Products of reaction of fullerene C_{60} with fuming sulfuric acid studied by IR and ESR spectroscopy

O. G. Garkusha,★ S. P. Solodovnikov, and B. V. Lokshin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: garkusha@ineos.ac.ru

The products of reaction of fullerene C_{60} with fuming sulfuric acid were precipitated from a solution with water and triethylamine and studied by IR and ESR spectroscopies. A comparison of the obtained data with the spectra of fullerene, dimers C_{120} and $C_{120}O$, and fullerene polymers produced by photopolymerization allowed the conclusion that fullerene polymers were formed by fullerene oxidation with fuming sulfuric acid.

Key words: fullerene C_{60}, fuming sulfuric acid, fullerene polymers, fullerene dimers, IR spectroscopy, ESR spectroscopy.

One of the most interesting areas of fullerene chemistry is the synthesis and study of the structure of fullerene C_{60} dimers and its oligomers and polymers. According to calculations,[1] the C_{120} dimer corresponding to [2+2]-cycloaddition is one of the most stable compounds of this type. Experimental studies showed that the C_{120} dimer, oligomers, and polymers are formed by the photopolymerization of C_{60} [2,3] at a high pressure[4] and by doping of C_{60} with alkaline metals.[5] The synthesis of the C_{120} fullerene dimer has been described in several works.[6—8] Another compound, $C_{120}O$, contains two C_{60} fragments bound *via* the furanoid cycle.[9,10]

The oxidation of fullerene C_{60} has been studied.[11—14] The temperature-dependent ESR spectrum of the product of reaction of crystalline C_{60} with fuming sulfuric acid suggested the presence in the reaction product of the dimer radical cations $C_{120}{}^{\bullet+}$ or oligomers $(C_{60})_n{}^{\bullet+}$ that formed by [2+2]-cycloaddition.[14] The lately found coincidence of the ESR spectra of the products of oxidation of C_{60} and C_{120} by fuming sulfuric acid confirmed cyclodimerization between $C_{60}{}^{\bullet+}$ and C_{60}.[15] The IR spectrum of the product of reaction of C_{60} with fuming sulfuric acid isolated after precipitation with water, has been published[11] without discussion.

In this work, the products of reaction of C_{60} with fuming sulfuric acid were studied by IR and ESR spectroscopies.

Experimental

Fullerene C_{60} (25 mg) was dissolved in fuming sulfuric acid (1 mL) at 50 °C. The crystals were completely dissolved within 30 min. The emerald solution that formed was added to water (120 mL). In experiments using neutralization with triethylamine, C_{60} (10 mg) was dissolved in fuming sulfuric acid (0.5 mL) and the solution was poured to excess triethylamine. After the acid was neutralized with triethylamine, water was added to the reaction mixture. In both cases, the product was formed as a brown precipitate, and the mother liquor gained an orange-yellow color. The brown precipitate was separated on a TsLN-2 centrifuge at 8000 min^{-1}. The obtained brown powder was five times washed with water using a Cole-Parmer Ultrasonic Cleaner 8891 ultrasonic bath with intermediate centrifugation and pH monitoring until the neutral value was achieved. After each washing, the isolated product was dried in air and then *in vacuo* at 10^{-3} Torr and 60 °C. In the case of precipitation with water, a brown powder (10 mg) containing fibrillar structures was obtained.

IR spectra of solid samples as pellets with CsI were recorded on a Nicolet, Magna-IR 750 FTIR spectrometer in a region of 4000—120 cm^{-1}. ESR spectra were recorded on a Varian E-12 ESR instrument.

Compounds C_{120} and $C_{120}O$ were synthesized by described procedures.[8,10]

Results and Discussion

Comparison of the IR spectra of the reaction products precipitated with water and triethylamine demonstrates the reproducibility of the results obtained using our procedure.

Based on the elemental analysis data, the formula $C_{60}(H_xSO_y)_4 \cdot zH_2O$ ($2 \ge x \ge 0.4$, $4 \ge y \ge 2$) has previously[11] been ascribed to the product of oxidation of C_{60} with fuming H_2SO_4. Hence, the fullerene structure was assumed to retain upon its sulfonation.

Distinctions in results of our work and earlier data[11] are caused, in our opinion, by the use of different procedures for the isolation of the final product. In our experi-

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ments, the reaction product was repeatedly washed with distilled water, whereas water was applied in earlier works[11] for precipitation only. According to X-ray fluorescence analysis, the substance obtained by us contains less than a percent of sulfur, while in the previously presented[11] reaction product the sulfur percentage was about 10%.

The IR spectrum of the product of reaction of fullerene C_{60} with fuming sulfuric acid before washing with water contains several bands (ν/cm^{-1}: 2925 s, 2545 m, 2470 sh, 1311 w, 1248 s, 1175 m, 1063 m, 1031 s, 863 m, 850 w, 599 m, 588 w, 576 m, 454 v.w, 431 w, 414 w, 279 v.v.w, and 190 m), which disappear after washing and isolation of the final product. Some of these bands are attributed to residual sulfuric acid (2925, 1175, 850, 599, 576, 454, 431, and 414 cm^{-1}), being detected by us in the reference spectra of the pellets with KBr treated with fuming sulfuric acid.

The IR spectrum of the reaction product isolated after repeated washing and drying is presented in Fig. 1 along with the spectra of fullerene C_{60} and dimers C_{120} and $C_{120}O$ recorded under identical conditions. The C_{60} molecule has the I_h symmetry, according to which the IR spectrum contains only four absorption bands attributed to vibrations of the F_{1u} symmetry: at 526, 576, 1182, and 1429 cm^{-1}. Detailed analysis of the spectra of the dimer molecules was not published. When C_{120} is formed, the symmetry of the molecule decreases to D_{2h}. Formally the decrease in symmetry should result in an increase in the number of bands in the IR spectrum to 134 ($44\ B_{1u} + 44\ B_{2u} + 46\ B_{3u}$). The symmetry of the $C_{120}O$ molecule is even lower (C_{2v}), and the expected number of bands is 270 ($92\ A_1 + 91\ B_1 + 87\ B_2$). In fact, the IR spectra of the dimers contain much more bands than the C_{60} spectrum; however, their number is much smaller than that predicted by the theory. This is explained by the closeness of frequencies of many vibrations resulting in their degeneration and by the low intensity of many bands.

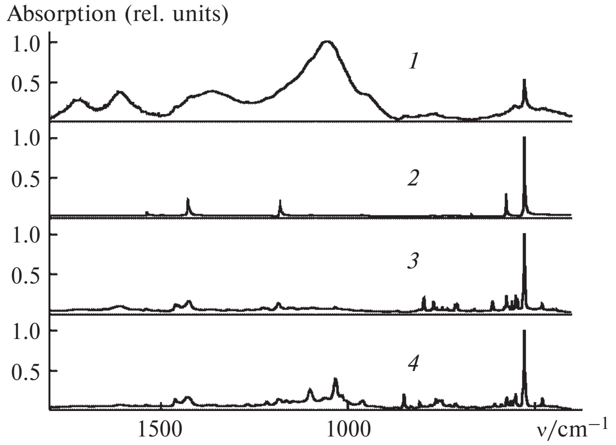

Fig. 1. IR spectra of the product of reaction of C_{60} with fuming sulfuric acid (*1*), fullerene C_{60} (*2*), C_{120} dimer (*3*), and $C_{120}O$ dimer (*4*).

Only the general pattern of the IR spectrum without analysis of frequencies and intensities has been published[7,16] for C_{120}. It was mentioned in the works[17,18] on quantum-chemical calculations of the vibrational spectra of C_{120} that the calculation results agree qualitatively with the experimental IR spectrum consisting of four groups of bands at ~500, 700—800, 1100—1200, and 1400—1500 cm^{-1}. The first two groups of the bands were attributed to radial movements of the C atoms, and the third and fourth groups were assigned to tangential vibrations. The works[9,10] on the synthesis of the $C_{120}O$ dimer contain no IR spectral data.

The IR spectrum of the C_{120} dimer recorded by us (see Fig. 1, curve *3*) agrees well with that of the C_{120} dimer prepared by the mechanochemical reaction of C_{60} with KCN.[7] In addition to the bands characteristic of C_{60}, the spectrum of C_{120} contains new low-intensity bands. IR spectrum of C_{120}, ν/cm^{-1}: 479 w, 526 w, 545 w, 550 w, 561 w, 570 v.w, 574 w, 581 v.w, 612 w, 661 v.w, 707 w, 711 w, 732 v.w, 738 v.w, 746 w, 762 v.w, 771 w, 797 w, 864 v.w, 1032 v.w, 1089 v.w, 1145 v.w, 1156 v.w, 1188 w, 1218 v.w, 1426 w, 1453 v.w, 1463 v.w, 1540 v.w, and 1617 v.w.

IR spectrum of $C_{120}O$ (see Fig. 1, curve *4*), ν/cm^{-1}: 478 w, 526 s, 551 w, 554 v.w, 564 w, 574 w, 576 v.w, 588 v.w, 606 w, 627 v.w, 659 v.w, 692 v.w, 711 w, 725 v.w, 747 v.w, 755 w, 765 w, 780 v.w, 796 v.w, 807 w, 831 v.w, 849 w, 960 w, 1016 v.w, 1033 m, 1063 v.w, 1101 m, 1147 v.w, 1166 v.w, 1181 w, 1188 w, 1218 w, 1245 v.w, 1269 v.w, 1306 v.w, 1324 v.w, 1339 v.w, 1359 v.w, 1374 v.w, 1429 w, 1463 w, 1542 v.w, and 1606 v.w. The most important distinction between the IR spectra of $C_{120}O$ and C_{120} is the occurrence in the first of them of medium-intensity bands at 1063 and 1101 cm^{-1}, which belong to vibrations of the C—O—C bridge between two fullerene rings.

The spectrum of the oxidation product of C_{60} with fuming sulfuric acid (see Fig. 1m curve *1*) sharply differs in shape from spectra *2—4* and contains several very broad and intense bands. In general pattern (double band at 1600—1700 cm^{-1}, broad structurized band at ~1400 cm^{-1}, intense broad band with a maximum at 1050 cm^{-1} and a shoulder at ~950 cm^{-1}) this spectrum resembles the spectra[3] of the photopolymerization products of C_{60}. Rather great number of very weak, narrow absorption bands and a strong "fullerene" band at 526 cm^{-1} are discernible against the background of these broad bands. Similarity of the spectra under discussion suggests that the polymerization products are also formed by the oxidation of C_{60} with fuming sulfuric acid. A series of very weak bands against the background of the intense broad bands of the polymers is observed in the approximately same spectral regions as those for C_{120} and $C_{120}O$ (ν/cm^{-1}: 478, 537, 553, 563, 576, 591, 600, 637, 660, 674, 700, 707, 713, 723, 731, 747, 765, 776, 781, 806, 823, 833, 839, 848, 1218, 1270). Thus, the data of IR spectroscopy indicate that the oxidation of C_{60} with fuming sulfuric acid possibly affords the polymeric and oligomeric products.

The presence of the strong band at 526 cm^{-1} in the IR spectra, which is also present in the spectra of C_{60}, C_{120}, and $C_{120}O$ can mean that some amounts of oligomers and dimers are present in the oxidation products along with polyfullerenes. For their identification the ESR spectra were studied. To generate paramagnetic centers, the reaction product was again oxidized with fuming sulfuric acid.

It was previously[15] shown that the ESR spectra of the oxidation products of C_{120} and $C_{120}O$ with fuming sulfuric acid can substantially differ. When C_{120} was oxidized, only the $C_{120}{}^{\cdot+}$ radical cation was detected. In the $C_{120}O$ oxidation product, the ESR spectrum contained the lines of the $C_{120}O^{\cdot\cdot 2+}$ biradical with the characteristic fine structure parameter $|D'| = 2.95$ mT [15] and specific ratio between the amplitudes of signals from $C_{120}O^{\cdot+}$ and $C_{120}O^{\cdot\cdot 2+}$, along with the spectrum of $C_{120}O^{\cdot+}$. The ESR spectrum of the oxidized product, which was precipitated with triethylamine, recorded at room temperature in a solution of fuming sulfuric acid (Fig. 2) consists of two signals (narrow and broad) with the axial anisotropy of the broad signal *g* factor. It can be assumed that the broad signal is attributed to the polyfullerene radical cation and the narrow line is assigned to the radical cations of low-molecular oligomers and $C_{120}{}^{\cdot+}$ and $C_{120}O^{\cdot+}$ dimers.

The ESR spectrum of the reaction product precipitated with water recorded with high amplification (Fig. 3) exhibits the fine structure lines with the parameters $|D'|/2 = 1.47$ mT and $|D'| = 2.95$ mT. The ESR spectra with these parameters were observed[15] for $C_{120}O$ oxidation, and they were attributed to the $C_{120}O^{\cdot\cdot 2+}$ radical dication. The delayed $C_{120}O^{\cdot\cdot 2+}$ rotation was previously[15] found in fuming sulfuric acid. The frequency of $C_{120}O^{\cdot\cdot 2+}$ rotation is $<8.4 \cdot 10^7$ s^{-1} at room temperature. Based on the *g* factor anisotropy (see Fig. 2) for the polyfullerene radical cations, we may conclude that the frequency of their rotation in a solution of fuming sulfuric acid is $<10^7$ s^{-1}. The integral intensity of the narrow signal is several percents of the intensity of the broad signal.

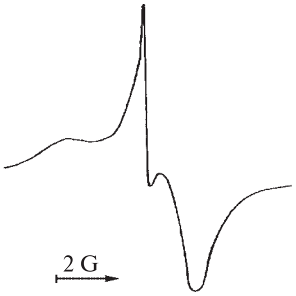

Fig. 2. ESR spectrum of the precipitated with triethylamine product of reaction of C_{60} with fuming sulfuric acid detected in a solution of fuming sulfuric acid at room temperature.

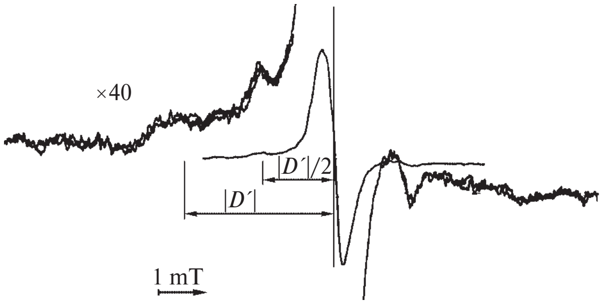

Fig. 3. ESR spectra of the water-precipitated product of reaction of C_{60} with fuming sulfuric acid measured at 77 K in a solution of fuming sulfuric acid.

The intensity ratio of the bands at 1057 and 526 cm^{-1} in the spectra of the reaction products isolated by precipitation with water and triethylamine differ sharply. For the sample precipitated with water this ratio is 2.4, whereas for the sample precipitated with triethylamine it is 11.3. Since the band at 526 cm^{-1} is present in the spectra of C_{60} and its C_{120} and $C_{120}O$ dimers, we can assume that this is related to the "terminal" fullerene units of the polymer. The decrease in the intensity of this band compared to that of the "polymeric" band at 1057 cm^{-1} indicates an increase in the degree of polymerization in the case of polymer precipitation from a solution with triethylamine compared to precipitation with water. In the spectra of the photopolymerization products this ratio equals 0.72 and 0.8, respectively,[3] which can be explained by the presence of free fullerene C_{60}.

Thus, analysis of the published data and those obtained in this work shows that the main product of reaction of C_{60} with fuming sulfuric acid is the polymer and the fraction of the C_{120} and $C_{120}O$ dimers is low. The relatively high (~40%) yield of the reaction product and simplicity of chemical operations allow us to propose this procedure for the synthesis of polyfullerenes.

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