Thermal degradation of the polymer obtained by oxidation of C_{60} fullerene by oleum

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Degradation of $(C_{60})_n$ polymer and the C_{120} and $C_{120}O$ dimers at different temperatures was studied by IR and ESR spectroscopy. The formation of C_{60} was revealed. The polymer stability was found to be higher than the stability of the dimers. Peculiar features of the IR spectra of three-dimensional "hyper-crosslinked" polymers obtained by liquid-phase polymerization of C_{60} are discussed.

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

Comparison of the IR spectra of the product obtained by oxidation of C_{60} by oleum[1] with the spectrum of a photopolymerized fullerene[2] revealed structural similarity of these compounds.

The most important features of the IR spectra of the sample obtained by liquid-phase polymerization of C_{60} fullerene[1,2] are a broad, intense structurized band with a maximum at 1050 cm^{-1} and the "fullerene" band at 526 cm^{-1} (the most intense band in the spectra of C_{60} fullerene, C_{120} and $C_{120}O$ dimers,[1] and the polymers prepared by polymerization of C_{60} at a high pressure).[3,4]

An important structural problem of the polymeric products is retention of the C_{60} units in the polymer structure. A possible solution is to study the reversibility of the polymerization process. If the polymer undergoes an *in vacuo* thermal degradation into fullerene units, this suggests that the polymer is comprised of C_{60} units linked by σ-bonds.

In our case this is of particular importance because of the use of highly aggressive chemical substance (oleum, fuming sulfuric acid) as initiator of cationic polymerization.

The above-mentioned reversibility was established in studies of the polymers prepared at a high pressure.[3,4] The depolymerization temperature of $(C_{60})_n$ (~520 K) was found to be much higher than the thermal degradation temperature of C_{120} (438 K).[4]

The aim of this work was to follow the changes in the IR spectra of the polymer during thermolysis and to compare them with the data on thermal degradation of the polymers prepared at a high pressure.

Experimental

The polymer/CsI pellets prepared following a standard procedure were heated *in vacuo* and then their IR spectra were recorded on a Nicolet Magna-IR 750 Fourier IR spectrometer in the spectral region 4000—400 cm^{-1}. The peak and integrated intensities of spectral bands were determined using the standard software of the spectrometer (OMNIC program) with inclusion of the base line. ESR spectra of the polymer/CsI samples were recorded on a Varian E-12 ESR spectrometer.

Compounds C_{120} and $C_{120}O$ were obtained following the known procedures.[5,6]

Results and Discussion

The changes in the spectra of the polymer on heating to 200 °C are shown in Fig. 1, *a*—*c*. The intensities of the narrow bands were estimated from the peak intensities, while those of the broad polymer bands were estimated from both the peak and integrated intensities.

Analysis of the IR spectra recorded after stepwise heating of the samples in the temperature range 120—200 °C (Δt = 20 °C) with an exposure time of 20 min (see Fig. 1, *a*, *b*) showed that both the peak intensity and the integrated intensity of the main "polymer" band at 1050 cm^{-1} decreased by 7% and 3%, respectively, relative to the corresponding initial values. At the same time, the peak intensity of the band at 526 cm^{-1} (fullerene cage "fingerprint" [1—4,7]) increased by 45%. This band was assigned to the terminal fullerene units. The "polymer"/"fullerene" band intensity ratio was shown to depend on the polymerization conditions.[1]

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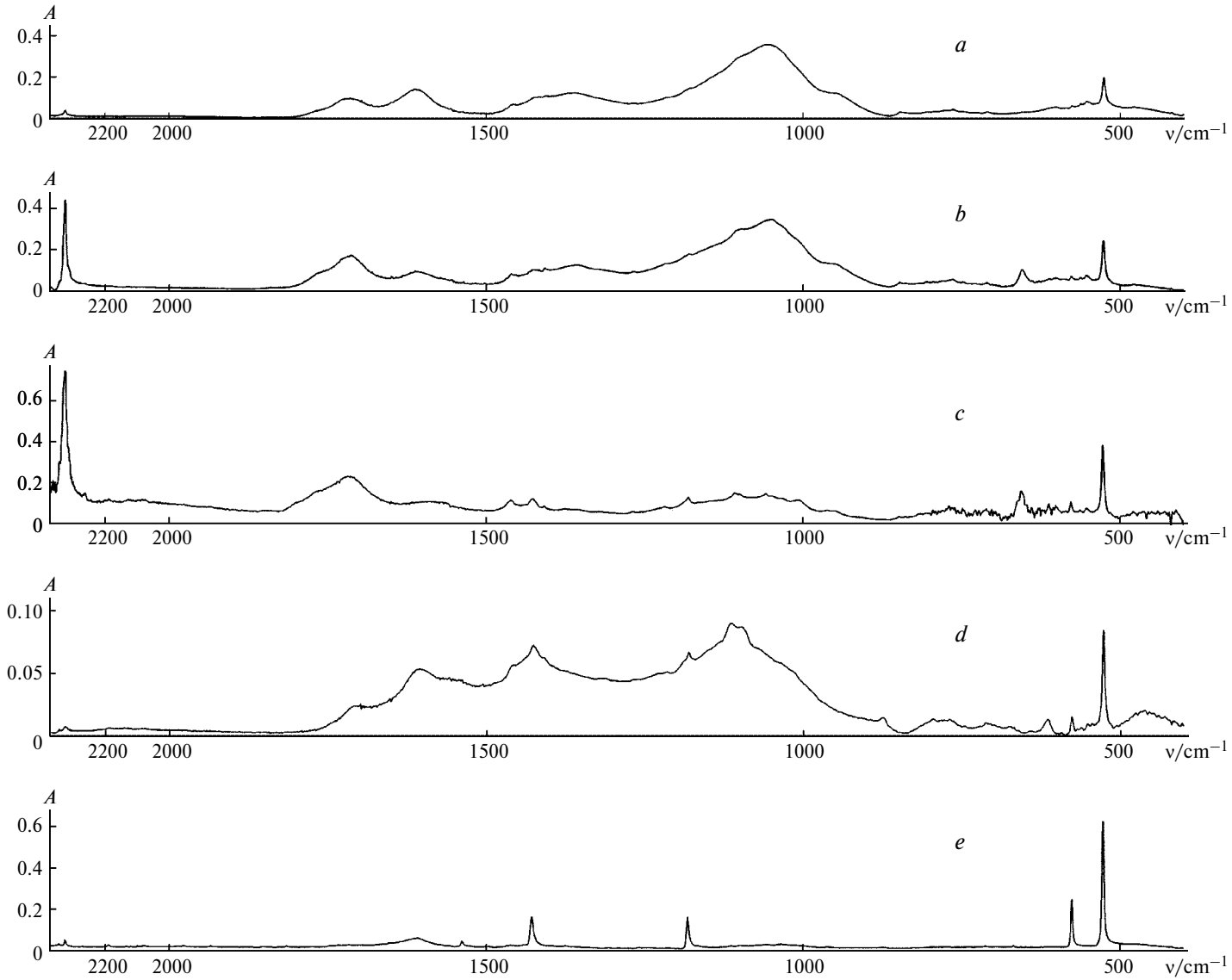

Fig. 1. IR spectra of $(C_{60})_n$ polymer before thermolysis (*a*), after thermal degradation in the temperature intervals 120—200 °C (*b*) and 200—280 °C (*c*), after heating at 450 °C for 30 min. (*d*), and the IR spectrum of C_{60} fullerene (*e*). The ordinate axes in the spectra *a*—*c* and *e* are presented in the same scale; for the spectrum *d* the scale is extended five-fold.

The frequency of the "fullerene" band in the spectra of both fullerene and its derivatives remains unchanged. Therefore, it is impossible to draw definite conclusions about the appearance of free fullerene in the sample based on the changes in the intensity of this band.

Because of this it is more convenient to use the adjacent band at 576 cm^{-1} (see Fig. 1, *e*) as an indicator of the presence of fullerene in the mixture with its derivatives. The peak intensity of this band in the spectrum of C_{60} fullerene is 2.75 times lower than that of the main "fullerene" band at 526 cm^{-1}. We used this coefficient for estimating the contribution of the C_{60} band to the total intensity of the "fullerene" band at 526 cm^{-1}. Comparison allows qualitative assessment of the ratio of free C_{60} fullerene to products of its polymerization.

More pronounced were the changes in the intensities of the bands at 1615 and 1720 cm^{-1}. Namely, the intensity of the former band nearly halved while that of the latter almost doubled in the above-mentioned temperature range. Noteworthy is that the spectrum of the initial polymer exhibits a weak band of the adsorbed carbon dioxide (at 2332 cm^{-1}). After heating the intensity of this band sharply increases (by a factor of nearly 15) and the band of the bending vibration of adsorbed CO_2 at 656 cm^{-1} also becomes observable.

Extension of the exposure time from 20 min to 1 h (at 200 °C) caused no significant changes in the band intensities. This was also observed at higher temperatures. In all cases raising the temperature first led to some decrease in the intensity of the "polymer" band at 1050 cm^{-1}; however, as the exposure time extended, the decrease in the band intensity was no longer observed. One can assume that some fraction or a structural fragment of the polymer undergo degradation at a certain temperature.

Thermolysis under mild conditions (below 200 °C) revealed a much higher stability of the polymer as compared to the C_{120} dimer, which is fully converted into C_{60} fullerene after 30 min at 200 °C.

The next series of measurements was carried out in the temperature range 200—280 °C at different exposure times (from 30 min to 1.5 h).

The "polymer" band was nearly unobservable in the spectrum recorded after heating to 280 °C (see Fig. 1, *c*). The contribution of the C_{60} absorption to the total intensity of the "fullerene" band at 526 cm^{-1} is 42% (calculated using the intensity of the band at 576 cm^{-1}). The "polymer" band intensity decreased substantially, while a number of weak narrow bands appeared against the background of this band. Weak bands at 1182 and 1429 cm^{-1} also correspond to C_{60} fullerene.

The spectral pattern observed differs from that of thermal degradation of the polymer prepared at a high pressure. At 200 °C, the IR spectra revealed a degradation of $(C_{60})_n$ into C_{60}.[3] It should be noted that comparison of the results obtained in different studies on the polymer degradation carried out under different conditions allows only qualitative conclusions.

There are several possible reasons for different patterns of the degradation processes in question. In our opinion, one of them is a different structure of the polymers prepared at a high pressure and by liquid-phase polymerization. The former group of polymers has one- or two-dimensional structures.[7] The corresponding IR spectra exhibit narrow bands (intense bands in the region 500—800 cm^{-1} and bands of lower intensity in the region 800—1500 cm^{-1}). The spectral patterns are only slightly different from those of the C_{120} and $C_{120}O$ dimers. These spectra exhibit no broad intense "polymer" band at 1050 cm^{-1} corresponding to the statistically averaged vibrational frequency of the simple C—C bond.

Carbon atoms constituting the C_{60} molecule are linked by a total of thirty unsaturated bonds. Dimerization causes saturation of five unsaturated bonds in each C_{60} unit. Therefore, the proportion between the saturated and unsaturated C—C bonds in the C_{60} unit of a linear polymer is 10 : 20 (main chain) and 5 : 25 (terminal C_{60} units). This count procedure ignores the C—C links between fullerene units.

In the case of liquid-phase polymerization one can assume the formation of not only linear polymers but also polymers with a three-dimensional structure and a much larger number of ordinary bonds. One central fullerene unit of "hyper-crosslinked" C_{60} can add up to six C_{60} units, all carbon atoms in the central unit being connected by ordinary bonds.

One can assume that degradation of the three-dimensional polymer into fullerene molecules is preceded by its fragmentation into planar and linear units.

Since no indications of fast polymer degradation were observed in the temperature range studied, we continued the investigation of thermolysis at higher temperatures.

The IR spectrum of the sample obtained by heating in the temperature range 300—450 °C (Fig. 1, *d*) is extended five-fold along the ordinate axis as compared to the spectra *a*—*c*, since the absorption intensity substantially decreases throughout the spectrum at these temperatures. All four C_{60} bands are clearly seen in the spectrum *d*. The calculated contribution of C_{60} to the intensity of the band at 526 cm^{-1} is 84%. At 450 °C, at three exposure times of 30 min the intensities of the IR bands in the spectrum of C_{60} passed through a maximum. This was accompanied by the appearance of a brown C_{60} film on the cold surface of the ampule in which thermolysis of the sample was performed.

In the case of a simple decomposition reaction, $(C_{60})_n \rightarrow nC_{60}$, sublimation of fullerene should cause decoloration of the sample. Nevertheless, the dark color of the sample retained during high-temperature thermolysis.

In this temperature range, graphitization of C_{60} begins,[8] which manifests itself as a sharp increase in the absorption intensity in the ESR spectrum.

In the temperature range 120—200 °C the ESR signal is three times more intense than the weak ESR signal of the initial polymer. The maximum ESR signal intensity (120 times higher than the intensity of the signal of the initial polymer) was obtained after heating at 450 °C for 30 min.

The three-dimensional structure is only one peculiar feature of the polymer obtained by liquid-phase oxidation. Another possible structural feature of the compound are "furanoid" bridges connecting the C_{60} units. This assumption was made after analysis of the ESR spectra.[1] The ESR spectrum of the polymer oxidized by oleum exhibited some components of the fine structure, which are typical of the $C_{120}O^{\bullet 2+}$ diradical cation.

The thermal stability of C_{120} has been the subject of a few studies;[4,9] however, this property of $C_{120}O$ has not been assessed so far. We studied thermal degradation of this oxygen-containing dimer in the temperature range 180—280 °C. At 180—250 °C and different exposure times (from 0.5 h to 1 h), no significant decrease in the IR band intensities was observed. Figure 2 presents the spectra of the initial $C_{120}O$ sample (*a*), after heating at 250 °C for 1 h (*b*), and after subsequent heating at 280 °C for 1 h (*c*). As can be seen, almost no decomposition of the dimer occurs at 250 °C. At 280 °C, the spectrum significantly changes, the characteristic narrow bands of C_{60} being clearly seen in addition to the weak bands of the initial dimer.

When discussing the thermal stabilities of C_{120} and $C_{120}O$, it is reasonable to compare them with those of cyclobutane and THF. The difference between the stabilities of the last two compounds is primarily determined by the absence of large strain in the THF molecule compared to cyclobutane.

Probably, it would be premature to write, based on the results obtained, the equation for the decomposition reaction as follows

$$2\,C_{120}O \longrightarrow 4\,C_{60} + O_2.$$

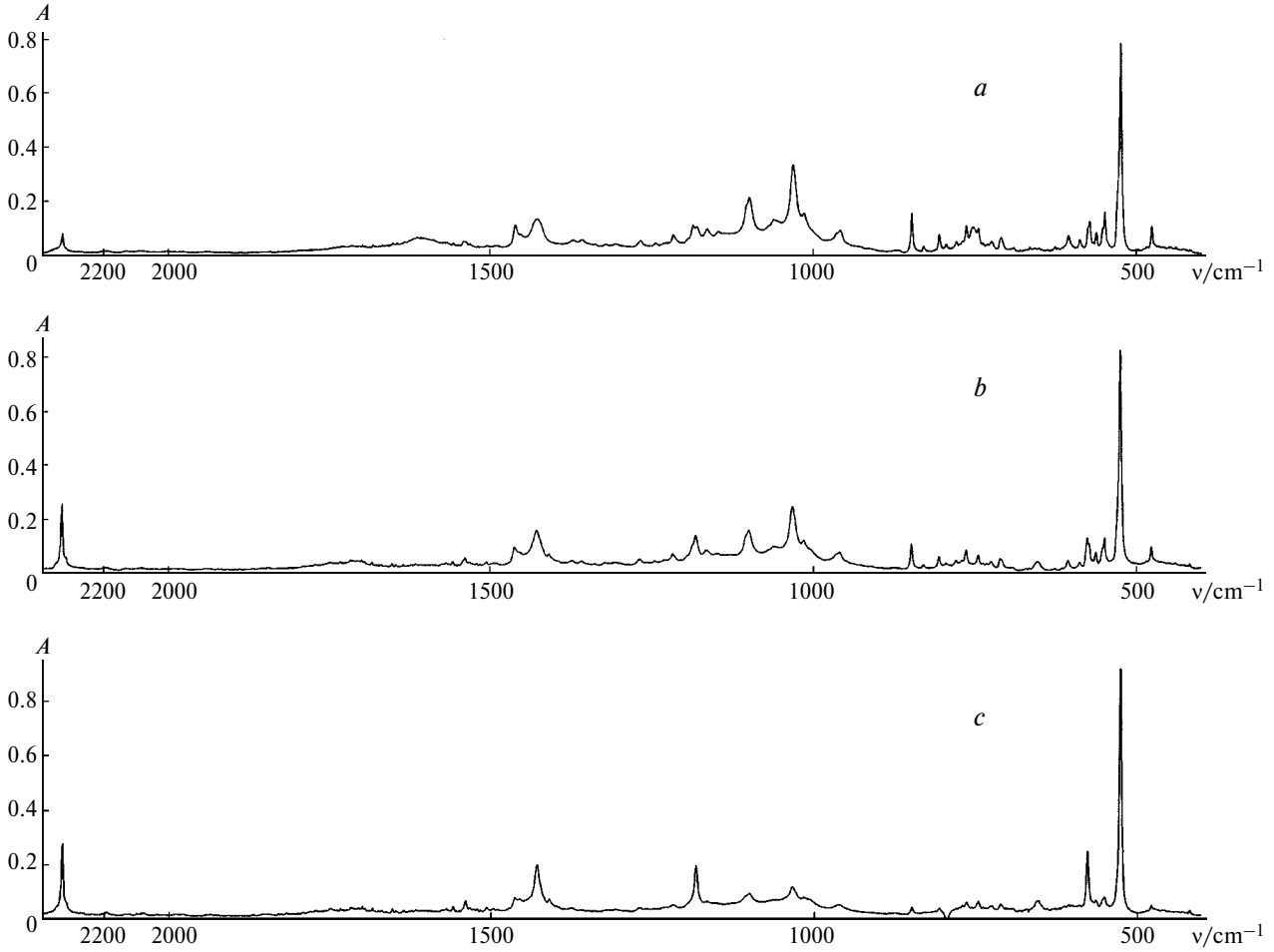

Fig. 2. IR spectra of $C_{120}O$ before and after heating: initial sample (*a*), the sample after heating in the temperature interval 180—250 °C (*b*), and after heating at 280 °C for 1 h (*c*).

However, the spectrum exhibited no new bands, except for the absorption band of the adsorbed carbon dioxide (see Fig. 2, *c*).

We first suggested the formation of CO_2 in the studies of polymer degradation at lower temperatures. But the lack of experimental data precluded formulation of the hypothesis concerning a possible source of carbon dioxide until studying the thermal degradation of $C_{120}O$.

The spectrum shown in Fig. 2, *b* exhibits no sharp decrease in the intensity of the $C_{120}O$ bands. At the same time an intense stretching vibration band of the adsorbed CO_2 at 2332 cm^{-1} and a band of lower intensity at 656 cm^{-1}, corresponding to the bending vibration, become visible. A possible source of CO_2 can be a carbonyl compound, a small amount of which is present in the sample, as indicated by the band at 1615 cm^{-1} (see spectrum *a* in Fig. 2). Noteworthy is that, in spite of different methods for the synthesis of $C_{120}O$ **6** and the polymer under study, the band at 1615 cm^{-1} and the next band at 1720 cm^{-1} are observed in the spectra of both compounds.

A decrease in the intensity of the band at 1615 cm^{-1} in the spectra of $C_{120}O$ and the polymer correlates with the appearance of the bands of adsorbed CO_2. As the carbonyl bands at 1615 and 1720 cm^{-1} disappear on prolonged heating *in vacuo*, the CO_2 bands also disappear, which could be attributed to desorption.

The most important results obtained in this work are as follows. We proved that the polymer structure comprises C_{60} units that form a three-dimensional network. The polymer structure contains a large number of saturated C—C bonds which determine the pattern of the IR spectrum.

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