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Synthesis of Fullerenol-70-d by Direct Oxidation and Its Identification

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Abstract—A procedure was developed for the synthesis of a water-soluble derivative of lower fullerene C_{70}, fullerenol-70-d, by direct homogeneous catalytic oxidation of C_{70} with alkali. Fullerenol-70-d was identified by electronic absorption and infrared spectroscopy and mass spectrometry.

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Lower fullerenes (C_{60} and C_{70}) are widely used in various fields of science and engineering. However, their application is severely restricted due to near-complete incompatibility with water and aqueous solutions. For example, the true solubility of C_{60} in water at 25°C is 1.3×10^{-11} g/l [1–5], and of C_{70}, 1.1×10^{-13} g/l [5–7]. The same applies to most derivatives of lower fullerenes, such halogen, oxo, amino, carboxy, etc.; as a rule, they are very poorly soluble in aqueous medium [5, 8]. The present study was aimed as developing methods for the synthesis and identification of a water-soluble C_{70} derivative which was called fullerenol-70-d. Hereinafter, by fullerenol-70-d we mean a mixture of polyhydroxylated fullerenes $C_{70}(OH)_n$ obtained by direct homogeneous catalytic alkaline oxidation of C_{70} (the index "d" in fullerenol-70-d stands for "direct oxidation"). As reported previously for fullerenols obtained from C_{60} [9], fullerenol-70-d may contain oxo hydroxy structures like $C_{70}(OH)_{n1}O_{n2}$ in addition to polyhydroxy fullerenes. Unlike fullerenols derived from C_{60}, the number of known procedures for the synthesis of analogous C_{70} derivatives is considerably smaller.

Chen et al. [10, 11] described a synthesis of polyhydroxylated C_{70} derivatives $C_{70}(OH)_n$ (n = 14, 16, 18, 20) by hydrolysis of polycyclosulfated intermediate compoounds $C_{70}(SO_4)_x$. It was also presumed [10] that the resulting compounds are soluble in water and that they can be used to obtain star-shaped polymers. However, no data on the stability and exact geometric structure of the obtained fullerenols were given in [10], and no probable hydroxylation mechanism was proposed. Wang et. al. [12] revealed possible geometric isomers, estimated the stability, and calculated thermodynamic parameters of fullerenols $C_{70}(OH)_n$ (n = 14, 16, 18, 20) [10] by semiempirical PM3 quantum-chemical calculations; the authors also advanced a plausible mechanism for the formation of fullerenols. According to [12], the most stable are those hydroxy derivatives where the hydroxy groups reside in the "equatorial belt region" of the C_{70} molecule. This is related to the fact that that the C–C bonds in the equatorial belt region are longer than in other regions of C_{70} polyhedron. As a result, mutual repulsion between the OH groups is weaker, and the molecule becomes more stable. Thus the relative stability of fullerenols increases with rise in the number of hydroxy groups in the equatorial belt region of C_{70} and decrease in the number of hydroxy groups above and below the equatorial belt. Xia et al. [13] synthesized nanocomposites by incorporating fullerenols $C_{60}(OH)_n$ and $C_{70}(OH)_n$ in SiO_2, SiO_2–TiO_2, GPTMS–SiO_2, and GPTMS–ATPS gels using the sol–gel process. The obtained nanocomposites containing water-soluble fullerenol were found to be thermally stable, and the optical liming effect of the fullerenols was studied [13].

Fullerenol $C_{70}(OH)_n$ was synthesized in [13] according to the following procedure. A solution of pure fullerene C_{70} in toluene was heated to the boiling point. After addition of metallic sodium, the solution turned brown, and a solid separated. The mixture was heated for 4 h under reflux and cooled, unreacted sodium was removed, and the solvent was distilled off at 60°C. The residue was subjected to hydrolysis and dissolved in distilled water to obtain a brown solution of fullerenol $C_{70}(OH)_{n1}O_{n2}$ which was characterized by electronic absorption and IR spectroscopy, and its thermal stability was studied by thermogravimetry.

Fullerene diols 1,2-$C_{70}(OH)_2$ and 5,6-$C_{70}(OH)_2$ were synthesized [14] and characterized by IR, NMR, and electronic absorption spectra, as well as by HPLC. Fullerene C_{70} was dissolved in 1,2,4-trichlorobenzene, a freshly prepared solution of RuO_4 in carbon tetrachloride was added, the resulting suspension was stirred for 3 h, the precipitate was filtered off, washed with several portions of toluene to remove unreacted C_{70}, and dispersed in aqueous dioxane, and hydrochloric acid was added. The suspension was subjected to ultrasonic treatment, toluene was added, the aqueous phase was separated, the organic phase was dried over anhydrous sodium sulfate, the drying agent was filtered off, and the filtrate was evaporated to dryness. The residue, a brown powder, was dissolved in toluene–dioxane and purified by liquid chromatography (silica gel, toluene–dioxane as eluent).

In the present work we tried to synthesize fullerenol-70 by direct homogeneous catalytic oxidation. This procedure was successfully used previously to obtain the closest analog of fullerenol-70, fullerenol-60 (or fullerenol-d) [9, 15, 16] and turned out to be the simplest and most accessible among known methods. As far as we know, it was not used to prepare fullerenols-70. The starting material was fullerene C_{70} with a purity of 99.9%, which was obtained according to Krätchmer at the “Innovations of Leningrad Institutes and Enterprises” Closed Corporation (St. Peterburg, Russia); benzene, methanol (analytical grade; Vekton, St. Petersburg), and 40% aqueous tetrabutylammonium hydroxide (analytical grade; Sigma–Aldrich) were also used.

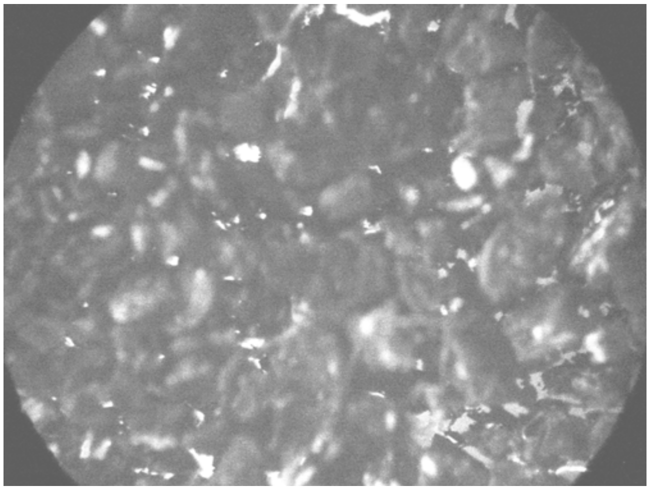

Fig. 1. Polarizing microscope image of crystals of fullerenol-70-d (magnification ×21).

The following procedure for the synthesis of fullerenol $C_{70}(OH)_x$ has been developed. A saturated solution of C_{70} (1 g) in benzene (500 ml) was prepared by isothermal saturation at 20°C for 8–10 h. The equilibrium solubility was assessed by spectrophotometry on a Specord M-32 instrument (Carl Zeiss) according to [17–19] and was ~1.30±0.05 g/l, which is very consistent with published data [19, 20]. The solution was filtered to separate undissolved C_{70}, 20 ml of 50% aqueous sodium hydroxide was added to the filtrate, and a 40% aqueous solution of tetrabutylammonium hydroxide (phase-transfer catalyst) was added under stirring until the mixture turned colorless. Benzene was distilled off from the mixture under reduced pressure (0.1 mm) for several hours, 100 ml of water was added to the residue consisting of a solid material and alkali solution, and the mixture was stirred for 10 h. An additional portion of water, 200 ml, was then added to complete the reaction, and the resulting red–brown solution was separated from the undissolved material by filtration through a “green band“ filter paper. The filtrate was concentrated to a volume of 50 ml on a rotary evaporator (0.1 mm), and 150 ml of methanol was added to precipitate fullerenol-70-d. The reprecipitation procedure was repeated three times, and the product was dried in a vacuum drying box for 4 h at 40°C (0.1 mm) to remove traces of methanol and benzene. The yield of oxo hydroxy fullerenol-70 was 225 mg (from 1000 mg of C_{70}). It was impossible to estimate the percent yield since the product was a multicomponent mixture of polysubstituted products which may be represented by the general formula $C_{70}(OH)_{n1}O_{n2}$ ($n1 \neq n2$). In any case, the yield was much lower than the yield of fullerenol obtained from C_{60} [9, 16] according to analogous

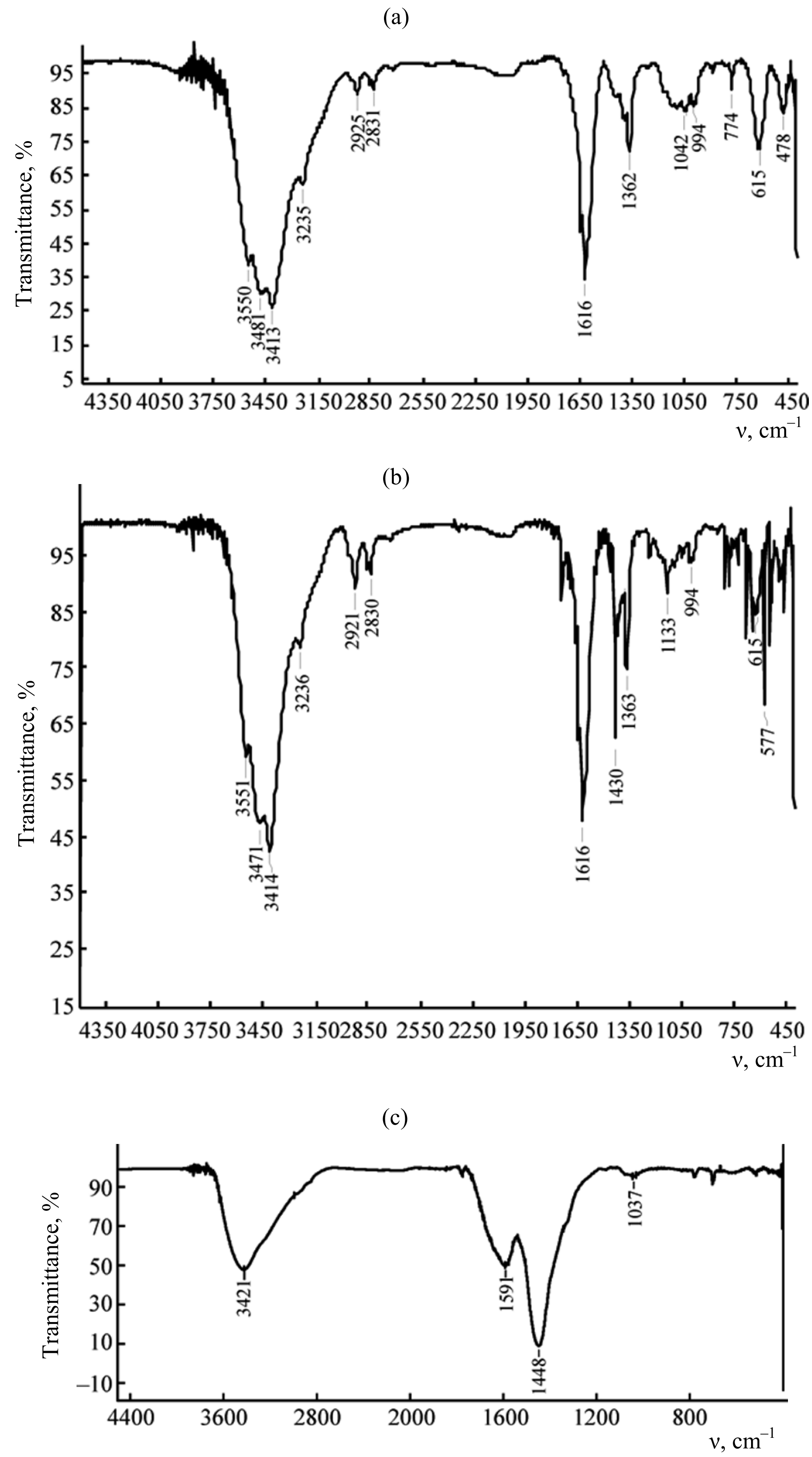

Fig. 2. IR spectra of (a) fullerenol-70-d, (b) fullerene C_{70}, and (c) fullerenol-d.

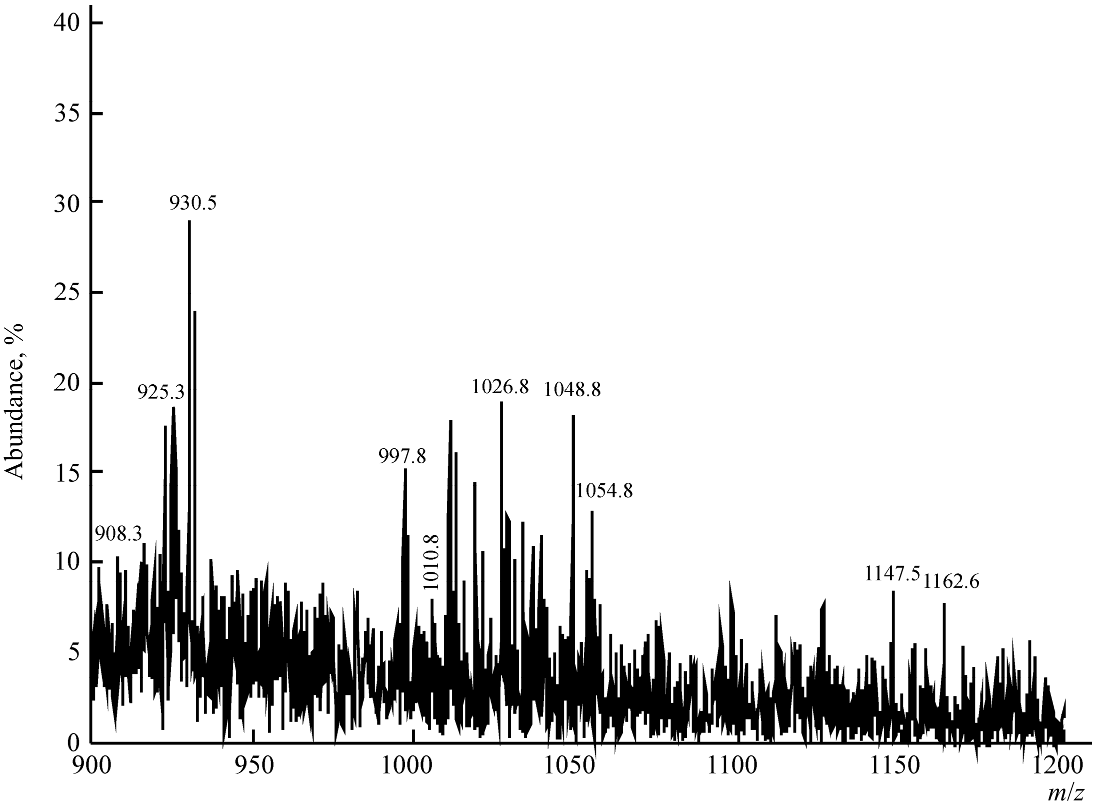

Fig. 3. A fragment of the mass spectrum of fullerenol-70-d; for comments, see text.

procedure (1000 mg from 1000 mg of C_{60}). Figure 1 shows a photograph of crystals of fullerenol-70-d (MIN-5 polarizing microscope, magnification ×21). No appreciable absorption was observed in the visible and near-UV regions (λ 300–900 nm) of the electronic absorption spectrum of fullerenol-70-d in water. In particular, there were no absorption bands at ~472 nm (C_{70}), ~335 nm (C_{60}, C_{70}), and 320–330 nm ($C_{60}Br_n$, n = 6, 8, 24) typical of lower fullerenes and many their derivatives in aromatic or nonaromatic solvents [21, 22]. These findings confirm the absence of unreacted C_{70} in the product. For identification purposes, the IR spectra of solid samples of fullerenol-70-d (in KBr; dried under argon) were recorded on a Shimadzu FTIR-8400S spectrometer in the frequency range from 400–4400 cm^{-1} (Fig. 2a). For comparison, the IR spectra of C_{70} (Fig. 2b) and solid fullerenol-d (Fig. 2c) are also given (published data). It is seen that some characteristic absorption bands of fullerenol-70-d and C_{70} coincide with each other, in particular those at 2830±1, 1616, 1362±1 cm^{-1}, weak low-frequency peaks at 994±1 and 615±1 cm^{-1}, and high-frequency triplet at 3414±5/3475±5/3550±5 cm^{-1}. Interestingly, essential differences were observed in the IR spectra of apparently related fullerenol-70-d and fullerenol-d. The latter lacked almost all peaks typical of fullerenol-70-d and fullerene C_{70} simultaneously, but new absorption bands appeared at 1448, 1591, and 1037 cm^{-1}. The high-frequency peak somewhat shifted relative to the above triplet (3421 cm^{-1}). On the whole, we can assert that the IR spectrum of fullerenol-70-d is quite informative and that it can be used to identify this compound. By analogy with fullerenol-d synthesized from C_{60} [9, 16] according to a similar procedure, it was reasonable to presume that the oxidation of C_{70} yield a complex mixture of products. For example, the oxidation of C_{60} leads to a mixture of polyhydroxy compounds $C_{60}(OH)_n$ and oxo hydroxy derivatives $C_{60}(OH)_{n1}O_{n2}$ or their sodium salts $C_{60}(OH)_{n1}O_{n2}(ONa)_{n3}$. In order to elucidate the composition of fullerenol-70-d we recorded its mass spectrum.

A typical mass spectrum of fullerenol-70-d (Agilent 1100 Series LC/MSD Trap; electrospray ionization; direct sample admission as a solution in DMSO without ionizing additives; capillary voltage 3500 V) is shown in Fig. 3. We can readily distinguish ion peaks corresponding to polyols $C_{70}(OH)_n$ where n varies over a wide range: $n = 4$ (*m*/*z* 908), $n = 5$ (*m*/*z* 925), …, $n =$ 10 (*m*/*z* 1010), …, $n = 19$ (*m*/*z* 1163). Also, ion peaks arising from sodium salts $C_{70}(OH)_{n1}(ONa)_{n2}$ are present: $n1 = 7$, $n2 = 1$ (m/z 998); $n1 = 8$, $n2 = 2$ (m/z 1054); etc. Figure 3 intentionally displays only the most informative fragment of the mass spectrum (m/z 900–1200); ion peaks with larger m/z values have low intensity, whereas lower m/z values correspond to fragment ions. The peak intensities in Fig. 3 are given relative to the intensity of the base peak with m/z 847 which is not shown; naturally, that peak cannot be assigned to any nondegraded ionized component of fullerenol-70-d. Nevertheless, the obtained hydroxylation product mixture may be described quite certainly on a qualitative level: (1) the product contains polyols $C_{70}(OH)_n$ and their sodium derivatives $C_{70}(OH)_{n1}(ONa)_{n2}$; (2) unlike hydroxylated fullerene C_{60} [9, 16, 23], the product contains neither polyoxo polyhydroxy compounds $C_{70}(OH)_{n1}O_{n2}$ nor their sodium salts $C_{70}(OH)_{n1}O_{n2}(ONa)_{n3}$; (3) the degree of hydroxylation of C_{70} is appreciably lower than the degree of hydroxylation of C_{60} (cf. $\Sigma n_i \approx 4$–19 for C_{70} and $\Sigma n_i \approx 12$–34 for C_{60} [9, 16, 23]); (4) unlike fullerenol-d, there are no multiply charged ions in the negative ion mass spectra of fullerenol-70-d, and no destructive ionization is observed.

In all calculations, the molecular weight of fullerenol-70-d was assumed to be equal to 1044 which corresponds to the formula $C_{70}(OH)_{12}$ {cf. M 1128 of fullerenol-d, $C_{60}(OH)_{24}$ [9, 16, 23]}.

To conclude, we have developed a procedure for the synthesis of fullerenol-70-d and identified it by IR spectroscopy and mass spectrometry.

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