

## Water-soluble polyketones and esters as the main stable products of ozonolysis of fullerene C<sub>60</sub> solutions

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Stable ozonolysis products of C<sub>60</sub> solutions in CCl<sub>4</sub>, toluene, and hexane were studied by elemental analysis, HPLC, and UV and IR spectroscopy. Polyketones and esters were established for the first time to be the main stable products, whose content increased during the whole ozonolysis time (1 h). Epoxides C<sub>60</sub>O<sub>n</sub> (*n* = 1–6) are accumulated within 1–3 min, and after 5 min of ozonolysis their concentration decreases to zero. Fullerene C<sub>60</sub> disappears from the reaction solution due to its conversion to oxides and mechanical capturing of C<sub>60</sub> by these oxides to form a precipitate. The oxidation of C<sub>60</sub> is completed in the solid phase by the formation of the C<sub>60</sub>O<sub>16</sub> oxide in which 9.68 O atoms fall on fullerene polyketones, 6 O atoms are attributed to esters, and 0.32 O atoms fall per epoxides. The optimum medium for preparation of the C<sub>60</sub> oxides is CCl<sub>4</sub> rather than traditional toluene, which reacts with ozone in the side reaction to form products containing active oxygen. The C<sub>60</sub> cage is ruptured during ozonolysis because of the C=C bond cleavage to form two C=O groups at the ends of the open hexagon. Ozonolysis of C<sub>60</sub> solutions in CCl<sub>4</sub> is efficient for synthesis of water-soluble fullerene oxides due to the high yield and solubility of polyketones and esters in water.

**Key words:** fullerene C<sub>60</sub>, ozonolysis, polyketones, esters and epoxides.

Oxidation of C<sub>60</sub> solutions with ozone is one of the first studied chemical reactions of fullerenes, which is being under study for more than a decade.<sup>1–20</sup> This reaction is of interest from the viewpoint of both establishment of the fundamental chemical properties of fullerene and ozone and the solution of the problem of oxidative functionalization of C<sub>60</sub>. Surprisingly, the most progress was achieved in studying the primary unstable products of ozonolysis of C<sub>60</sub>. For example, primary fullerene ozonide C<sub>60</sub>O<sub>3</sub> formed by the [6,6]-addition of O<sub>3</sub> to the C=C bond of the C<sub>60</sub> cage, which is rapidly ruptured to epoxide C<sub>60</sub>O and singlet oxygen <sup>1</sup>O<sub>2</sub>, has recently<sup>17</sup> been isolated for the first time and identified. However, many important aspects of C<sub>60</sub> ozonolysis remain unstudied so far. The main of them are the identification of stable products, the influence of the solvent nature on the oxidation rate and composition of the products, and the elucidation of conditions under which the C<sub>60</sub> cage begins to decompose. The above studies contain many contradictory data. For example, the C<sub>119</sub> cluster was identified<sup>2</sup> by mass spectrometry as a product of C<sub>60</sub> ozonolysis in toluene. However, this result has not been confirmed

later.<sup>6</sup> The solubility<sup>4</sup> and insolubility<sup>6</sup> of the C<sub>60</sub>O<sub>n</sub> epoxides (*n* = 1–5) in toluene were also reported. In Refs. 5 and 8, toluene (traditional solvent) is considered inert toward ozone in the presence of C<sub>60</sub>, while the authors<sup>11</sup> believe that toluene is oxidized by ozone like other aromatic hydrocarbons. These authors assume that some intermediate of this reaction can also oxidize C<sub>60</sub>, although, according to published data,<sup>8</sup> ozone is considered to be the only oxidant in the interaction with C<sub>60</sub>. When studying the reaction of C<sub>60</sub> with ozone, the attention was concentrated on the mechanism of formation and properties of the C<sub>60</sub>O<sub>n</sub> epoxides (*n* = 1–6) (hereafter epoxides), and the data on fullerene ketones and polyketones (hereafter polyketones) are restricted by the detection of the absorption band of the C=O group at 1725 cm<sup>–1</sup> in the IR spectra of the precipitates. The exception is presented by published data<sup>6</sup> on a weak signal in the <sup>13</sup>C NMR spectrum at δ 211 assigned to the C=O group of fullerene diketone C<sub>60</sub>(=O)<sub>2</sub>. However, taking into account that C<sub>60</sub> contains 30 C=C bonds, one can expect that products containing a much greater number of the C=O groups can be formed along with C<sub>60</sub>(=O)<sub>2</sub>

due to ozonolysis. On the contrary, based on the calculations of the thermal effects and activation energies of several elementary steps of the [6,6]-addition of O<sub>3</sub> to the C=C bond of the C<sub>60</sub> cage, the authors<sup>18</sup> concluded that the main stable products of C<sub>60</sub> ozonolysis should be epoxides rather than polyketones. According to the scheme proposed<sup>6</sup> for ozonolysis of C<sub>60</sub>, the only route of C<sub>60</sub>(=O)<sub>2</sub> formation is the interaction of a reaction intermediate (oxofullerenecarbonyl oxide) with toluene or xylene. This evokes an important question: can fullerene oxides be formed by ozonolysis in solvents containing no hydrogen? We have previously<sup>12,15</sup> found that the ozonolysis of C<sub>60</sub> solutions produces products in both the ground and excited states, and this is precisely the emission of the excited states of the \*O=C<sub>60</sub>(=O)<sub>m</sub> polyketones (*m* = 1–19) which is responsible<sup>19</sup> for the bright chemiluminescence (CL) accompanying the ozonolysis of C<sub>60</sub>. No experimental proofs for the formation of fullerene esters (hereafter esters) due to C<sub>60</sub> ozonolysis can be found in literature. The problem about the completeness of C<sub>60</sub> oxidation by ozone to oxy derivatives remained unsolved,<sup>1–20</sup> because the reaction solutions contain significant amounts of C<sub>60</sub> according to the known data of analyses by HPLC and mass spectrometry. In addition, data on the conversion of C<sub>60</sub>, which could attribute the corresponding results of analysis of the products to a particular depth of C<sub>60</sub> oxidation are lacking (the exception is the publication<sup>5</sup> indicating that the ozonolysis was performed to the 30% conversion of C<sub>60</sub>). Taking into account that C<sub>60</sub> is formed<sup>21</sup> by the thermal decomposition (110 °C) of the C<sub>60</sub>O epoxide (obtained by another reaction), we can assume that the signals of C<sub>60</sub> detected in the mass spectra can be the result of the decomposition of the ozonolysis products when analyses are performed by this method.

This work is devoted to the identification of stable ozonolysis products of C<sub>60</sub> solutions, studies of the influence of the solvent nature and, in particular, a possibility of the formation of polyketones with the number of the C=O groups greater than two, and elucidation of a possibility of the appearance of polyketones in solvents containing no hydrogen. The main task of the study is to answer the following question: are epoxides indeed the main stable ozonolysis products or polyketones and esters are additionally formed in noticeable amounts? A special attention is also given to the spectrophotometric study of the stability of the C<sub>60</sub> cage during ozonolysis of its solutions.

### Experimental

Commercial C<sub>60</sub> (99.9%) obtained in an arc discharge between graphite electrodes was used. The purity of C<sub>60</sub> was monitored by HPLC, elemental analysis, and by absorption spectra of its solutions at 200–800 nm. Ozone was obtained in a labora-

tory ozonator supplied by O<sub>2</sub> or air dried by passing through columns with 98.3% H<sub>2</sub>SO<sub>4</sub>, NaOH flakes, and zeolites 4 Å. NaOH, KOH, CaCl<sub>2</sub>, and HCl (reagent grade) and bidistilled water were used. 1,4-Dioxane (special purity grade) containing no admixtures of carbonyl compounds was purified by a known procedure.<sup>22</sup> 1,2-Dichlorobenzene (DCB) was purified by double distillation. Toluene and hexane were boiled and distilled above Na metal; CCl<sub>4</sub> (pure grade) was purified according to a described procedure,<sup>22</sup> washed six times with a large volume of water, dried above CaCl<sub>2</sub>, ozonated until the minimum CL brightness accompanying this process was achieved, refluxed for 2 h, and kept above zeolite 4 Å. Methanol was distilled above (MeO)<sub>2</sub>Mg, and admixtures of carbonyl compounds were removed according to known procedures.<sup>23,24</sup> A commercial 98% solution of Et<sub>3</sub>Al in gasoline was distilled *in vacuo* (15 Torr, 383 K). To remove moisture and oxygen, argon was passed through a PG instrument (gas absorber) consisting of columns packed with alumina, zeolite, and the supported nickel catalyst, and equipped with the Petryanov molecular filter. Solutions of C<sub>60</sub> were prepared (and stored) in the dark by the dissolution of a fullerite weighing sample in an argon atmosphere. In a typical experiment, solutions with [C<sub>60</sub>]<sub>0</sub> = 1.6 · 10<sup>−4</sup> mol L<sup>−1</sup> and a volume of 10 mL at 300 K were ozonated by bubbling an O<sub>3</sub>–air (0.7 mmol of O<sub>3</sub> h<sup>−1</sup>) or O<sub>3</sub>–O<sub>2</sub> (1.4 mmol of O<sub>3</sub> h<sup>−1</sup>) mixture. In both cases, the composition of the ozonolysis products was the same, and they contained no possible nitrogen-containing admixtures. Ozonolysis was carried out at 300 K in a quartz cell (diameter 35 mm, height 15 cm) placed in a copper unit, whose temperature was maintained constant. The reaction was periodically stopped by switching-off the O<sub>3</sub> flow, a residue of O<sub>3</sub> was removed with an argon flow, and then samples of the reaction mixture were taken. The samples were centrifuged to separate the solution and precipitate. The precipitates were washed with toluene and hexane (or CCl<sub>4</sub>) until a washing solution showed no carbonyl compounds and peroxides (analysis for the C=O and –OO– groups). The samples were analyzed by measuring the absorption spectra in the IR (solutions and precipitates) and UV-visible (solutions) regions and by HPLC (solutions) and elemental analysis (precipitates). Additionally, to establish the composition of the precipitates, they were dissolved in DCB, and the resulting solutions were analyzed by HPLC. When choosing the solvent for these experiments, we used the known data,<sup>25</sup> according to which DCB is one of the best solvents for C<sub>60</sub> (27 and 7 mg mL<sup>−1</sup>). It turned out that the former value is invalid, and at −20 °C the maximum solubility of C<sub>60</sub> in DCB is at most 7 mg mL<sup>−1</sup>. The content of oxygen in the precipitates was determined by elemental analysis (maximum error 2.0 rel.%) from the difference after the content of C and H was subtracted and by the direct analysis of samples using a described method<sup>26</sup> in the form of CO after decomposition at 1333 K in the presence of active carbon prepared on nickel followed by chromatography on a column packed with molecular sieves 5 Å. Polyketones were identified by the colorimetric method<sup>23,24</sup> measuring the intensity of the UV absorption band at λ = 490 nm of fullerene 2,4-dinitrophenylhydrazine formed by the treatment of an oxidate sample dissolved in MeOH with 2,4-dinitrophenylhydrazine. Esters were determined by saponification according to a published method<sup>27</sup> accepted for analysis of hydrocarbon esters by the treatment of a precipitate sample with 2 mL of a 0.09 M solution of KOH in EtOH and heating in a water bath for 1.5 h. Then phenolphthalein (1 droplet) was

added, and an excess of unreacted alkali was titrated with a 0.01 *M* solution of HCl. The procedure was improved for AcOEt. The content of oxygen of the epoxide group was determined by hydrochlorination according to a described procedure<sup>24</sup> used for analysis of hydrocarbon epoxides. For this purpose, the precipitate was placed in dioxane, treated with 0.5 mL of a 0.09 *M* solution of HCl, and heated for 30 min at 90 °C. Then EtOH (5 mL) and phenolphthalein (1 drop) were added, and the mixture was titrated with a 0.1 *M* solution of NaOH in MeOH. The procedure was improved for epichlorohydrin. The content of active oxygen in precipitates and solutions was determined (after O<sub>3</sub> was thoroughly removed with argon) by iodometric titration in a glacial AcOH medium according to a published procedure.<sup>27</sup>

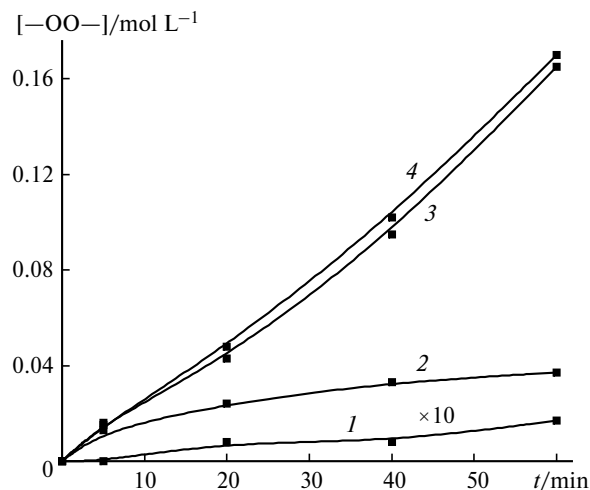
Elemental analysis of precipitates were carried out on a Carlo Erba-1106 elemental analyzer. A Hewlett—Packard chromatograph (series 1050, UV detector ( $\lambda = 313$  nm), column 250×4.6 mm, stationary phase (C18)—Zorbax OD5, eluant CHCl<sub>3</sub>—PhCH<sub>3</sub>—MeOH (1 : 1.1 : 1.3) mixture) was used for HPLC. The composition of the reaction mixture was determined by the integration of the areas of chromatographic peaks using an HP 3396A integrator. Absorption spectra were recorded on Specord M40 (UV-visible region) and Specord IR-75 spectrophotometers and on a Nicolet Magna-750 FTIR spectrometer (IR region).

## Results and Discussion

To study the influence of the solvent nature on the composition of products and oxidation rate of fullerene and a possible involvement of the solvent in this process, C<sub>60</sub> solutions were ozonated in solvents with and without hydrogen, namely, toluene, hexane, and CCl<sub>4</sub>, respectively. When bubbling O<sub>3</sub> through these solutions of C<sub>60</sub>, the formation of brown precipitates starts already after 2—5 min. The precipitation has previously been observed only when solutions of C<sub>60</sub> were ozonated in toluene.<sup>6–12,15,17</sup> Thus, the fact mentioned in Ref. 4 that a toluene solution of C<sub>60</sub> retained homogeneity upon ozonolysis is likely incorrect. The ozonation of the solvents in the absence of C<sub>60</sub> gives no colored products. Therefore, the brown color of the precipitates is caused by the oxy derivatives of C<sub>60</sub>, which is confirmed by an analogous color of the precipitates obtained in solutions of CCl<sub>4</sub>, which is inert toward ozone.<sup>27</sup>

### Influence of C<sub>60</sub> on the interaction of O<sub>3</sub> with toluene.

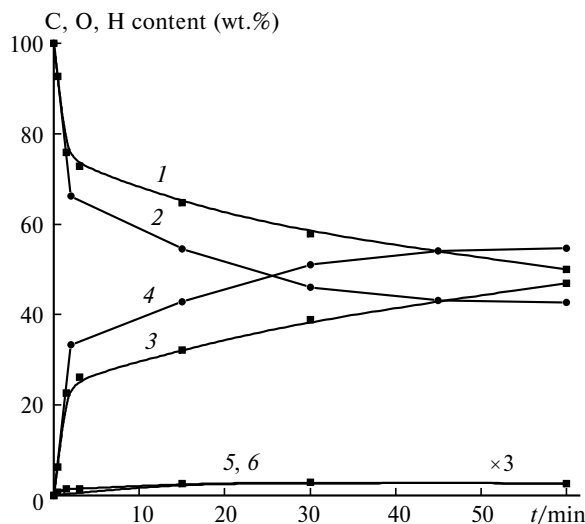
Since distinct published data on the influence of C<sub>60</sub> on the interaction of ozone with the traditional solvent (toluene) are lacking, we studied the formation of toluene derivatives containing active oxygen (AO). This process was determined by iodometric titration in the presence and absence of C<sub>60</sub>. As it turned out, the presence of C<sub>60</sub> in toluene sharply decreases the content of compounds with AO in a solution (Fig. 1). However, its amount in the precipitate is sufficiently high in the presence of C<sub>60</sub> as well. A much higher content of AO in the precipitate ( $1.0 \cdot 10^{-3}$  moles after 40 min of ozonolysis) com-



**Fig. 1.** Content of active oxygen (AO) in the solutions and precipitates as a function of the ozonolysis time (*t*) (volume 10 mL, bubbling rate 1.4 mmol of O<sub>3</sub> h<sup>−1</sup>): C<sub>60</sub> solution in toluene (1), toluene (2), and the total content of AO (solution + precipitate) upon ozonolysis of toluene (3) and a C<sub>60</sub> solution in toluene (4); [C<sub>60</sub>]<sub>0</sub> =  $1.6 \cdot 10^{-4}$  mol L<sup>−1</sup> (1, 4).

pared to the low content of C<sub>60</sub> in the initial solution ( $1.6 \cdot 10^{-6}$  moles) indicates that AO is a product of the ozonolysis of toluene rather than C<sub>60</sub>. Of course, this does not exclude a possibility of formation of C<sub>60</sub> derivatives containing AO; however, if they are present, then their amounts are much smaller and disguised by the corresponding toluene derivatives. Based on published data<sup>28–30</sup> on the ozonolysis of aromatic hydrocarbons, we believe that toluene ozonide is the most probable poorly soluble product of this reaction.

**Elemental analysis of precipitates.** According to the results of elemental analysis of the precipitates, when the ozonolysis time of C<sub>60</sub> solutions increases, the carbon content decreases considerably, the oxygen content increases, and the hydrogen content increases insignificantly (Fig. 2). A faster decrease in the carbon content takes place at short exposures of the reactions (5 min), and the addition of oxygen to the C<sub>60</sub> cage becomes slower (see Fig. 2). The equally low content of hydrogen (relatively to that of carbon and oxygen) in the ozonolysis products of C<sub>60</sub> solutions in toluene and CCl<sub>4</sub> implies that the products contain no hydrogen-containing C<sub>60</sub> derivatives. When the reaction is carried out in toluene, the carbon content in the precipitate decreases more slowly than that in CCl<sub>4</sub> (see Fig. 2), which can be explained by the consumption of ozone for toluene oxidation to form derivatives with AO. Since CCl<sub>4</sub> contains no hydrogen, we can conclude that the latter appears due to water admixtures in the precipitate, which is highly hygroscopic. Based on the fact that all hydrogen is introduced into the precipitate as an admixture of adsorbed water, we subtracted the hydrogen of water and established the molecular formulas



**Fig. 2.** Changes in the content of carbon (1, 2), oxygen (3, 4), and hydrogen (5, 6) in the precipitates obtained by the ozonolysis of a solution of C<sub>60</sub> ( $1.6 \cdot 10^{-4}$  mol L<sup>-1</sup>) in toluene (1, 3, 5) and CCl<sub>4</sub> (2, 4, 6) ( $t$  is the ozonolysis time).

of the fullerene oxy derivatives formed at different exposures of ozonolysis (Table 1).

The temperature has no noticeable effect on the composition of the ozonolysis products. For example, the results of elemental analysis of the precipitate obtained from the sample taken after the 5-min ozonolysis of a C<sub>60</sub> solution in toluene at 300 K are close to published data<sup>6</sup> (in parentheses) on the ozonolysis of toluene solutions of C<sub>60</sub> at 195 K: C, 50.95% (50%); H, 3.2% (3%); O (direct determination), 45.77% (from the difference, 47%). The ozonolysis time or the amount of consumed ozone is not presented,<sup>6</sup> as in the most other studies on the ozonolysis of C<sub>60</sub>.

**HPLC data for reaction solutions.** The results of HPLC only for toluene solutions of C<sub>60</sub> have recently been described.<sup>3,5,8–11,17,19</sup> We carried out HPLC of reaction so-

lutions in CCl<sub>4</sub>, hexane, and toluene. The absolute retention times of peaks in the chromatograms obtained by us ( $t_r$ ) and in Ref. 7 ( $t_r^7$ ) after the ozonolysis of toluene solutions of C<sub>60</sub> differ substantially likely due to different compositions of the eluent used for HPLC. However, the general views of the compared chromatograms are very close. When the peaks of C<sub>60</sub> are matched, the  $t_r^7$  values for C<sub>60</sub>O, C<sub>60</sub>O<sub>2</sub>, C<sub>60</sub>O<sub>3</sub>, C<sub>60</sub>O<sub>4</sub>, and C<sub>60</sub>O<sub>5</sub> (including isomers) differ slightly from  $t_r$  of the corresponding peaks in our chromatograms (Fig. 3). The average difference between the positions of the peaks of C<sub>60</sub> and epoxides is  $t_r - t_r^7 = 2.6$  min. The authors of Ref. 7 identified the peaks of epoxides by the application of a complex of methods of analytical and preparative HPLC and mass spectrometry with electro- and laser-desorption ionization of samples. Based on these data and taking into account the analogy of the chromatograms compared, we assigned the peaks in Fig. 3 to the same epoxides C<sub>60</sub>O<sub>*n*</sub> ( $n = 1–5$ ). The same view of the chromatograms of reaction solutions in toluene, CCl<sub>4</sub>, and hexane suggests (which correlates with the results of elemental analysis) that the formation of the products of C<sub>60</sub> ozonolysis involves no solvent and contains no its fragment.

Note that the used HPLC procedure makes it possible to monitor only products of non-deep C<sub>60</sub> oxidation. Indeed, the C<sub>60</sub> peaks in the chromatograms of the reaction solutions disappear already at short exposures of ozonolysis. For example, after the 3.5-min ozonolysis of a solution of C<sub>60</sub> in CCl<sub>4</sub> and precipitation, the HPLC chromatogram of the reaction solution contains no peaks of C<sub>60</sub> and epoxides.

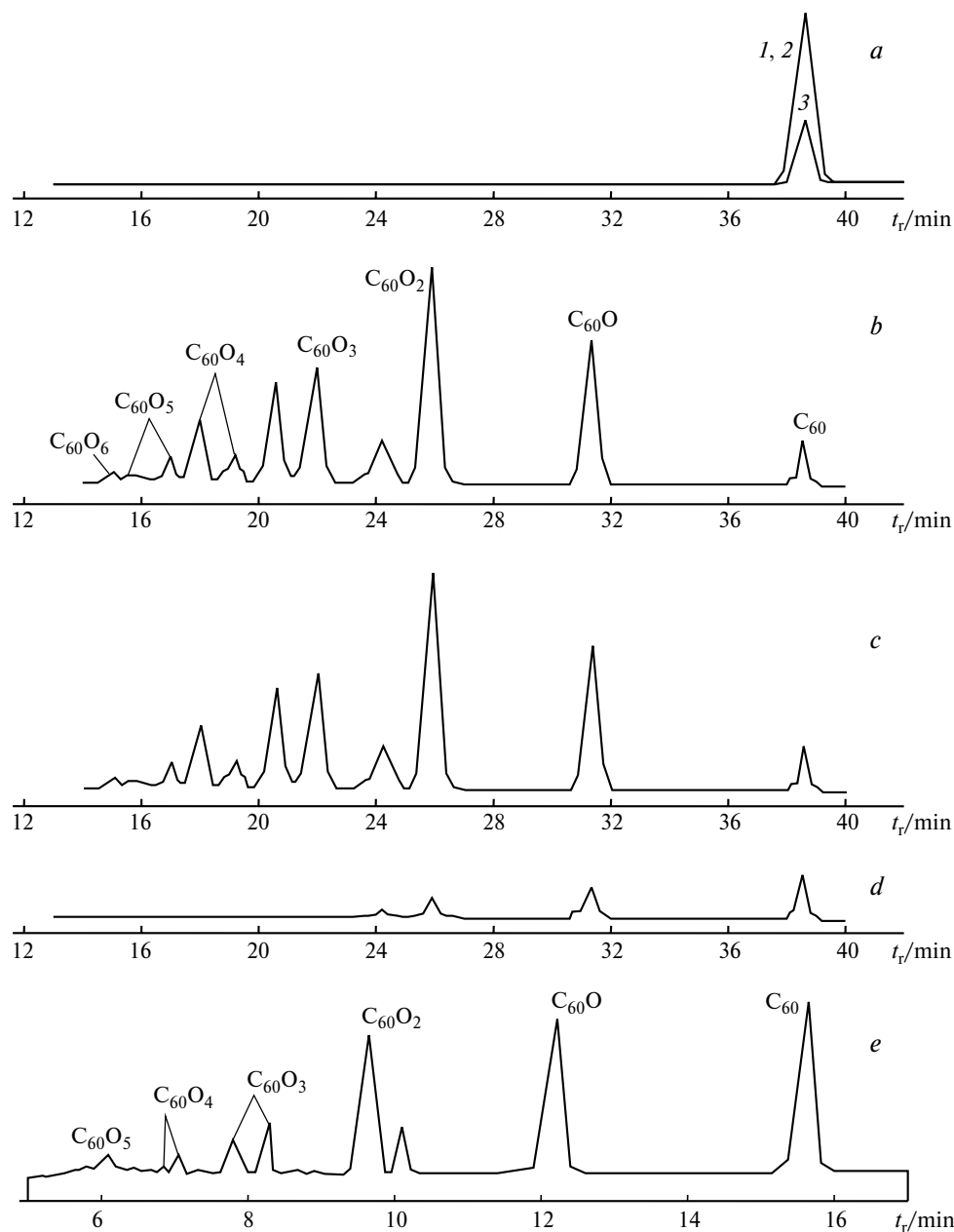
The kinetic dependences (Fig. 4) plotted by the change in the areas of the corresponding peaks in the chromatograms for the samples taken at different ozonolysis times of toluene solutions of C<sub>60</sub> demonstrate the accumulation and consumption of the epoxides in the solution. These kinetic curves are similar to those obtained previously<sup>11</sup> for the epoxides containing one–three O atoms. In addition, we also succeeded to monitor the kinetics of accumulation and consumption of the epoxides containing four and five O atoms. Analogous kinetic curves for the ozonolysis of C<sub>60</sub> in CCl<sub>4</sub> differ only by the faster formation of maxima (are not presented).

The solvent nature affects the rate of C<sub>60</sub> disappearance from the reaction solution. For example, in toluene the C<sub>60</sub> content is close to zero after 3 min of ozonolysis, whereas in CCl<sub>4</sub> and hexane it is close to zero after 1.5–2 min and 25 s, respectively. Thus, the rate of C<sub>60</sub> consumption in reaction solutions decreases in the series hexane > CCl<sub>4</sub> > toluene (see Fig. 4). The faster disappearance of C<sub>60</sub> in CCl<sub>4</sub> compared to toluene is caused by the fact that in CCl<sub>4</sub> ozone reacts only with C<sub>60</sub>, while in toluene ozone is also consumed in the side reaction with the solvent. Taking into account that hexane is oxidized by ozone more slowly than toluene,<sup>28</sup> we did not under-

**Table 1.** Elemental composition of the precipitates as a function of the ozonolysis time ( $t$ ) for C<sub>60</sub> solutions in CCl<sub>4</sub> ( $[C_{60}]_0 = 1.6 \cdot 10^{-4}$  mol L<sup>-1</sup>,  $V = 10$  mL,  $T = 298$  K)

$t/\text{min}$	Composition	
	total	without H <sub>2</sub> O
3.5	C <sub>60</sub> H <sub>37</sub> O <sub>31</sub>	C <sub>60</sub> O <sub>14</sub> *
5	C <sub>60</sub> H <sub>19.2</sub> O <sub>25</sub>	C <sub>60</sub> O <sub>16</sub>
15	C <sub>60</sub> H <sub>35.1</sub> O <sub>35.4</sub>	C <sub>60</sub> O <sub>18</sub>
30	C <sub>60</sub> H <sub>40.65</sub> O <sub>51.25</sub>	C <sub>60</sub> O <sub>31</sub>
45	C <sub>60</sub> H <sub>47.12</sub> O <sub>56.48</sub>	C <sub>60</sub> O <sub>33</sub>
60	C <sub>60</sub> H <sub>44.82</sub> O <sub>57.5</sub>	C <sub>60</sub> O <sub>35</sub>

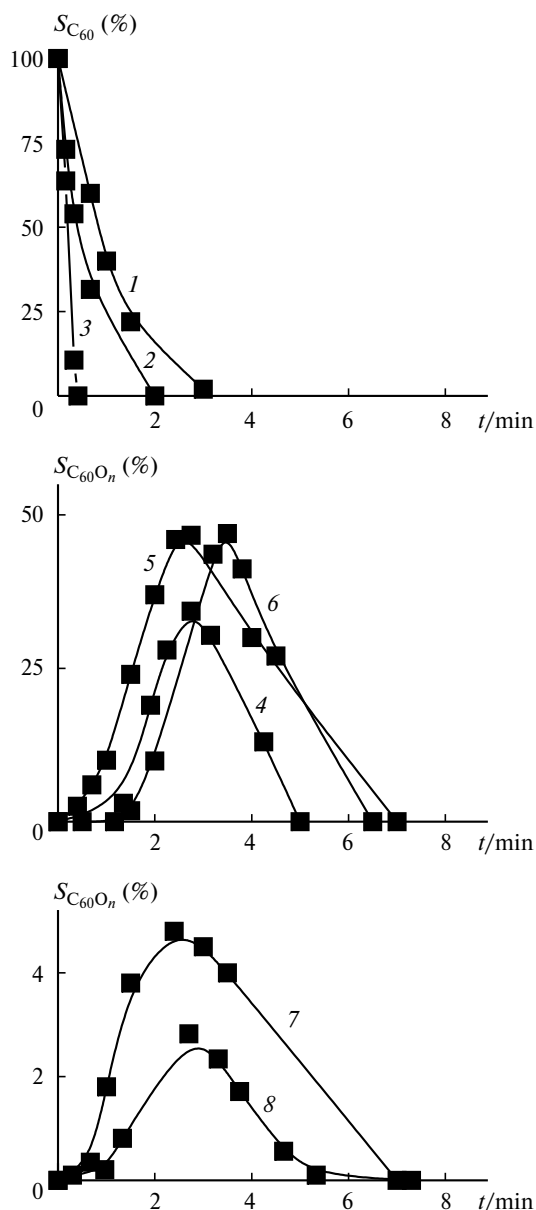
\* Calculated for reacted C<sub>60</sub> taking into account the 72.5% conversion of C<sub>60</sub>.



**Fig. 3.** Chromatograms detected by HPLC for the initial solutions of  $C_{60}$  in toluene (1),  $CCl_4$  ( $1.6 \cdot 10^{-4}$  mol  $L^{-1}$ ) (2), and hexane ( $0.6 \cdot 10^{-4}$  mol  $L^{-1}$ ) (3) (a) and the reaction solutions upon ozonolysis of  $C_{60}$  in toluene (b),  $CCl_4$  (c), and hexane (d). The ozonation time is 0.5 (b), 0.66 (c), and 0.33 min (d). Curve e corresponds to the ozonation of  $C_{60}$  in toluene according to published data<sup>7</sup> (ozonation time is not indicated).

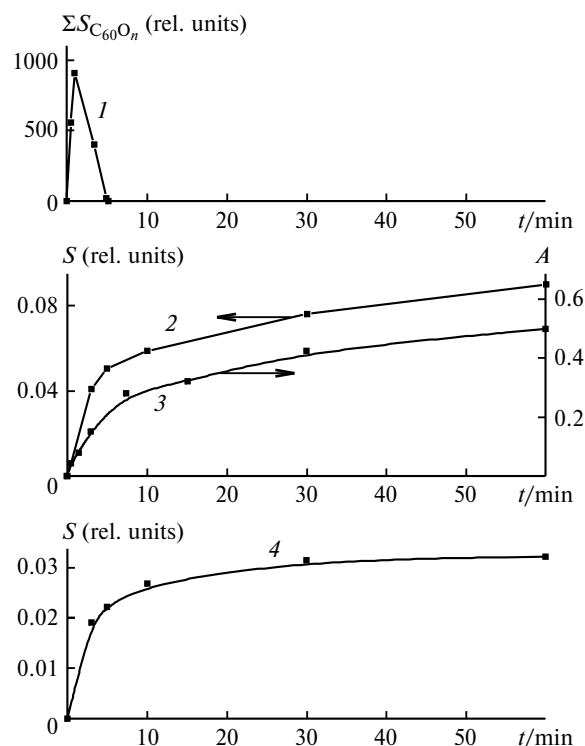
stand, at the first sight, why the rate of  $C_{60}$  disappearance in hexane was higher than that in toluene. As it turned out,  $C_{60}$  disappears from the reaction solution upon ozonolysis due to the chemical transformation into the oxy derivatives and also due to the mechanical capturing into a precipitate, *i.e.*, the absence of  $C_{60}$  in the solution does not imply that it has transformed completely into oxides, which was established by the HPLC analysis of solutions of the reaction precipitates in DCB. After the precipitate

corresponding to the molecular formula  $C_{60}O_{14}$  (see Table 1) was completely dissolved in DCB (stirring for 2 h), the chromatogram of the resulting solution contained peaks of fullerene and its oxides:  $C_{60}$ , 42.1%;  $C_{60}O$ , 43.3%; and  $C_{60}O_2$ , 14.6% (the total areas of the peaks of  $C_{60}$  and epoxides was taken as 100%). The conversion of  $C_{60}$  determined from the difference of the surface areas of the  $C_{60}$  peaks in the chromatograms of a solution of  $C_{60}$  before ozonolysis and a solution of the



**Fig. 4.** Concentrations of  $C_{60}$  and  $C_{60}O_n$  ( $n = 1-5$ ) in the reaction solutions as functions of the ozonolysis time ( $t$ ) according to the HPLC data: content of  $C_{60}$  in toluene (1),  $CCl_4$  ( $[C_{60}]_0 = 1.6 \cdot 10^{-4} \text{ mol L}^{-1}$ ) (2), and hexane ( $[C_{60}]_0 = 0.6 \cdot 10^{-4} \text{ mol L}^{-1}$ ) (3); content of the epoxides  $C_{60}O$  (4),  $C_{60}O_2$  (5),  $C_{60}O_3$  (6),  $C_{60}O_4$  (7), and  $C_{60}O_5$  (8) in toluene. Curves 1–8, change in the areas of peaks ( $S$ ) in the HPLC chromatograms (the area of the initial solution of  $C_{60}$  was accepted for 100% (1–3), the sum of the areas of the peaks of  $C_{60}$  and  $C_{60}O_n$  was taken as 100% (4–8)).

precipitate in DCB is 72.5%. The complete disappearance of  $C_{60}$  in the reaction system (solution and precipitate) occurs at the fifth minute of ozonolysis, and the precipitate corresponds to the molecular formula  $C_{60}O_{16}$  (see Table 1). This precipitate is also dissolved completely on stirring for 2 h in DCB, and its chromatogram con-



**Fig. 5.** Content of the sum of the  $C_{60}O_n$  epoxides ( $n = 1-5$ ), polyketones, and esters as a function of the ozonolysis time ( $t$ ) of  $C_{60}$  solutions in  $CCl_4$  ( $1.6 \cdot 10^{-4} \text{ mol L}^{-1}$ ): sum of the areas of HPLC peaks of the epoxides ( $\Sigma S_{C_{60}O_n}$ ) in solutions obtained by the dissolution of the precipitates in DCB (1), areas of the absorption maxima ( $S$ ) of the  $C=O$  groups at  $1736 \text{ cm}^{-1}$  in the IR spectra of the precipitates (2), absorbance ( $A$ ) at  $\lambda_{\text{max}} = 490 \text{ nm}$  of solutions obtained by the treatment of the precipitates with a solution of 2,4-dinitrophenylhydrazine in MeOH (3),  $S$  of the  $C-O-C$  groups at  $1100-1200 \text{ cm}^{-1}$  in the IR spectra of the precipitates (4).

tains peaks of only two epoxides:  $C_{60}O_2$  (57.14%) and  $C_{60}O_3$  (42.86%) (the total area of peaks of epoxides is taken as 100%). The areas of peaks of these epoxides are 1.13 and 0.85%, respectively, of the area of the initial peak of  $C_{60}$  before oxidation. Upon ozonolysis for more than 5 min, no epoxide peaks are detected in the chromatogram of a solution of the precipitate in DCB (Fig. 5).

Based on the aforesaid, we can conclude that the faster disappearance of  $C_{60}$  in hexane compared to that in toluene is caused by capturing of  $C_{60}$  by the precipitate, which formed more rapidly in this solvent due to the very low solubility of  $C_{60}$  in hexane (therefore, it is necessary to work with saturated solutions). This results in the situation that the chromatograms obtained by HPLC in hexane contain a less number of peaks (only peaks of  $C_{60}$ , a less intense peak of  $C_{60}O$ , and very weak peaks of the  $C_{60}O_2$  isomers are detected) (see Fig. 3).

With an increase in the ozonolysis duration, the solubility of the products in the initial (nonpolar) solvents decreases and their solubility in polar solvents (methanol,

acetone, water) increases. This is related to an increase in the polarity of the products with an increase in the number of the O atoms added to the fullerene cage. The precipitate obtained by the ozonolysis of a solution of  $C_{60}$  in  $CCl_4$  is completely dissolved in water when  $C_{60}O_{18}$  is formed (hereinafter oxygen of adsorbed water is subtracted).

Thus, it has been established for the first time that the ozonolysis of fullerene  $C_{60}$  results in its disappearance from the reaction solution due to two processes: chemical transformation into the oxy derivatives and mechanical capturing to the precipitate. The oxidation of  $C_{60}$  is completed already in the solid phase to the moment of formation of the  $C_{60}O_{16}$  precipitate.

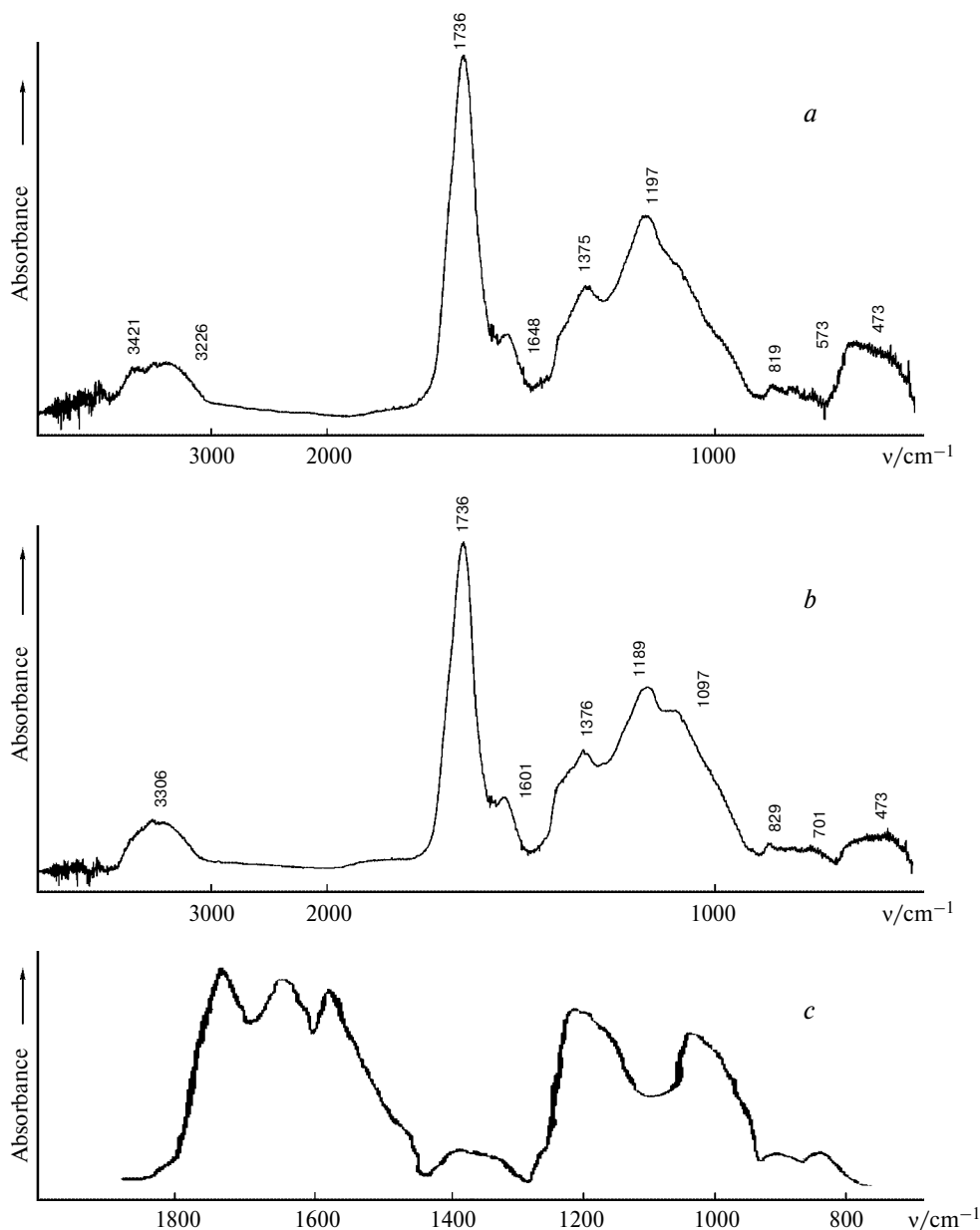
No epoxides are found among the products upon ozonolysis longer than 5 and 7 min (in  $CCl_4$  and toluene, respectively). In fact, for HPLC of a solution of the precipitate (ozonolysis for >5.5 min in  $CCl_4$ ) in DBC, peaks of epoxides are not detected at all. This allows an important conclusion to be made that the epoxides are not predominant products and, moreover, they can be considered as intermediates of the ozonolysis of solutions of  $C_{60}$ , which disappear almost entirely to the moment of complete  $C_{60}$  oxidation to the oxy derivatives.

It is of interest that the  $C_{60}O_n$  epoxides with  $n = 5$  and 6, which are distinctly detected at short exposures of ozonolysis (0.5–3.5 min), are characterized by a low yield compared to  $C_{60}O_n$  ( $n = 1, 2$ ). The epoxides containing seven and more O atoms are not formed upon ozonolysis. However, the fluoro derivatives of  $C_{60}$  containing 18 oxygen atoms, which were obtained by another method, were described.<sup>31</sup>

**IR spectra of products.** The IR spectra of the products of  $C_{60}$  ozonolysis are presented for the first time in Fig. 6. The IR spectra of the reaction solutions (are not presented) and precipitates (see Fig. 6) obtained after the ozonolysis of  $C_{60}$ , regardless of the solvent nature, exhibit the disappearance of the characteristic bands of  $C_{60}$  (1183 (s), 1425 (m), 577 (m), 527  $cm^{-1}$  (m)) and the appearance of the same set of new bands, whose positions undergo no significant changes: 1736 (vs, C=O), 3306–3292 (s) and 1601–1604 (w, OH) (absent from the spectrum of the solution), and 1376  $cm^{-1}$  (w,  $C_{60}-O_2$ ). In addition, an unidentified band appears in the region of 400–700  $cm^{-1}$  (m) with weak maxima at 473 and 573  $cm^{-1}$ . The most intense band at 1736  $cm^{-1}$  unambiguously belongs to the keto group. After the precipitate was heated in a toluene solution of  $Et_3Al$  (110 °C, 7 h), this band disappeared completely, which is characteristic<sup>32</sup> of the reaction of  $Et_3Al$  with aliphatic ketones. The band of C=O primarily appears in the reaction solution before its homogeneity was distorted, it is much more narrow, and its maximum is detected at shorter wavelengths (1711  $cm^{-1}$ ). This is likely related to the fact that polyketones, which are better soluble in the starting sol-

vents, contain a less number of the C=O groups. A broad band at 3306–3292  $cm^{-1}$  (s) and a more narrow band at 1601–1604  $cm^{-1}$  (w) for the precipitate are attributed (by us and authors of Ref. 6) to the OH group of adsorbed water. However, our interpretation of its nature is substantiated by both the elemental analysis data and the appearance of this band in both toluene and  $CCl_4$ . In addition, the spectrum of the solution does not exhibit the band of the OH group even at long exposures of ozonolysis (30 min), which confirms the conclusion about the high hygroscopicity of the precipitate. The intensity of the bands at 3306–3292  $cm^{-1}$  and 1601–1604  $cm^{-1}$  for the IR spectra of the precipitates obtained from solutions in  $CCl_4$  is much higher than that for toluene solutions, which is likely related to the higher solubility of water in the first solvent. We do not exclude that at deep ozonolysis the CO–H groups of the different types can contribute along with water to the absorption at 3306–3292  $cm^{-1}$ . Finally, the last "constant" band at 1376  $cm^{-1}$  is close to that at 1382  $cm^{-1}$  previously<sup>33</sup> assigned to the absorption of molecular oxygen added to the  $C_{60}$  cage on heating of fullerite in air ( $\geq 523$  K), which, according to the conclusion,<sup>33</sup> decreases the symmetry to induce the IR activity of  $O_2$  molecules. We believe that the assignment of the band at 1376  $cm^{-1}$  similar to that in published data<sup>33</sup> is reasonable from several common properties of the samples obtained by us by ozonolysis and in Ref. 33 by the treatment of fullerite with oxygen, namely, the presence of epoxide and carbonyl groups linked to the fullerene cage. We assign the short-wave shift of the band at 1376  $cm^{-1}$  (relatively to the band at 1382  $cm^{-1}$ ) to a higher degree of symmetry decrease due to the great distortion of the  $C_{60}$  cage during ozonolysis of its solutions compared to the fullerite sample subjected to oxygen. This is confirmed by the fast disappearance upon ozonolysis of the IR bands characterizing the electronic structure of the  $C_{60}$  cage (1183, 1425, 577, and 527  $cm^{-1}$ ), while these bands are retained<sup>33</sup> for a longer time upon treatment with oxygen.

In addition to these "constant" bands, other bands are also observed, whose position changes with an increase in the ozonolysis duration. For example, an intense broad single band at 1197  $cm^{-1}$  (vs) detected at the fifth minute of ozonolysis becomes more intense (30th min) and is broadened and split into two components: a band at 1189  $cm^{-1}$  (m) and a shoulder at 1097  $cm^{-1}$  (m) (see Fig. 6). Later (60th min) these components are transformed into two bands at 1104 and 1178  $cm^{-1}$  (are not presented). The band at 1197–1200  $cm^{-1}$  cannot belong to fullerene, because it is much broader than the very narrow fullerene band (closest to the band under discussion) at 1187  $cm^{-1}$ , and such a great shift (by 10  $cm^{-1}$ ) is not characteristic<sup>9,34,35</sup> of transformations of the C=C bonds of the fullerene cage into the C–C bond. The assignment of the band at 1197  $cm^{-1}$  to the epoxide ring



**Fig. 6.** IR spectra of the precipitates obtained after 5 (a) and 30 min (b) of ozonolysis of C<sub>60</sub> solutions in CCl<sub>4</sub> or toluene ( $1.6 \cdot 10^{-4}$  mol L<sup>-1</sup>) and the fullerene nanotube after ozonation (98 min) (c). The intensities of maxima of spectra a and b are matched.

linked with the C<sub>60</sub> cage (the "epoxide" band of hydrocarbons appears<sup>36</sup> at 1250  $\text{cm}^{-1}$ ) can be ruled out on the basis of analysis of published data.<sup>9,34,35</sup> Indeed, the IR spectra of the C<sub>60</sub>O and C<sub>60</sub>O<sub>2</sub> epoxides obtained by the photo-oxidation of a benzene solution of C<sub>60</sub> with oxygen<sup>34</sup> and by the oxidation of toluene solutions of C<sub>60</sub> with *m*-chloroperbenzoic acid<sup>9</sup> or methyl(trifluoromethyl)dioxirane,<sup>35</sup> respectively, do not contain this band. In addition, the spectra of these epoxides contain bands at 1427.8, 1184.6, 575.4, and 526.0  $\text{cm}^{-1}$ , whose position is almost the same as that of the corresponding bands of C<sub>60</sub>, and

they are only insignificantly broadened, although remain rather narrow. In the spectra obtained, the bands of C<sub>60</sub> disappear very rapidly (for 30 s), indicating that the fullerene cage is decomposed during ozonolysis due to the cleavage of both  $\pi$ - and  $\sigma$ -components of the C=C bonds of hexagons, while in the spectra of the epoxides the  $\sigma$ -component, according to published data,<sup>9,34,35</sup> is retained. According to the known data for hydrocarbons,<sup>22</sup> the absorption bands obtained by us for the precipitates at 1100–1200  $\text{cm}^{-1}$  could also belong to vibrations of the C—O bonds of compounds containing AO (peroxides,



ozonide). However, after the precipitates were heated (80 °C, 1 h), the intensity of the band at 1100–1900  $\text{cm}^{-1}$  remains virtually unchanged. The same assignment can be valid for the band at 1100–1900  $\text{cm}^{-1}$ , whose intensity is enhanced with an increase in the ozonolysis exposure along with the intensity of the band at 1736  $\text{cm}^{-1}$ , *i.e.*, it can be attributed to vibrations of the C–C bonds in the C–C=O species, as it has been made previously<sup>37</sup> for diketone  $\text{C}_{60}(\text{=O})_2$  obtained by the argon laser irradiation of the  $\text{C}_{60}$  film supported on KBr in an  $\text{O}_2$  atmosphere. However, the band maximum observed in Ref. 37 lies at a shorter wavelength (1000  $\text{cm}^{-1}$ ). Therefore, it seems more correct to assign the band at 1100–1200  $\text{cm}^{-1}$  to vibrations of the C–O–C group of ester. The argument in favor of this assignment is provided by published results,<sup>38</sup> according to which the band at 1200  $\text{cm}^{-1}$  in the IR spectrum of the product of ozonolysis of the fullerene nanotube (see Fig. 6) was also assigned to the C–O–C group of ester. Note that the spectrum of the ozonated nanotube<sup>38</sup> and the spectra obtained by us for ozonolysis of  $\text{C}_{60}$  solutions have several common features (see Fig. 6): 1739 and 1736  $\text{cm}^{-1}$  (C=O), 1380 (in Ref. 38 this band was not identified), 1200, and 1100–1200  $\text{cm}^{-1}$  (C–O–C). However, the IR spectra compared exhibit distinctions. For example, our spectrum contains no bands at 1650 (C=O vibrations of quinoid structures), 1581 (C=C), and 925  $\text{cm}^{-1}$  (was not identified<sup>38</sup>). It is of interest that the band at 1650  $\text{cm}^{-1}$  has<sup>38</sup> almost the same intensity as the band at 1739  $\text{cm}^{-1}$ . We believe that our assignment of the band at 1601–1604  $\text{cm}^{-1}$ , which is closest to the band at 1581  $\text{cm}^{-1}$ , to the absorption of adsorbed water rather than to vibrations of the C=C bond is correct, because the number of C=C bonds decreases and the absorption intensity at 1601–1604  $\text{cm}^{-1}$  increases along with the absorption at 3306–3292  $\text{cm}^{-1}$  with an increase in the ozonolysis time of solutions of  $\text{C}_{60}$ .

The comparison of the IR spectra of the precipitates obtained by the ozonolysis of  $\text{C}_{60}$  solutions and the IR spectra of the epoxides presented previously<sup>9,34,35</sup> demonstrated that these spectra are absolutely different. This is one more evidence that the epoxides are not predominant products of the ozonolysis of  $\text{C}_{60}$ .

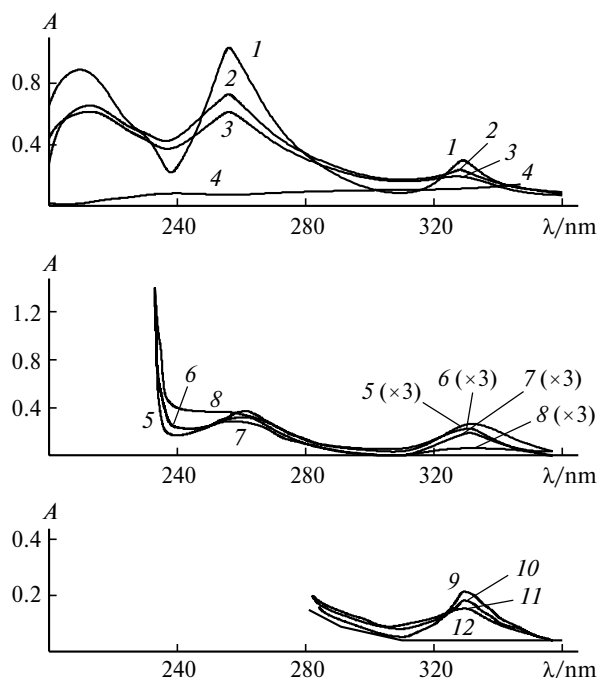
For the additional identification of polyketones among the ozonolysis products of  $\text{C}_{60}$  solutions, we applied for the first time the colorimetric method, which has previously been used<sup>22,23</sup> to identify aliphatic carbonyl compounds. After dissolution of the solid precipitates in MeOH and treatment of this solution with a methanolic solution of 2,4-dinitrophenylhydrazine, the solution gains a cherry color characteristic of 2,4-dinitrophenylhydrazones. Successful analysis is favored by the high solubility of the solid oxidate in MeOH (the complete solubility is achieved after 15 min of ozonolysis when  $\text{C}_{60}\text{O}_{18}$  is formed). As can be seen from the data in Fig. 5, the

kinetic curves of polyketone accumulation obtained by measuring the intensity of the absorption bands of the cherry-colored solution at 490 nm and 1736  $\text{cm}^{-1}$  are parallel for the precipitates and demonstrate a continuous increase in the content of the C=O groups during the whole ozonolysis process (1 h).

Thus, the formation of polyketones and esters begins in the liquid phase and continues in the solid phase with an increase in the number of C=O groups linked to the fullerene cage.

The identical IR absorption spectra of the products obtained by the ozonolysis of  $\text{C}_{60}$  solutions in toluene and  $\text{CCl}_4$  provide an important conclusion that the presence of a hydrogen-containing substrate in a solution is not necessary for the formation of ketones and polyketones. Therefore, there are other routes of formation of carbonyl derivatives of  $\text{C}_{60}$  in addition to the reaction proposed<sup>6</sup>: epoxidation of hydrogen-containing solvents or aromatic additives by the ozonolysis intermediate oxofullerene-carbonyloxide. Moreover, in solvents containing no hydrogen, such as  $\text{CCl}_4$ , the formation of polyketones *via* the mechanism of solvent epoxidation<sup>6</sup> is completely ruled out.

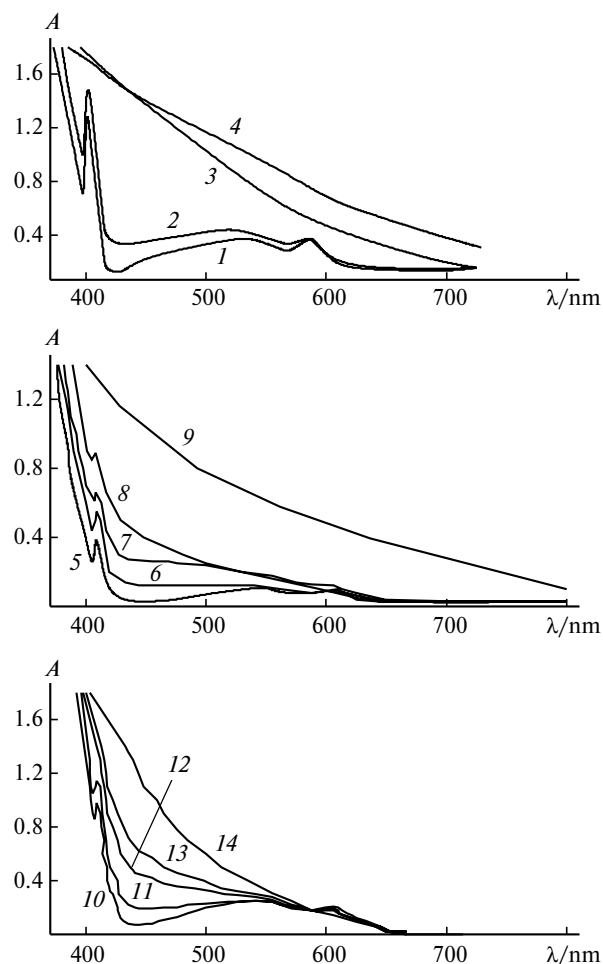
**Decomposition of the  $\text{C}_{60}$  cage during ozonolysis.** In addition to IR bands, three UV bands in the absorption spectra of solutions at 208, 256, and 330 nm are<sup>9,34,35,39</sup> the characteristic properties of the electronic structure of the  $\text{C}_{60}$  cage. Therefore, to solve the problem about the stability of the  $\text{C}_{60}$  cage toward ozone, we measured the absorption spectra at different exposures of  $\text{C}_{60}$  ozonolysis in hexane,  $\text{CCl}_4$ , and toluene. Already at the first seconds of ozonolysis of  $\text{C}_{60}$  solutions in hexane, the intensity first decreases, and then the bands at 208, 256, and 330 nm disappear completely (Fig. 7). An analogous situation is observed for the ozonolysis of  $\text{C}_{60}$  in other solvents (see Fig. 7), *i.e.*, the bands at 256 and 330 nm disappear gradually. The smaller number of bands detected in these solvents compared to hexane is caused by the intrinsic absorption of  $\text{CCl}_4$  and toluene in the region of observation of the corresponding bands of  $\text{C}_{60}$ . The following changes in the characteristic bands of  $\text{C}_{60}$  are observed in the long-wave region of the spectrum during ozonolysis: a decrease in the intensity and gradual disappearance of a sharp peak at 408 nm and broader maxima at 540 and 600 nm (Fig. 8). As known, the  $\text{C}_{60}\text{O}_n$  epoxides ( $n = 1\text{--}4$ ), obtained by the photooxidation of a benzene solution of  $\text{C}_{60}$  with oxygen<sup>34</sup> and the oxidation of a toluene solution of  $\text{C}_{60}$  with *m*-chloroperbenzoic acid<sup>9</sup> or oxidation of fullerene with PhOI in the presence of the  $\text{Fe}^{\text{III}}$  complexes as catalysts (cytochrome P450),<sup>40</sup> exhibit the cleavage of the  $\pi$ -component of the C=C bonds and retention of the C–C bond, due to which the bands of  $\text{C}_{60}$  at 208, 256, and 330 nm remain in the UV spectral region, and a sharp peak at 424 nm appears in the long-



**Fig. 7.** UV absorption spectra of the reaction solutions upon ozonolysis of C<sub>60</sub> in hexane (1–4), CCl<sub>4</sub> (5–8), and toluene (9–12): ozonolysis time 0 (1, 5, 9), 3 (2), 5 (3), 10 (6, 10), 12 (4), 20 (7, 11), and 40 s (8, 12); *l* = 0.1 (1–4) and 0.01 cm (5–12). [C<sub>60</sub>]<sub>0</sub> =  $6 \cdot 10^{-5}$  (1) and  $1.6 \cdot 10^{-4}$  mol L<sup>-1</sup> (5, 9).

wave part of the spectrum instead of the sharp peak of C<sub>60</sub> at 408 nm. Comparison of these data and results of our spectrophotometric study of the ozonolysis of C<sub>60</sub> solutions suggests the following. First, epoxides are not predominant stable reaction products; otherwise, all three bands of C<sub>60</sub> would retain in the UV part of the spectrum, as it takes place for the oxidation of C<sub>60</sub> with other oxidants. Second, ozonolysis decomposes the C<sub>60</sub> cage due to the cleavage of the  $\pi$ - and  $\sigma$ -components of the C=C bonds with hexagon opening and formation of two carbonyl groups at its ends. The latter is confirmed by our data on the detection of a band at 1736 cm<sup>-1</sup> for the products and a band at 490 nm appeared after the treatment of the oxidate with 2,4-dinitrophenylhydrazine (see above).

**Chemical analysis of ozonolysis products of a C<sub>60</sub> solution in CCl<sub>4</sub>.** The above-described results of testing the products of C<sub>60</sub> ozonolysis by HPLC, elemental analysis, and UV–IR spectrophotometry were confirmed by chemical analyses of the precipitates obtained at the fifth minute of ozonolysis, *i.e.*, to the moment of complete transformation of C<sub>60</sub> into solid oxy derivatives with the molecular formula C<sub>60</sub>O<sub>16</sub>. As shown above, the products are absent from a solution to this moment. The number of epoxide oxygen atoms established by the hydrochlorination of the precipitate with a solution of HCl and the subsequent determination of the decrease in the acid by



**Fig. 8.** Absorption spectra of the reaction solutions upon ozonolysis of C<sub>60</sub> in the visible region in hexane (1–4), CCl<sub>4</sub> (5–9), and toluene (10–14): ozonation time 0 (1, 5, 10), 3 (2), 5 (3), 9 (4), 10 (6), 15 (11), 20 (7, 12), 40 (8, 13), and 60 s (9, 14). [C<sub>60</sub>]<sub>0</sub> =  $6 \cdot 10^{-5}$  (1) and  $1.6 \cdot 10^{-4}$  mol L<sup>-1</sup> (5, 10).

titration with a solution of NaOH turned to be 0.32 (2%). The number of ester oxygen atoms is much greater (equal to 6), which was determined by the saponification of the precipitate with a solution of KOH followed by the titration of the unreacted alkali with HCl. The number of carbonyl oxygen atoms (9.68) was determined from the difference between the total number of O atoms (16) and the total number of epoxide (0.32) and ester (6) O atoms. The yield of polyketones and esters is 60.5 and 37.5%, respectively. The results of chemical analyses agree well with the larger area of the absorption band of the C=O groups at 1736 cm<sup>-1</sup> compared to the area of the C–O–C groups at 1100–1200 cm<sup>-1</sup> in the IR spectra of the precipitates and very small areas of HPLC peaks of the epoxides for solutions of these precipitates in DCB. Therefore, the predominant products of ozonolysis of C<sub>60</sub> solutions are polyketones and esters, whose content increases

during the whole process (see Fig. 5), while the content of the epoxides reaches a maximum after ~1 min and equals zero to the moment, which insignificantly exceeds the time necessary for the 100% conversion of C<sub>60</sub>.

The results of the present study show that the ozonolysis of C<sub>60</sub> solutions produces polyketones and esters with the controlled number of carbonyl and ester O atoms added to the fullerene cage. Polyketones and ester are of interest for testing the biological activity and as photosensitizers due to their high solubility in water. In addition, they are promising as basic reagents for the synthesis of polyfunctional fullerene derivatives using the experience on the transformation of hydrocarbon ketones and esters. It is established that toluene, which is often used as a solvent in many reactions of C<sub>60</sub>, is less appropriate for the preparation of oxy derivatives by the ozonolysis of C<sub>60</sub> because of the side reaction of ozone with toluene. The optimum medium for the preparative controlled synthesis is CCl<sub>4</sub> in which by-products are not formed.

It should be noted in conclusion that our identification of polyketones and esters as the main stable products proves that the results of the known quantum-chemical calculations,<sup>13,16,18</sup> which indicate that the epoxides are the main ozonolysis products of C<sub>60</sub> solutions, are inconsistent with the experimental data.

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