SYNTHESIS AND REACTIVITY OF HIGHER FULLERENES

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Introduction

One of fundamental tasks in chemistry of fullerenes is investigation of reactivity of higher fullerenes. In contrast to fullerenes C_{60} and C_{70}, reactivity of higher fullerenes C_{76}, C_{78}, C_{84}, C_{86} C_{90} has not been studied because of the problem of synthesizing them in preparative quantities [1]. The problem originates from limited accessibility of higher fullerenes and the task of isolation of pure products, which requires expensive and laborious multi-step high-performance liquid chromatography (HPLC). As a result, accessibility of pure higher fullerenes in milligram quantities impedes progress in chemistry of these compounds. Conventional methods of synthesis and isolation from soot allow the preparation of extracts with very low content of higher fullerenes, 1-3 % of extract weight [2]. Isomerically individual higher fullerenes are isolated from extracts by preparative high-performance liquid chromatography (HPLC). However, because of low content of higher fullerenes in extracts, chromatographic isolation is a very laborious procedure. Individual higher fullerenes are still unaccessible to researchers because of being expensible: the price of fullerene C_{78} is ~200 $/mg. Thus, there are only very few publications dedicated to the synthesis of higher fullerene derivatives and the study of their reactivity [1, 3].

Thus, in our work we especially focused on the tasks related to the development of electric arc synthesis of soot with high content of higher fullerenes, optimization of reaction conditions, search for methods of efficient isolation of higher fullerenes from soot, and the development of effective procedures of synthesis trifluoromethyl derivatives of higher fullerenes.

Results and Discussion

Higher fullerenes C_{76}, C_{78}, C_{84}, C_{86} and C_{90} were prepared by the electric arc method. The content of higher fullerenes in synthesized soot was enhanced as follows: 1) simultaneous evaporation of two graphite electrodes located at 4-5 cm from each other, i.e. two parallel arcs burning; 2) evaporation of a composite graphite electrodes comprising K, Y, La, Ce or Gd. An M/C ratio, the distance between electrodes, helium pressure and arc current were varied in experiments. As a result, optimal conditions for synthesis of soot with high content of higher fullerenes were found. It was shown that the addition of 1 at.% of K, Y, La, Ce or Gd to graphite electrodes or the evaporation of two parallel arcs provides a 2-3 times higher content of higher fullerenes in fullerene containing soot

Higher fullerenes were isolated by extracting with o-xylene or o-dichlorobenzene from fullerene containing soot in argon atmosphere in boiling solvents. The maximal content oh higher fullerenes in extracts was 12 mol.%. Pure higher fullerenes were isolated from fullerene extracts by HPLC (*Cosmosil Buckyprep* column, toluene as eluent). As a result, chromatographically pure higher fullerenes were prepared in quantities which allowed their chemical properties to be studied.

Reactivity of higher fullerenes C_{76}, C_{78}, C_{84} and C_{90} in high-temperature reactions with trifluoroiodomethane was studied. For the first time a series of isomerically pure trifluoromethyl derivatives of higher fullerenes: C_2-(C_{76}-D_2(1))$(CF_3)_{10}$, C_1-(C_{76}-D_2(1))$(CF_3)_{10}$ (четыре изомера), C_2-(C_{78}-D_3(1))$(CF_3)_{10}$, C_s-(C_{78}-C_{2v}(2))$(CF_3)_{10}$, C_2-(C_{78}-C_{2v}(2))$(CF_3)_{10}$, C_1-(C_{78}-C_{2v}(3))$(CF_3)_{12}$, C_1-(C_{84}-C_2(11))$(CF_3)_{12}$, D_2-(C_{84}-D_2(22))$(CF_3)_{12}$, C_2-(C_{84}-D_2(22))$(CF_3)_{12}$, C_1-(C_{90}-C_1(32))$(CF_3)_{12}$ was isolated and analyzed. Single crystals of C_2-(C_{78}-D_3(1))$(CF_3)_{10}$, C_S-(C_{78}-C_{2V}(2))$(CF_3)_{10}$ were grown and their structures were determined from X-ray analysis. It was found that topology of the cage of fullerene C_{78} determines the arrangement of ten CF_3 groups on the carbon cage. In the C_{78} molecule with D_3 symmetry (Fig. 1a), ten CF_3 groups are attached in *para* positions of the six-membered cycles which form two symmetric ribbons on the carbon cage, while in the C_{78} molecule with C_{2V} symmetry (Fig. 1b), ten CF_3 groups are located on a single ribbons of edge-sharing *p*-$C_6(CF_3)_2$ hexagons.

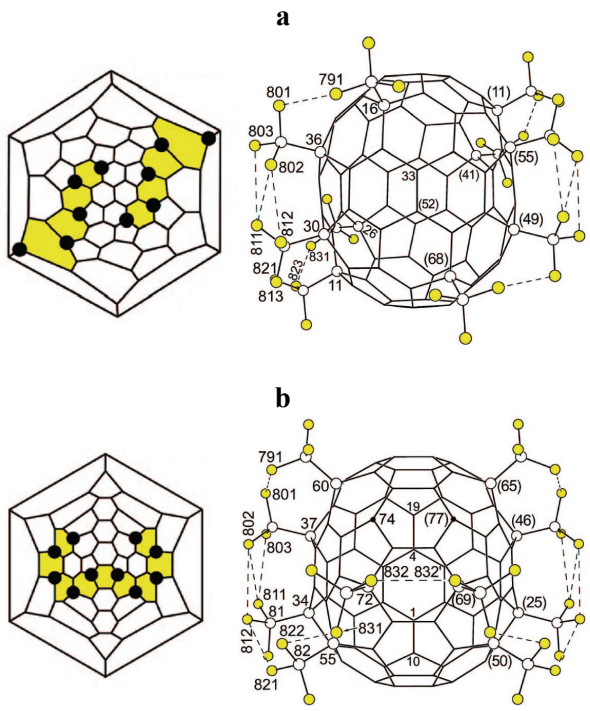

Fig. 1. Structures and Schlegel diagrams for a) C_2-(C_{78}-D_3(1))$(CF_3)_{10}$ and b) C_S-(C_{78}-C_{2V}(2))$(CF_3)_{10}$ molecules. Carbon atoms to which CF_3 groups are attached are marked by black dots.

Conclusions

Pure higher fullerenes C_{76}, C_{78}, C_{84}, C_{86} and C_{90} were synthesized by electric arc method and isolated by HPLC in quantities which allowed their properties to be studied. For the first time a series of isomerically pure trifluoromethyl derivatives was synthesized *via* the reaction of trifluoroiodomethane with higher fullerenes at 520-550°C, isolated by HPLC and characterized by mass spectrometry and ^{19}F NMR spectrometry.

The analysis of structural data allows one to formulate the following principles of the addition of bulky substituents such as one CF_3 to higher fullerenes: 1) the main addition-pattern is *para*- and/or *meta*-addition on six-membered cycles of the carbon cage; 2) a preferable mutual arrangement of pairs of substituents is the formation of one or several ribbons of edge-sharing *p*-$C_6(CF_3)_2$ hexagons of a cage; 3) 1,4-addition of bulky substituents does not involve the "most reactive" double bonds of fullerene, which are involved in 1,2-addition.

The work was supported by the Program N 27 "Fundamentals of basic research for nanotechnologies and nanomaterials of Basic Research of Presidium of RAS.

References

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