A mass spectrometric study of the vaporization and the heats of sublimation of trifluoromeyhylated [60]fullerene compounds

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The rising interest to the fullerenes and their derivatives is related to their special properties appearing both on macroscopic, and on microscopic level. Of the known fullerene derivatives, the trifluoromethyl ones are of particular interest. Like fluorofullerenes, they possess electron-acceptor properties, being promising compounds for further chemical modifications, but exhibit higher resistance to thermal decomposition and hydrolysis, a feature facilitates their storage and subsequent use as reagents [1].

All methods of trifluoromethylation (synthesis with the use of silver trifluoroacetate and the reaction with CF_3I) result in formation of wide variety of products with different number of groups, attached to the carbon cage, And the sublimation of final products from the reaction mixtures is one of the most important stage of purification in both methods.

Sublimation studies have been performed for isomerically pure $C_{60}(CF_3)_{12}$ [2] and for $C_{60}(CF_3)n$ (n = 6–16) mixture in the temperature range 300–550K. The Knudsen effusion method with the mass-spectrometric detection of vaporization products was used. Saturated vapor pressure and the enthalpy and entropy of sublimation for the S_6 isomer of $C_{60}(CF_3)_{12}$was obtained for the first time.

It is known that electron impact ionization method has a significant drawback when it is used for analysis of trifluoromethyl derivatives that is severe fragmentation down to bare fullerene ions. So the individual mass-spectrum for pure $C_{60}(CF_3)_{12}$ (70 eV) was than used for the interpretation of mass-spectra of mixture. The relative vapor pressures and heats of sublimation was obtained for compounds, containing 6–16 CF_3 groups. A significant difference in fragmentation channels between $C_{60}(CF_3)_{14,16}$ and other derivatives was observed.

This work was supported in part by the Russian Foundation for Basic Research (project no. 05-03-32916a)

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Annealing of CN_x nanotubes and nanofibers

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Carbon nanotubes and carbon – nitrogen (CN_x) nanofibers are perspective materials for use in numerous fields. To improve working characteristics of carbon and CN_x nanomaterials the purification from metal catalysts and amorphous carbon is necessary.

In the given work we are presenting the investigations of influence of high temperature annealing in argon atmosphere on purity and structural changes of CN_x nanofibers grown in the high isostatic pressure apparatus by graphite direct resistive heating in nitrogen atmosphere under pressure up to 70 MPa and temperature 1800°C. Detailed description of experimental procedure has been presented in [1]. The characteristic property of these CN_x nanofibers is their bamboo – like structure

In this work we made annealing of by temperature up to 2500°C in argon gas media under pressure in range 1-2 MPa on the very experimental apparatus which was used by CN_x nanofibers synthesis. We used increased argon pressure to improve refinement conditions from metal vapor by increase gas convection under increased pressure. Before and after annealing the CN_x nanomaterial was analyzed by transmission electron microscopy using Jeol JEM-200CX. Raman scattering spectra of the deposit were collected with a Jobin Yvon HR 640 spectrometer with Princeton Instruments Inc. CCD matrix cooled with liquid nitrogen.

The high temperature annealing leads to full removal of catalytical metal particles and amorphous carbon. The last one probably graphitizates and becomes transformed in a onion – like structure. It is significant that quantity of bamboo-like nanofibers with numerous inner diaphragms decreases appreciably after annealing. Nanofibers with large cells predominate.

After annealing at 2500°C we observed appearance of strongly reformatted nanofibers and nanotubes with drastic local widening of walls. The most deformated sections were filled by carbon inside. The nanotubes can have channel with smooth relief of inner surface while there are widenings in outer surface. The surface distortions relates obviously with structural changes. It could be supposed that high solution of carbon in iron takes place by melting of iron particles and this process increases by increasing gas pressure. Due to high saturation of iron by carbon the volume of particle is increased and this process can lead to transformation of walls and to structural changes.

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Structure and optical properties of astralens

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High Resolution Transmission Electron Microscopy (HRTEM) provided a direct evidence of the polyhedral multi-shell fullerene-like structure of astralen particles. The polyhedra consist of large well-ordered flat sp^2 graphitic faces connected by defective corner regions with presumably pentagon-like structure. The spacing of lattice fringes is ~0.340 nm. This value coincides with that obtained in HRTEM micro-diffraction and XRD measurements and close to the (002) inter-plane distance in graphite. The size distribution of astralen particles is determined. It is shown that the expectation value for the astralen size is 40 nm and the variance is 140 nm^2. The transmission spectrum of astralen is uniform in visible and NIR spectral range. The singlet molecular oxygen generation was found and studied by means of luminescence and chemical traps methods in astralen suspensions in water, alcohol and carbon tetrachloride and on surfaces of astralen coatings in air. The established fact of singlet oxygen generation at the interaction of photoexcited astralens with molecular oxygen confirms the existence of a singlet-triplet structure of the astralen electronic states.

Physicochemical compatibility of fullerene C_{60} with *tetrakis*(4-amino-5-phenoxy)phthalocyanine

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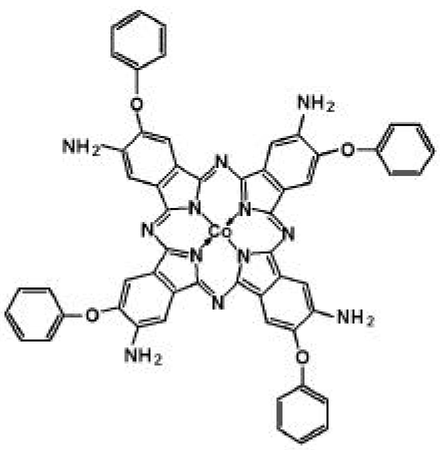
Donor-acceptor systems of the phthalocyanine–fullerene type show unique photophysical properties in solution and, hence, are of great interest as a basis of photoresponsive composite materials. However practical application thereof is hampered by poor compatibility of fullerene with conventional phthalocyanines and consequently a lack of efficient charge transfer between the components in the solid state. Therefore this work was planned as a first systematic attempt to reveal physicochemical factors promoting compatibility of fullerene with ?-donor molecular partners of the phthalocyanine nature.



As a partner of fullerene, cobalt phthalocyanine Pc (structure, [1]) with the strong electron-donor (amino) and steric (phenoxy) molecular entities was chosen. Homoaggregation of such Pc occurs by the van-der-Waals mechanism and is not accompanied by collectivization of the ?-electron density within the aggregates. Compatibility was studied by Langmuir–Blodgett (LB) technique, optical spectroscopy and optical polarizing microscopy.

The homogeneous ternary Pc–C_{60}–H_2O nanosystem was found to be aggregately stable within a very broad interval of the Pc/C_{60} ratio; it might be freely compressed and efficiently transferred onto a hydrophilic quartz plate. The thin solid Pc–C_{60} compositions at the ratio ranging from 1:1 to 1:8 were prepared by both LB technique and solution casting. Electronic spectra of the LB films are strictly additive and characterized by a low base-line even at the 60^0 tilting of the film-covered plate with respect to the incidence beam. In the spectra of the cast films, bands of “false charge transfer” usually interpreted as a sign of intense fullerene–donor interactions [2] are found. Morphology of the LB films is studied in detail as a function of the Pc/C_{60} ratio and a number of plate-dipping into the Pc–C_{60}–H_2O nanosystem.

Conclusion A key molecular factor controlling the homogeneous nanostructure of the studied composites seems to be the amino-group attached directly to the phthalocyanine macrocycle. As for the microhomogeneity, it is limited by poor film-forming properties of chosen Pc.

The work is supported by the Russian Foundation for Basic Research (Grants 06-03-96308 and 07-03-00145) and the Russian Academy of Sciences (Program P7/03).

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The stable products of the Ñ$_{70}$ fullerene reaction with ozone in solution

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For the first time total and relative contents of stable products of Ñ$_{70}$ fullerene ozonolysis in CCl_4 and î -dichlorobenzene have been identified with HPLC, UV, IR spectroscopy, element and chemical analyses. At the moment of 100 % conversion of Ñ$_{70}$ the mixture of products is produced and corresponds to formula: Ñ$_{70}$Î$_{14.3}$Í$_{0.21}$ (epoxides / polyketones / polyesters / secondary ozonides fullerene (SOZF) / acids = 1.07 / 6 / 6 / 0.21 / 1.02). Epoxides of Ñ$_{70}$ contain less number of oxygen atoms Ñ$_{70}$Î$_{n}$ (n = 1?4) in comparison with Ñ$_{60}$Î$_{n}$ (n = 1?6). Polyketones, polyesters, acids and SOZF collect during the total time of Ñ$_{70}$ ozonolysis (1 h). The kinetic curve of Ñ$_{70}$Î$_{n=1?4}$ accumulation has the maximum on 0.5 min, and epoxides are absent among products after 3.5 min ozonolysis due to transformation into others oxygen containing fullerene derivatives.

Fullerene Ñ$_{70}$ unlike to Ñ$_{60}$ is completely oxidized with ozone in a liquid phase. The rate constants for oxidation of Ñ$_{70}$ with ozone in CCl_4 have been measured ($k = 0.7 \cdot 10^4$ $L \cdot mol^{-1} \cdot s^{-1}$), its value is higher than that for Ñ$_{60}$ ozonolysis, which has been measured before ($k = 1.2 \cdot 10^3$ $L \cdot mol^{-1} \cdot s^{-1}$). Ñ$_{70}$ fullerene shows more reaction ability to ozone, than Ñ$_{60}$. It can be explained by lower symmetry of C_{70} molecules, containing in the tops of ellipsoidal framework Ñ=Ñ bonds with higher reaction ability.

High solubility of Ñ$_{70}$ oxiderivatives (OD) in water has been detected, that can offer the Ñ$_{70}$ ozonolysis for producing of water-soluble Ñ$_{70}$ derivatives, which are perspective in pharmacology and medicine. Hydrolysis of SOZF generated fullerene polyketones and H_2O_2 takes place at dissolution of OD in water. H_2O_2 has been identified by iodometric titration and by color reaction with diphenylcarbazide. Activation energy of SOZF hydrolysis, measured by inclination linear dependence (R=0.97) ln of maximal CL intensity (accompanying hydrolysis) from Ò$^{-1}$, equals to 12.4±0.7 $kcal \cdot mol^{-1}$. SOZF has been found to be much less stable and destruct not at 300?Ñ (as it was considered earlier), but at room temperatures as a result of interaction with moisture traces from the air.

This work was supported by the program of the Department of chemistry and sciences about materials of the RAS

Industrial complex for the production of light- and heavy fullerenes

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An original fullerene production complex is developed by the authors for the production, extraction and separation of the light- and heavy fullerenes [1-2].

The complex contains the following apparatuses.

The fullerene soot production reactor. The operation volume is 25l, the producibility is (100-120) g/h, continious operation time exceeds 12h, the fullerene content in the soot is 12 – 14 mas.%, the fractional content of the fullerene mix is the following: 65-70 mas.% of C_{60}, 25–30 mas.% of $Ñ_{70}$, upto 5 mas.% of the mix(C_{76} + C_{78} + C_{84} + C_{90}…), the half of these last ones being $Ñ_{84}$.The analyses methods are outlined in [3].

The fullerene mix production extractor. The operation volume is 2l, producibility– 400 g/cycle, the cycle time exceeds 5h, the efficiency is higher than 98 rel. mas.%.

The separator for the pure C_{60} fullerene production. The operation volume is 10l, the producibility is 100g of the $Ñ_{60}$ fullerene/cycle, the cycle time is no longer than 22h, the $Ñ_{60}$ purity is (99.5–99.9) rel.mas.%, the $Ñ_{60}$ fullerene loss is not in excess of 5 rel. mas.%,

The separator for the production of pure C_{70} fullerenes, individual heavy fullerens or/and their mixture. The separator operation volume is 12l, the producibility is (7-9) g of the $Ñ_{70}$ fullerene/cycle, (1.0–1.2) g of the heavy fullerene mix/cycle, (200–250) mg of the $Ñ_{84}$ fullerene/cycle, (5–10) mg of the $Ñ_{90}$ fullerene/cycle, the cycle time is no longer than 5days, the $Ñ_{70}$ purity is 99 rel.mas.%, the purity of the heavy fullerene mixture is (98–99) rel.mas.%, the $Ñ_{84}$ purity is 99 rel.mas.%, the $Ñ_{90}$ purity is 99 rel.mas.%, the loss of the $Ñ_{70}$ fullerene and of the individual heavy fullerenes are not in excess of 10 rel. mas.% and 10 rel. mas.% subsequently.

Auxiliary facility: vacuum rotational evaporator, vacuum dry box, vacuum contra-flow extractor (of the Soxlet type) for the individual fullerene (and their mixtures) solvent concentration increase, for drying and removing the remainders of the solvents.

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Stability of linear $(C_{20})_k$ complexes of the smallest fullerenes C_{20}

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Thermal stability of covalently bound $(C_{20})_k$ chains consisting of C_{20} fullerenes is examined numerically through molecular dynamics simulations at various temperatures making use of transferable tight-binding interatomic potential. It is shown that the finite lifetimes of these metastable systems are determined by three different processes: the decay of one of the C_{20} fullerenes (as in the case of an isolated C_{20} fullerene [1]), the fusion of two C_{20} fullerenes into the C_{40} cluster (as in the case of a $(C_{20})_2$ dimer [2, 3]), and the separation of one of the C_{20} fullerenes from the chain. The activation energies of the former two processes are somewhat lower than those for C_{20} and $(C_{20})_2$ systems but nevertheless rather high to ensure the macroscopically long lifetimes of $(C_{20})_k$ chains at room temperature.

The work was supported in part by the Russian Foundation for Basic Research (project no. 06-02-16406).

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Synthesis of fullerenols in preparative scale

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Water-soluble fullerene derivatives are of grate interest as biological active compounds for using in biomedicine. Fullerenols (polyhydroxylated fullerene) are one of the most hydrophilic derivatives of fullerene C_{60} as biological active compounds itself and as precursors of biological active compounds for biomedical applications can be synthesized by different methods [1-3].

In this work, fullerenols were synthesized by the modified procedure [2] in alkali medium with TBAH as catalyst and 1,2,4 – trimethylbenzene as a solvent. The difficulty of fullerenols preparation in large scale is connected with small solubility of fullerene in solvents so 1,2,4 – trimethylbenzene was used as a solvent. The solubility of fullerene C_{60} in 1,2,4 – trimethylbenzene about 14 times larger than in benzene which makes it possible to increase the scale preparation of product. The using of chlorobenzene derivatives or naphtalene derivatives as a solvents in which solubility of C_{60} in about 20–40 times larger than in benzene are not suitable owing to their toxic properties.

On HPLC data fullerenols owing to very high hydrophilic properties can be used for the determination of void volume of columns in reversed phase liquid chromatography.

For characterization of prepared fullerenols different methods such as IR, TG, ^{13}C NMR and ^{1}H NMR, DSC were applied. Results of investigation of fullerenols by these methods are discussed.

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Effect of the composition of initial fullerites on the structure and properties of nanocrystalline carbon phase formed in metallic matrix under pressure

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The methods of X-ray diffraction, high-resolution electron microscopy, and microdurometry were used to study the products of the transformation of different fullerites in the mixture with iron powder under a pressure of 3-5 GPa under quasihydrostatic conditions at a temperature of 1200°C. The initial fullerites were taken as pure crystals C_{60} and C_{70}, their artificial dispersed mixtures containing from 3 to 80 wt.% C_{70}, and a soot extract. Loading of pure C_{60} under the above conditions results in the retention of fullerene C_{60} molecules. The initial fullerite mixture containing more than 15% C_{70} is transformed into X-ray amorphous phase with an "elastic" hardness (resistance to purely elastic deformation in the absence of residual plastic deformation) more than 10 GPa. A superhard phase (with the "elastic" hardness exceeding 14 GPa) is formed from pure C_{70}, while from a mixture of C_{60} and C_{70} it is formed only in the case of soot extract containing >20% C_{70}. The HREM images of the X-ray amorphous superhard carbon phase exhibit nanoscale regions of parallel bent layers. The interlayer spacings in such phases were determined according to the positions of the gravity centers of the diffused Bragg peaks in the X-ray diffraction patterns to be 3.4-3.6 A. An increase in the C_{70} content in the initial mixture increases both the amount of graphite in the synthesized phase and the fraction of carbon atoms diffusing into the iron matrix with the formation of martensite and carbides.

The work was supported by the Russian Foundation of Basic Research, projects nos. 05-03-32763 and NSh-1190.2006.3

Method of sublimation and self-assembly for fullerenes separation

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Conventional methods for fullerenes isolation and separation are based on their solubility in the organic solvents. It has been shown [1-3] that it is impossible to isolate the C_{74} fullerene by extraction and C_{80} could be isolated by this way only partially. Obtained results are explained either by insolubility of carbon clusters or by unstable structure that leads to rapid polymerization under even slight exposure on the soot. Therefore gradient sublimation of the insoluble and unstable carbon clusters in the inert atmosphere or vacuum based on the dependency of sublimation temperature on molecule size has been proposed as the method for isolation and separation of fullerenes.

In the present work possibility of fullerene separation by sublimation from carbon soot and by self-assembly during crystallization from solutions onto different substrates has been investigated. Ability of carbon clusters to self-assembly was used for simultaneous separation and surface modification in order to reduce duration and rate of exposure.

To separate fullerenes by sublimation apparatus for maintenance of temperature gradient was developed. Infrared spectroscopy, UV-Vis-spectroscopy and MALDI-TOF-mass-spectrometry was used for comparative analysis of proportion of fullerenes mixture isolated either by sublimation or self-assembly. Effect of substrate nature on the composition and morphology of fullerene crystals obtained by sublimation and self-assembly was established.

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Synthesis and properties of sodium fullerides

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Owing to small atomic radius of sodium, the properties of sodium fullerides are rather different as compared to those of heavy alkali metal (K, Rb, Cs) fullerides. This is evident from the following: Na_3C_{60} is not a superconductor; disodium fulleride Na_2C_{60} were found to be existed, planar polymeric layers were formed in Na_4C_{60}; and sodium clusters were observed in Na_xC_{60}, x ? 6.

The aim of this work was the study of possibility of synthesis of sodium nanoclusters intercalated in fullerite C_{60}.

To synthesize sodium fullerides, we used three methods: electrochemical intercalation of sodium ions into fullerite under potential difference in a solid electrochemical cell; high pressure-high temperature treatment of solid sodium and fullerite mixture in a steel ampoule, and interaction of sodium hydride and solid C_{60} under high temperature.

Sodium fullerides Na_xC_{60} (x?1) synthesized using the electrochemical technique show mixed electronic and ionic cunductivity, with almost equal contribution of electronic and ionic conductivity constituents. The reverse linear function of the cell unit and filleride composition was brought to display. XRD- and differential scannig calorymetry data indicate polymerization (dimerization) of fullerite upon the synthesis.

Sodium fullerides Na_xC_{60}, where x = 1, 4, 6, were synthesized under high pressure–high temperature treatment. Fullerides Na_2C_{60} and Na_4C_{60} were synthesized using electrochemical and hydryde techniques. The samples obtained were invesigated using X-ray, calorymetric and ^{23}Na and ^{13}C NMR methods. Polymerization of sodium fulleride with different stoichiometry results in various polymer formation. According to the ^{23}Na NMR studies, the state of sodium in fullerides Na_xC_{60} depends not only on their composition, but also on preparation technique. For every studied composition, the states with full charge tranfer from sodium atom to carbon cage were observed in the Na - C_{60} system. In the ^{23}Na NMR spectrum of electrochemically synthesized Na_4C_{60} sample, the line at 535 ppm was observed. This line is not typical for either ionized or metallic state (1130 ppm) and can be explained by the formation of sodium clusters in voids of the C_{60} crystalline structure.

Intercalation of C_{60} with N_2 molecules. X-ray data.

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Solid C_{60}-N_2 solutions have been investigated in a wide temperature range (6 - 293 K) using X-ray methods. It is found that on interstitial molecular impurity has a considerable effect upon the structural properties, the orientational phase transition and the orientational glass in C_{60}. In contrast to atomic impurities, the N_2 molecules intercalated into C_{60} cause some deformation of the cubic cell and a 0.2% increase in the lattice parameter at room temperature. This excess over the value for pure C_{60} persists down to T = 6 K. On heating, the lattice parameter of the solid solution approaches the a-value of pure C_{60} in the region of T_c. On cooling, T_C of the C_{60}-N_2 solution is lower then that of pure C_{60}. T_c and the temperature-induced change in the lattice parameter have a hysteresis, which is observed both on heating and cooling. The distinctions in the behavior of solid C_{60}-N_2 solutions and solutions with atomic impurities are largely determined by the noncentral component in the molecular interaction and by possible ordering of the molecular impurity in the octahedral sites at low temperatures.

Spectroscopic evidence for the reaction of C_{60} with side-chain groups in Alkylbenzenes

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Basically, the chemical derivatization has been among important subjects in C_{60} chemistry (1). Concerning polyaromatic derivatization, Olah et al (2) prepared polyarenefullerenes by reaction of both pure C_{60} and C_{60}/C_{70} mixture with aluminum trichloride in benzene and/or toluene and the products where characterized by ^{1}H and ^{13}C NMR spectroscopy. He also suggested that the reaction take place under relatively strong Friedel-Craft acid catalysis *via* electrophilic fullerenation of the aromatics. In 1992 Taylor et al (3) reported formation of aryl derivative of C_{60} upon electrophilic aromatic substitution catalyzed by iron (III) chloride. Then, the structures of polyarenefullerenes of both C_{60} and C_{70} were characterized extensively by different spectroscopic methods (4). In this work, we report our observations about the possible products from the reaction between alkylated benzene ring with C_{60} in the presence of di-*tert*-butyl peroxide as oxidant. We also interested in the other reactive sites except for the aromatic rings. The 500-MHz ^{1}H NMR spectrum in those reaction products as ethylbenzene and triethylbenzene show characteristic bands which has been reported for C-H fullerene skeletal hydrogens (5). Furthermore, the observation of new absorption bands in the ^{13}C NMR spectrum at sp^3 as well as sp^2 regions confirms the kinds of the reaction products. A closer look at $\delta(^{13}C)$ of the dept absorption bands show that the newly-formed CH_n ($n = 0$ or 2) are prominently formed at sp^3 region. Considering both ethylbenzene and triethylbenzene structures, this would be possible where only the terminal CH_3 groups take part in the reaction with C_{60} backbone and finally change to CH_2 groups.

The work is fully supported by RIPI at National Iranian Oil Company.

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Supramolecular approach to modification of surfaces – formation of coatings based on fullerene derivatives

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The formation of fullerene containing layers is of great interest with respect to transferring fullerene unique properties to various materials by surface tailoring. In the present study a supramolecular approach to coating (“films”) preparation and electrochemical properties of these films are reported.

Electrode (ITO, glassy carbon) surfaces are modified by immobilizing fullerenopyrrolidines in a $(C_8H_{17})_4NBr$ matrix, and by either self-assembling layers based on fullerene adducts or rubbing attachment of an active substance. The coatings were studied by cyclic voltammetry, optic spectroscopy, X-ray diffraction, and atomic force microscopy.

To reveal the effect of addends in the Ñ$_{60}$ molecule on kinetics and thermodynamics of redox transformations of fullerenes immobilized on electrodes, we studied fullerene and various pyridyl substituted fullerenopyrrolidines films using cyclic voltammetry in 0.5 Ì KCl/H_2O and 0.1M $(C_4H_9)_4NBF_4$/AN. We suggest that kinetics of redox transformations of individual fullerenes is defined mainly by changes in structures of pristine films during their cathodic doping. It was also shown that formal potentials corresponding to redox conversions of fullerenes in a solid cationic matrix are defined by the energy of the interaction of fullerene anions formed with matrix cations. The result of this interaction is a shift of potentials of film cathodic doping to less negative values. The introduction of substituents with increased donor ability in fullerenopyrrolidine provides higher energy of the interaction of fullerene anions with matrix cations.

Investigation of physical properties and reactivity of $Li_{12}C_{60}$

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In the last years the interest in $Li_{12}C_{60}$ has increased significantly as a consequence of its perspective and varied properties. The gas-phase synthesis of Li containing fullerene compounds as well as the electrochemical method and the reaction in the liquid ammonia are rather difficult. We proposed a simple method for preparing the $Li_nC_{60}(THF)_x$ (n = 1-12) stoichiometric compounds in toluene solution with preliminary synthesis of lithium naphthalenide [1].

In the present work the thermal stability of $Li_{12}C_{60}$ was investigated by means of TGA (Termal Gravimetric Analysis) under nitrogen atmosphere. $Li_{12}C_{60}$ is stable up to 190°C. A Li> C_{60} electron transfer has been revealed by the IR, Raman and ^{13}C NMR spectroscopy. The tangential vibrational frequencies $F_{1u}(4)$ (1346 cm^{-1}) and $A_g(2)$ (1427 cm^{-1}) are lower than those in neutral C_{60} (1429 and 1468 cm^{-1}, respectively). The ^{13}C chemical shift changes from 142.8 ppm (pristine C_{60}) to 185 ppm. Reactivity of $Li_{12}C_{60}$ was studied by interaction with Me_3SiCl, t-BuBr, $PhCH_2Br$, MeI. Prepared compounds $(Me_3Si)_{12}C_{60}$, t-$Bu_{12}C_{60}$, $(PhCH_2)_{12}C_{60}$ and $Me_{12}C_{60}$ were characterized by the TGA and HPLC methods, the IR and NMR spectroscopy as well as by the negative ion DCI mass-spectrometry for $(Me_3Si)_{12}C_{60}$.

$Li_{12}C_{60}$ can be a base for preparation of lithium batteries. It was shown that the $Li_{12}C_{60}$ unit can store up to 120 hydrogen atoms in the molecular form [2]. The organic and organoelement fullerene compounds with certain properties prepared on the basis of $Li_{12}C_{60}$ can be perspective precursors for new materials.

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Theoretical study of the poly(trifluoromethyl)fullerenes

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Polytrifluoromethylated fullerenes are among the most widely studied polyfunctionalyzed fullerene derivatives. Recently, a number of isomers of $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_n$ compounds with $n = 2$-18 compounds were have been isolated and structurally characterized (see [1,2] and references therein). A large amount of structural information thus obtained for a broad range of degree of functionalization makes possible to rationalize various regiochemical trends of the trifluoromethylation process.

The isomeric composition of the reaction products obtained at elevated temperature is usually likely to be controlled by the thermodynamic factors. Therefore, one can anticipate that the experimentally observed isomers should be among the most energetically favorable ones. Unfortunately, a complete survey of all possible structures is impossible due to an exponential growth of their number. The unavoidable empirical restrictions that can be imposed on a set of isomers to be considered (such as based on symmetry or addition patterns) may sometimes result in a loss of some important structures.

Here we suggest the following scheme purported to standardize the approach to theoretical prediction of the thermodynamically preferable isomers and to formulate efficient general restrictions. It is assumed that formation of $C_{60/70}(CF_3)_n$ compounds proceeds via n sequential stages of addition of CF_3 groups. The number of theoretically possible products of the very first stages is small enough to take them all into account. On the following stages only the most stable isomers within the given energy gap are selected as precursors for further addition and all possible products of attachment of one more CF_3 group to any of them are subjected to the subsequent act of selection.

The above approach results in considerable simplification of the computational procedure due to dramatic shortening of the lists of relevant structures. Our energy-based criterion appears to combine sufficient reliability and high restrictive power thus requiring no additional empirical restrictions to be used. The results and applicability limitations of this approach to the analysis of poly(trifluoromethyl)fullerenes at the AM1 and DFT levels of theory are discussed.

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Theoretical study of isomerization of fullerene derivatives via transfer and substitution of addends

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High-temperature syntheses of some classes of fullerene derivatives like fluorides and hydrides are known to yield the most thermodynamically stable isomers. These observations suggest some sort of thermodynamic control in isomer formation. Indeed, it has been shown directly that formation of some fullerene compounds requires rearrangement of addends (see, e.g., [1]). However, possible mechanisms of such processes still need to be investigated.

Here we report our computational results on energetics of some reactions that might be expected to serve as elementary stages of complex rearrangement processes. These reactions include transfer of an addend between the two sites belonging to same or different fullerene cages and isomerizational substitution, i.e. replacement of a given addend with a remotely attaching one accompanied by redistribution of the π-electron density. The systems containing fluorine, hydrogen, and CF_3 addends have been treated at the DFT level of theory and the activation barriers of typical processes have been calculated. We present a summary of the data obtained and discuss the probable rearrangement pathways.

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