PM3 method in the ROHF approximation. Calculation showed that the cyclopentadienyl fullerenyl radical (**1a**) is thermodynamically most stable (ΔH^0_f = 716.5 kcal mol^{-1}). In this radical, a lone electron is delocalized over five C atoms in the five-membered ring of the fullerene skeleton. Elimination of any other Cl atoms results in a product (**1b**) with a higher enthalpy (ΔH^0_f = 721.2 kcal mol^{-1}) (Fig. 2).

In the presence of PBN, the ESR spectra exhibit, along with signals from compound **2**, a triplet of doublets from different nitroxyl radicals. The HFC constants, a_N and $a_{\beta\text{-}H}$, depend on the nature of a solvent. In the case of toluene, a_N and $a_{\beta\text{-}H}$ are equal to 13.9 and 2.45 G, respectively, while in benzene they are 13.8 and 1.8 G. These values coincide with those found for spin adducts of benzyl and phenyl radicals with PBN.[7]

One can assume that the Cl atoms released upon decomposition of **1** detach an H atom from toluene or benzene, thus generating benzyl and phenyl radicals that are detected by ESR as spin adducts with PBN. The results obtained indicate that $C_{60}Cl_6$ can be used as a source of Cl atoms in homolytic chain processes.

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