INTRODUCTION

 Fullerites have been shown to undergo considerable destruction when heated to 400–600°C in an oxidative atmosphere. A good absorbent, fullerite readily allows various gases (primarily oxygen) to fill the octapores of its crystal lattice. During the extraction of fullerenes from fullerene-containing soot with organic solvents, fullerenes either form complexes with hydrocarbons [1] or the solvent residues are sealed in intercrystallite space [2]. These impurities introduce defects to the crystal lattice, leading to decomposition of the frameworks of fullerene molecules upon heating.

The oxidation of chromatographically purified C60 fullerite was studied by thermogravimetric analysis in [3]. It had the lowest maximum mass loss temperature (444°C vs. 629, 644, and 565°C for diamond, graphite, and soot, respectively) at a heating rate of 1 K/min. The reason for the higher activity of fullerene with O2 compared to other allotropic forms of carbon was considered [3] to be a conformational strain of the C60 molecule.

As is well known [4], the surface layers of C60 fullerite are polymerized under the action of light. This hinders its interaction with the environment; e.g., lowers the rate of dissolution in organic solvents. Ellipsometric and Rutherford backscattering studies [4] show that a stable surface layer 15 nm thick forms when C60 films were exposed to air for several minutes (C : O = 10 : 1). Heating the films in vacuum at 180°C caused the disappearance of this layer within 2 h.

Comparing the activities of different types of fullerenes, the authors of [5] concluded on the basis of quantum-mechanical calculations that the chemical activity of the C70 fullerene molecule was higher than that of C60, though C70 is energetically more stable than C60. However, studies of the oxidation of C60 and C70 films and polycrystalline samples by X-ray absorption, photoelectron, and IR diffuse reflectance spectroscopy and thermal analysis [6, 7] show that above the temperatures of the onset of gasification (297°C), the activity of C60 and C70 in reactions with molecular oxygen is the same. Heating fullerenes in air or under low vacuum gives rise to epoxide fragments and C–O and C=O groups.

Differences in the molecular (electronic and geometrical) structure of C60 and C70 lead to different activation energies at the first stage of oxygen intercalation. At 27°C, the activation energy of O2 intercalation of C70 fullerene is low; for C60, it is negligible and cannot be evaluated. Thus higher fullerenes are more liable to oxidation at 27°C than C60. At the same time, the authors of [7] assumed in analyzing CO and CO2 effusion upon heating that the rate of framework decomposition of C70 was higher than that of C60. Isothermal storage made it possible to correlate the difference in the oxidation of C60 and C70 with the kinetics of oxygen diffusion in fullerite, which is more hindered in C70. Furan-bridged dimers that formed while oxidation of fullerenes can affect further oxidation; the oxidation and thermal stability of C60 and C70 dimers is lower than that of the corresponding monomers [8].

The problems of the oxidation/decomposition of fullerenes are thus important in studies with heating to 400–600°C. A comparative analysis of the behavior of C60 and C70 considers only the differences in the molecular geometry, but ignores the specifics of their crystallization from solutions, intercalation with solvent molecules, crystal morphology, etc. Our IR spectroscopy study [9] of fullerites recrystallized at room temperature and containing residual toluene showed...
that pronounced oxidation of C\textsubscript{70} started at higher temperatures than that of C\textsubscript{60}.

The aim of this study was a comparative investigation of the decomposition of C\textsubscript{60} and C\textsubscript{70} fullerites and mixtures of C\textsubscript{60}/C\textsubscript{70} (14 wt % C\textsubscript{70}) during annealing at 445°C in air.

EXPERIMENTAL

Studies were performed on powdered samples of C\textsubscript{60} (99.95 wt %) and C\textsubscript{70} (98 wt %) obtained at the Institute of Organometal Chemistry, Russian Academy of Sciences, ZAO Fullerene Center (Nizhni Novgorod). C\textsubscript{60} fullerite was chromatographically purified and annealed in dynamic vacuum to remove residual toluene (according to IR data, it contained almost no toluene; spectrum 1, Fig. 1). C\textsubscript{70} fullerite was prepared as two samples. The first sample was prepared by the same procedure as C\textsubscript{60} and contained a certain amount of residual toluene (according to IR data, it contained almost no toluene; spectrum 3, Fig. 1). The second sample was obtained by vacuum resublimation and contained no toluene (spectrum 2, Fig. 1). The C\textsubscript{60}/C\textsubscript{70} sample (14 wt % C\textsubscript{70}) was obtained via the Kretschmer technique of extraction with boiling toluene and crystallization in a rotary evaporator (spectrum 4, Fig. 1).

To evaluate mass loss during oxidation/decomposition, fullerite powders were weighed before and after annealing. Fullerite samples (16 mg) were placed in a muffle furnace and annealed in air at 250 and 445°C for 2 h. Their mass was controlled using an MV 210-A electronic balance (ZAO Sartogosm) to an accuracy of 0.03 mg. The IR spectra were studied on an FSM 1202 IR-Fourier spectrometer with a resolution of 1 cm\textsuperscript{-1} (14 scans). KBr pellets were prepared for spectrum recording (1:250). Micrographs of the crystals were obtained on a Philips SEM-515 scanning electron microscope (accelerating voltage, 10 kV). The fullerite powder was held on the sample stage with a thin layer of electro-conductive alcohol-soluble nickel-containing glue.

The composition of the samples was evaluated on an Agilent 1100 chromatograph with a diode matrix detector (Cosmosil Buckyprep column 4.6 × 250 mm, toluene eluent, 1 mL/min, wavelength 290 nm). For pure C\textsubscript{60} and C\textsubscript{70} fullerenes, the chromatograph was calibrated for six concentrations of 0.3 to 0.03 mg/mL.

RESULTS AND DISCUSSION

Figure 2 presents the IR spectra of fullerenes C\textsubscript{60} and C\textsubscript{70} annealed in air at 445°C (2 h). Let us first compare the degree of decomposition of the frameworks of C\textsubscript{60} and C\textsubscript{70} as a result of the oxidation of the samples containing no residual toluene (spectra 1 and 2, respectively). According to Fig. 2, C\textsubscript{70} was oxidized more actively than C\textsubscript{60}. This is also indicated by the considerable weakening of the characteristic absorption bands of C\textsubscript{70} and the appearance of 1600 and 1727 cm\textsuperscript{-1} bands due to C=O bond vibrations. After annealing at 445°C for 2 h, the loss of C\textsubscript{60} fullerite was 26.4 wt %, and the loss of C\textsubscript{70} was 19.1 wt % (Table 1). The oxidation of C\textsubscript{70} was more profound, evidently explaining the slight difference in the mass loss of C\textsubscript{60} and C\textsubscript{70}. The mass loss related to the decomposition of C\textsubscript{70} and evolution of CO and CO\textsubscript{2} were compensated by the formation of oxides.
At the first stage, the oxidation is probably accompanied by polymerization of the surface layer of crystallites [4]. This can lead to the formation of furan-bridged polymers. As is known [10], the rate of polymerization under UV irradiation of fullerene C₆₀ was higher than that of C₇₀. In addition, oxygen intercalation into C₆₀ fullerite was more active [6]. C₇₀, which is chemically more active [5], was actively oxidized with ambient oxygen at the next stage. Oxygen was added to the C₇₀ in the equatorial or nearly equatorial region of the molecular surface [9]. As a result of the nucleophilic reaction, the strains were higher than in C₆₀. The C₇₀ molecule thus became more strained and liable to destruction as a result of oxidation.

Any comparative analysis of the intensity of fullerene oxidation must consider the crystal size and morphology. Figure 3 presents micrographs of the initial C₆₀ and C₇₀ samples. The C₆₀ fullerite powder consists of globular crystals with sizes of 70 to 300 µm (Fig. 3, 1); C₇₀ obtained by sublimation (Fig. 3, 3) is loose powder with a developed surface in which small crystals (2–10 µm) coagulate into particles of up to 200 µm in size. The large specific surface area of C₇₀ microcrystals creates favorable conditions for oxidation/decomposition. Based on the crystal morphology of C₆₀ and C₇₀, we may assume that C₇₀ is oxidized more actively in air than C₆₀.

The effect of the residual solvent on the oxidation requires a separate consideration. Let us compare the oxidation of C₇₀ samples with residual toluene (in the form of crystal solvates) and without it. Quantitative determination of the residual solvent content is difficult because of problems in preparing the calibrating reference samples (specifics of the dissolution of fullerenes, the presence of impurities and oxides in the reference fullerite samples, etc.). We can nevertheless evaluate the content from the IR spectra (from the area of the 725 cm⁻¹ absorption band of toluene) using a C₆₀/C₇₀ sample with 1.05% toluene (TGA data) as a reference (Table 1). The toluene content in the C₇₀ sample was 0.5 wt %. To study the effect of the residual toluene on the oxidation/decomposition of fullerenes, the C₇₀ samples with toluene and without it (spectra 3 and 2, respectively; Fig. 2) were annealed at 445°C. The mass loss of the C₇₀ sample with toluene was ~76.8 wt %, four times greater than the loss for the C₇₀ sample without toluene (Table 1). The IR spectra of both samples indicate that fullerenes were considerably oxidized with formation of carbon–oxygen double bonds (1600 and 1727 cm⁻¹ absorption bands, respectively). The intensity of the absorption bands related to the characteristic vibrations of C₇₀ in the sample with toluene fell considerably after annealing.

We may thus conclude that the presence of residual solvent in C₇₀ fullerite led to considerable decomposition of molecules. The ratio of the mass losses of the samples (Table 1) also indicate that the presence of a solvent initiated the decomposition/sublimation of fullerenes. Since the fullerene molecules in the C₇₀⋅

![Figure 2](image-url)

**Fig. 2.** IR spectra of fullerenes after annealing at 445°C (exposure, 2 h): (1–4) see Fig. 1.

**Table 1.** Mass loss (Δm) of C₆₀ and C₇₀ fullerenes and C₆₀/C₇₀ mixture after annealing at 445°C (2 h)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Δm, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀ reference</td>
<td>26.4</td>
</tr>
<tr>
<td>C₇₀ reference (without toluene)</td>
<td>19.1</td>
</tr>
<tr>
<td>C₇₀ reference (with toluene)</td>
<td>76.8 (0.5)</td>
</tr>
<tr>
<td>C₆₀/C₇₀ mixture</td>
<td>83.2 (1.05)</td>
</tr>
</tbody>
</table>

Note: The mass of residual toluene is indicated in parentheses.
C₆H₅CH₃ crystal solvate are isolated from one another by solvent molecules, the sublimation temperature can decline. This difference in the intensity of oxidation of C₇₀ fullerite samples can also be explained by differences in the crystal size and morphology. C₇₀ (with residual toluene) consists of orthorhombic twin crystals with sizes from 30 to 650 µm (Fig. 3, 2). At first glance, the larger (but porous) C₇₀ crystals obtained by sublimation (Fig. 3, 3) should be oxidized more actively. During the thermal destruction of crystal solvates and the removal of toluene, however, C₇₀ fullerite is considerably loosened, facilitating oxygen diffusion into deeper layers of the crystal. Based on these data, it is believed that the decomposition of C₇₀ is affected by the dispersity of the initial sample and the sample obtained after the evaporation of the solvent with which C₇₀ forms mixed molecular crystals.

The C₆₀/C₇₀ mixture of fullerenes oxidized even more actively; its oxidation/decomposition was revealed by IR spectroscopy at temperatures as low as 150–200°C. The IR spectrum of the C₆₀/C₇₀ sample annealed at 445°C (spectrum 4, Fig. 2) corresponds to a highly oxidized state (the absorption bands related to the vibrations of the carbonyl group). Moreover, the intensity of the absorption bands of fullerenes fell appreciably. The initial mixture contained a large amount of residual toluene, 1.05 wt %, whose removal during the annealing (as in the case of C₇₀) led to loosening of fullerite, creating favorable conditions for sublimation/oxidation. Photos 4a and 4b in Fig. 3 show micrographs of the initial C₆₀/C₇₀ mixture of

Fig. 3. SEM micrographs of fullerite microcrystals: (1–4) see Fig. 1.
fullerenes. The C\textsubscript{60}/C\textsubscript{70} sample was platelike crystals with sizes from 200–300 to 500–800 µm (crystallized fullerite was scraped off from the inner surface of the crystallizer flask). The surface was smooth or highly developed (depending on whether the surface was in contact with the flask). The fragment sizes ranged from 1.5 × 1.5 to 4 × 8 µm. The initially porous structure of the C\textsubscript{60}/C\textsubscript{70} sample became more liable to intercalation with molecular oxygen and hence to oxidation upon heating because of the decomposition of its crystal solvates [11]. This led to considerable mass loss (~83.2 wt % after annealing in air at 445 °C for 2 h, Table 1).

As is well known [12], the decomposition of C\textsubscript{60} molecules on impurities begins to avalanche upon heating. The highest degree of oxidation, forming epoxides, oxidoannulenes (C\textsubscript{60}O\textsubscript{n} and C\textsubscript{70}O\textsubscript{n}, where n = 1–3) and furan-bridged dimers (C\textsubscript{120}O\textsubscript{n} and C\textsubscript{140}O\textsubscript{n}, where n = 1, 2) is observed at 250 °C for fullerenes containing the residual solvent. For comparative evaluation of fullerene loss during oxidation, the C\textsubscript{60} and C\textsubscript{70} samples recrystallized from toluene solutions at room temperature were therefore annealed at 250 °C. According to our IR data, both samples contained residual toluene (spectrum 1, Fig. 4; spectrum 1, Fig. 5), as indicated by the 725 cm\textsuperscript{-1} absorption band. According to our estimates, the starting samples contained ~0.5 wt % (C\textsubscript{60}) and ~2.5 wt % (C\textsubscript{70}) residual toluene (Table 2).

In the C\textsubscript{70} sample, toluene was part of the regular crystal solvate structure. In C\textsubscript{60}, toluene was preserved in a small amount on the boundaries of crystallites as a result of the decomposition of the crystal solvate during the evaporation of the mother solution. By annealing in air for 2 h at 250 °C, toluene was completely removed from the C\textsubscript{70} fullerite, while in C\textsubscript{60} its content fell to ~0.06 wt % (spectrum 3, Fig. 5; spectrum 2, Fig. 4, respectively). As is shown by the IR data, oxidation was inconsiderable: the absorption bands related to the C–O–C bond vibrations were barely discernable in the spectrum of the C\textsubscript{60} sample and were missing from the spectrum of C\textsubscript{70}. The spectrum also did not show the formation of carbonyl groups due to cleavage of the molecules' carbon framework. The mass loss was 1.1 and 7.5 wt % for C\textsubscript{60} and C\textsubscript{70}, respectively (Table 2). C\textsubscript{70} fullerite is evidently more liable to oxidation/decomposition when the solvent is removed.

After annealing at 250 °C for 2 h, C\textsubscript{60} formed C\textsubscript{120}O oxides and dimers. The IR spectrum (spectrum 2, Fig. 4) shows weak absorption bands corresponding to the C–O–C stretching vibrations at 849 (epoxide) and 1032 (ether) cm\textsuperscript{-1} [13]. In contrast to the oxidoannulene C\textsubscript{60}O, whose ether bridge is the result of the incorporation of the oxygen atom during the cleavage of the single bond, C\textsubscript{60}O epoxide is formed on the C=C double bond. The 849 and 1032 cm\textsuperscript{-1} bands can thus be attributed to the C–O–C vibrations of epoxides and oxidoannulenes, respectively. As is well known [14], C\textsubscript{60}O monoxide is unstable and combines with C\textsubscript{60} molecules to form C\textsubscript{120}O dimers, in which the fullerene molecules are linked by a furan bridge.

The absorption bands corresponding to the C–O–C vibrations in the polymer structures of fullerenes are

<table>
<thead>
<tr>
<th>Sample</th>
<th>m\textsubscript{1}, wt %</th>
<th>m\textsubscript{2}, wt %</th>
<th>Δm, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{60}</td>
<td>0.5</td>
<td>0.06</td>
<td>1.1</td>
</tr>
<tr>
<td>C\textsubscript{70}</td>
<td>2.5</td>
<td>–</td>
<td>7.5</td>
</tr>
</tbody>
</table>
thus localized in the range of ether absorption 1200–1000 cm\(^{-1}\) [13]. In our experiments, we were obviously dealing with a variety of structures that can form in solid-state synthesis [15] involving simultaneous thermolysis and photolysis. C\(_{60}\)O epoxides and oxidoannulenes formed first and C\(_{120}\)O dimers formed second. Synthesis of C\(_{60}\)O\(_n\) and C\(_{120}\)O\(_n\) (\(n > 1\)) was also possible. In the IR spectrum, all of these structures correspond to the absorption bands of C–O–C vibrations at ~849 cm\(^{-1}\) (epoxides) and 1200–1000 cm\(^{-1}\) (Fig. 4).

It is important to note that under the same conditions of annealing, the absorption bands attributed to C–O–C bond vibrations almost disappeared from the IR spectrum of C\(_{70}\) (spectrum 2, Fig. 5).

The samples were then additionally annealed for 2 h at 250°C. The absorption bands in the IR spectra of the samples (spectrum 3, Fig. 4; spectrum 2, Fig. 5) indicated that oxides and furan-bridged dimers were present and profound oxidation occurred when the frameworks of C\(_{60}\) and C\(_{70}\) molecules opened. In the spectrum of C\(_{60}\), this corresponds to the stronger bands at 849 and 1032 cm\(^{-1}\) and to the 1615 and 1727 cm\(^{-1}\) bands characteristic of C=O vibrations. In the spectrum of C\(_{70}\), the absorption bands of the carbon–oxygen double bond appeared (1615 and a doublet at 1720 and 1734 cm\(^{-1}\)). C–O–C vibrations were also noted; at 1220–1260 cm\(^{-1}\) and a weak band at 1017 cm\(^{-1}\). The absorption bands at 1615 and 1727 cm\(^{-1}\) correspond to the C=C and C=O stretching vibrations of diketones, respectively; those at 1720 and 1734 cm\(^{-1}\), to the C=O stretching vibrations of conjugated esters and diketones. Absorption in the range 1220–1260 cm\(^{-1}\) corresponds to the C–O–C asymmetric stretching vibrations of esters [16].

At increased exposure times, C\(_{60}\) fullerite thus continued to be oxidized, forming oxides and oxidoannulenes with negligible decomposition of the molecular framework. At the same time, the character of IR absorption in the spectrum of C\(_{70}\) points to the predominant formation of oxidoannulenes with the cleavage of single C–C bonds and more profound (relative to C\(_{60}\)) decomposition of molecules, liberating CO and CO\(_2\). According to high-performance liquid chromatography (HPLC) data, the C\(_{60}\) fullerite sample contained C\(_{60}\)O and C\(_{120}\)O oxides (5 wt % each) and higher C\(_{60}\)O\(_n\) oxides (\(n > 1\)). The C\(_{70}\) sample contained only traces of oxides (C\(_{70}\)O and C\(_{60}\)O because of the C\(_{60}\) impurity).

The IR and HPLC data revealed a considerable difference between the behavior of C\(_{60}\) and C\(_{70}\) molecules during the heating of the corresponding fullerite samples in air, both with and without the residual solvent. During prolonged annealing (for 4 h at 250°C), C\(_{70}\) fullerite decomposed more than C\(_{60}\). The decomposition of the carbon skeleton of the C\(_{60}\) molecule was possibly retarded during the annealing of fullerite in air because of the formation of a polymerized surface layer. The C\(_{70}\) molecule, however, forms C\(_{70}\)O oxides but no polymers and readily decomposes at the C–O–C bond.

We suggest the following stages of fullerite reactions with molecular oxygen during heating in air. At the first stage, fullerenes differ in their activity because of the geometrical peculiarities (surface curvature) of their molecules. When the heating time increases or the annealing temperature rises to 445°C, the polymerization and deformation of the carbon framework of molecules due to the addition of oxygen atoms dominates in the oxidation/decomposition of fullerene molecules. The C\(_{70}\) molecules decompose when the annealing time is increased at 250°C, forming carbon–oxygen double bonds; for C\(_{60}\) fullerite, the formation of epoxides and dimers dominates. At 445°C, we observe the active oxidation of C\(_{70}\) mole-
molecules with the opening of frameworks and oxidation on the C=O bond. The same conditions of annealing did not result in the decomposition of C_{60} molecules. The mass loss of the C_{70} sample with residual solvent considerably increased at 445°C (fourfold, relative to the sample without toluene) due to the destruction of molecules and the formation of CO and CO_2. The solvent effect during oxidation/decomposition reveals itself as crystallites disintegrate because of the decomposition of crystal solvates.

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REFERENCES


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