Formation of secondary fullerene ozonides in the ozonolysis of C_{60} solutions and chemiluminescence upon their hydrolysis

R. G. Bulgakov,[a]★ E. Yu. Nevyadovsky,[a] Yu. G. Ponomareva,[a] D. Sh. Sabirov,[a] and S. D. Razumovsky[b]

[a] *Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru*

[b] *N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 119991 Moscow, Russian Federation*

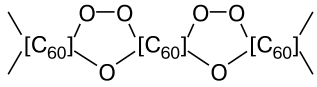
The formation of secondary fullerene ozonides (SFOs) in the ozonolysis of C_{60} solutions in CCl_4 has reliably been determined for the first time; SFOs are accumulated during the whole ozonolysis time as a suspension in CCl_4. Hydrolysis of the SFOs results in chemiluminescence (CL) ($I_{max} = 2.65 \cdot 10^8$ photon s^{-1} mL^{-1}), whose spectra contain maxima at 558, 608, and 685 nm. The most probable CL emitters are excited fullerene polyketones. Hydrogen peroxide was identified as a stable hydrolysis product of the SFOs by the color reaction with diphenylcarbazide and CL arisen upon the addition of an aqueous solution of $FeSO_4 \cdot 9H_2O$ to the hydrolyzate of the SFO. Chemiluminescence upon hydrolysis is a selective test for SFOs and allows one to find them in a complex mixture of the ozonolysis products of C_{60}. The rate constant and activation energy of SFO hydrolysis were determined from the kinetic measurements of CL. For SFO hydrolysis several probable reactions were proposed, including the formation of the CL emitters, and their heat effects were estimated using the PM3/RHF and AM1/RHF semiempirical methods for one- and two-cage model structures of SFOs.

Key words: fullerene C_{60}, secondary ozonides, hydrolysis, chemiluminescence.

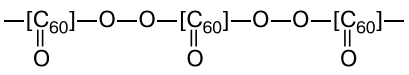
Most progress in studying the mechanism and ozonolysis products of fullerenes was achieved in the identification and studies of properties of primary fullerene ozonides (molozonides) $C_{60}O_3$ **1** and $C_{70}O_3$ **2** formed upon ozonolysis (at 0 and −16 °C) of fullerene solutions due to the addition of ozone to the [6,6]-bond (C=C) of hexagons. Molozonides rapidly decompose to epoxides $C_{60}O$ ($C_{70}O$) and oxygen. As known,[3,4] much more stable (even at 293—298 K) secondary ozonides are formed upon hydrocarbon ozonolysis due to the rearrangement of unstable molozonides. A question about the formation and identification of secondary fullerene ozonides (SFOs) or other fullerene derivatives containing active oxygen, *i.e.*, O—O group, remains unanswered until presently for several reasons.[5,6]

First, the structures of these compounds are interpreted ambiguously, *i.e.*, they are presented simultaneously as ozonides, peroxides, and bisperoxides.[5,6] Therefore, fullerene derivatives containing active oxygen are presented[5] by three various methods (structures **I**, **II**, and **III**; symbol [C_{60}] designates an open cage linked to the carboxyl and ketone groups). Note that only structure **I** contains the ozonide (1,2,4-trioxolane) cycle.

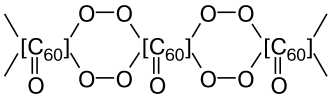
Second, arguments[5,6] in favor of SFO formation seem to be insufficient because of the following concepts. According to published data,[5,6] the main property indicating



I



II



III

the formation of SFO is the appearance of a band at 1090 cm^{-1} in the IR spectra of the solid ozonolysis products of C_{60} solutions and its disappearance on heating and treatment with chemical reagents. It should be noted that this band (more exactly, it should be named a shoulder) is weak and detected against the background of the much stronger band of ethers at 1213 cm^{-1}. The band at 1090 cm^{-1} disappeared only at very high temperature (573 K)[5] or upon the treatment of the solid ozonolysis product[5] with a 7% aqueous solution of KI or ultra-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1322—1329, August, 2006.

1066-5285/06/5508-1372

sonication of its solution in an AcOH + H_2O mixture followed by reflux for 3 h with zinc powder at 373 K.[6] This drastic treatment results in the disappearance of the band at 1090 cm^{-1} and also in substantial changes in the adjacent, more intense bands in the IR spectra of the ozonolysis products. For instance, after heating of the precipitates (573 K), the bands at 1213 and 1396 cm^{-1} are shifted to 1227 and 1385 cm^{-1}, respectively. The above described treatment of the ozonolysis products results in the appearance of several narrow low-intensity peaks (their nature is not discussed) at 1400—500 cm^{-1}, precisely in the region containing (before the treatment) an intense band at 1213 cm^{-1} with a weak band at 1090 cm^{-1} in the descending branch. As follows from Ref. 5, SFOs are stable on storage under ambient conditions. Such a remarkably high stability of the SFOs seems surprising because organic[7,8] and inorganic compounds containing active oxygen decompose, as a rule, at $T \leq 150$ °C. It is difficult to explain stability of SFOs because of high strain of the spherical structure of the fullerene cage. The conclusion about the formation of fullerene derivatives containing active oxygen was made[5] on the basis of iodometric titration of an aqueous solution of the precipitate obtained by the ozonolysis of C_{60} solutions in toluene. However, it has earlier been shown[9] that the determination of "fullerenic" active oxygen by iodometric titration of the ozonolysis products of toluene solutions of C_{60} is problematic because of the low content of this active oxygen caused by a low concentration of fullerene ($[C_{60}]_0 \leq 10^{-3}$ mol L^{-1}). Due to this, "fullerenic" active oxygen is disguised by large amounts (up to 10^{-1} mol L^{-1}) of active oxygen, being the oxidation product of toluene with ozone.

To establish more reliably the formation of fullerene derivatives containing active oxygen upon ozonolysis of C_{60} solutions and to identify the nature of these compounds, specifically attributing them to peroxides, bisperoxides, or ozonides, we studied the effect of KI solutions, water, and temperature on the ozonolysis products of C_{60} solutions in CCl_4 using traditional dark physicochemical analytical and chemiluminescence (CL) methods, whose efficiency in studying the properties of hydrocarbons containing active oxygen is well known.[10—12]

Experimental

Purity of fullerite C_{60} (99.9%, synthesized by the electric arc method at the G. A. Razuvaev Institute of Organometallic Chemistry, Nizhnii Novgorod) was monitored by a known method[9]; O_3, CCl_4, and Ar were purified as described earlier[9]; H_2SO_4, $K_2Cr_2O_7$, HCl, $Na_2S_2O_3$, $FeSO_4 \cdot 9H_2O$, 35% solution of H_2O_2, Et_2O, diphenylcarbazide (high-purity grade), I_2 (reagent grade), and water (bidistillate) were used. For synthesis of C_{60} derivatives containing active oxygen, solutions of C_{60} in CCl_4 ($[C_{60}]_0 = 1.6 \cdot 10^{-4}$ mol L^{-1}) were oxidized with ozone[9] in a CL cell. Depending on the ozonolysis exposure (OE), we obtained either homogeneous solutions (OE ≤ 0.5 min) or a suspension of brown precipitates (OE ≥ 2 min) containing, in addition to active oxygen, fullerene expoxides, polyketones, and polyethers, whose analysis have been described in detail earlier.[9] The "fullerenic" active oxygen in these products was analyzed using a modified iodometric spectrophotometric procedure[13—15] used for analysis of active oxygen in hydrocarbons. For this purpose, the liquid or solid products were treated with a solution of KI in an AcOH (10 mL) + H_2O (1 mL) mixture and stored for 10 min in the dark under argon. Then the absorbance of the solution in 0.1-cm quartz cells was measured at λ_{max} = 360 nm relative to water. The content of active oxygen was calculated from the calibration line ($R = 0.986$) of the dependence of the absorbance on the iodine concentration in the mixture prepared by dissolution of a weighed sample of I_2 (0.03540 g) in an AcOH (50 mL) + H_2O (5 mL) mixture. Before hydrolysis (immediately after ozonolysis) a residue of O_3 was removed with argon passed through the solution for 15 min. Hydrolysis was carried out in the same CL cell with the optically transparent bottom. The cell was placed in a light-proof chamber of an installation for CL measurements. Temperature was measured with a copper—constantan thermocouple. Ozonolysis products (solid or their suspension in CCl_4) were hydrolyzed using two methods. In the first case, water (1 mL, T = 293 K) was fed by a doser to a CL cell filled with a suspension of solid ozonolysis products in CCl_4 (20 mL, T = 293.8 K). In the second case, a thoroughly stirred suspension of solid ozonolysis products in CCl_4 (1 mL, T = 273—293.8 K) was fed within 0.5 s by a doser to a cell with CCl_4 (10 mL, T = 293.8—338.5 K) and water ($1 \cdot 10^{-2}$ mol L^{-1}, analysis according to Fischer[16]). After hydrolysis the IR spectra of solid precipitates, which were formed after water removal from the hydrolyzates *in vacuo* (1 Torr, T = 293 K), were measured in parallel experiments, and solutions prepared by dissolution of similar precipitates in CCl_4 were studied by HPLC. Procedures of HPCL and IR spectroscopy have been described earlier.[9] Hydrogen peroxide in the SFO hydrolyzate was carried out[17] was qualitatively determined from the appearance of the red-violet color in the ethereal layer formed upon the addition to the hydrolyzate of an aqueous solution of H_2SO_4 (0.9 mol L^{-1}), diethyl ether, a 5% aqueous solution of $K_2Cr_2O_4$, and diphenylcarbazide. An installation for CL and procedures for measuring the kinetics and CL spectra have been described earlier.[18] Absorption spectra were recorded on Specord M-40 (UV and visible regions) and Specord IR-75 (IR region) spectrophotometers. ^1H NMR spectra were measured on a Jeol FX-90Q spectrometer (D_2O as solvent, acetone as internal standard).

Results and Discussion

Spectrophotometric determination of fullerene derivatives containing active oxygen. Specific features of iodometric analysis of SFOs are not discussed in Ref. 5. We found that after dissolution in water of the solid ozonolysis products (or their suspensions in CCl_4) intensely colored dark brown solutions (aqueous phase) were formed even at rather low fullerene concentrations ($[C_{60}]_0 = 1.6 \cdot 10^{-4}$ mol L^{-1}). In thin layer (0.1 cm) these solutions do not absorb in the visible spectral region. Their absorption spectra at first time are presented in Fig. 1.

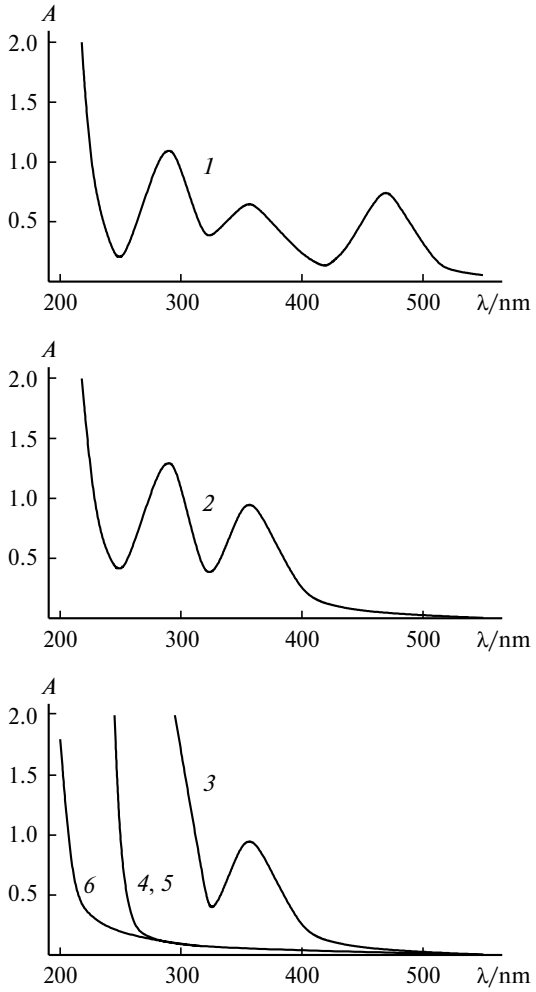


Fig. 1. Absorption spectra of solutions of I_2 (*1—3*) and ozonolysis products of C_{60} (*4—6*): a solution of I_2 in an AcOH—H_2O (10 : 1 vol/vol) mixture in the absence (*1*) and presence of KI ($3 \cdot 10^{-1}$ mol L^{-1}) (*2*); a solution of the ozonolysis products of C_{60} in CCl_4 after addition of 1 mL of a 50% solution of KI in H_2O and 10 mL of AcOH (*3*); a solution of the ozonolysis products of C_{60} in CCl_4 after addition of 1 mL of H_2O and 10 mL of AcOH (*4*) followed by addition of 1 mL of H_2O (*5*) and subsequent dilution with water by 15 times (*6*); l = 0.1 cm, rate of ozone supply $W(O_3)$ = 1.4 mmol h^{-1}, T = 293 K, $[C_{60}]_0$ = $1.6 \cdot 10^{-4}$ mol L^{-1}.

The intense color of the solution impedes visual determination of active oxygen. No distinct substantiation of application of these or another maxima of I_2 to spectrophotometric analysis of organic peroxides and no absorption spectra are available from literature.[13—15] We carried out preliminary experiments on studying the effect of the medium on the absorption spectra of I_2. For instance, the absorption spectrum of a solution of I_2 in an AcOH—H_2O mixture has three absorption maxima at 286, 360, and 470 nm, while only two maxima at 286 and 360 nm are observed in the presence of KI (see Fig. 1). It is known[13] that I_2 with KI forms the KI_3 complex and, hence, the

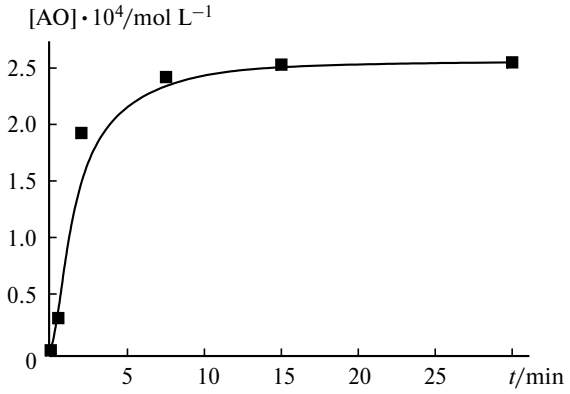


Fig. 2. Change in the SFO content at different durations of ozonolysis of C_{60} solutions in CCl_4; AO is active oxygen.

disappearance of the maximum at 470 nm in the presence of KI is due to the absence of free I_2 in the solution because KI_3 is formed. When I_2 is treated with $Na_2S_2O_3$ in an AcOH—H_2O mixture in both the absence and presence of KI, all absorption bands disappear. Therefore, all the three absorption bands are appropriate for determination of I_2; however, since this procedure is carried out in excess KI, active oxygen in the fullerene derivatives was analyzed by λ_{max} = 360 nm.

Thus, the formation of fullerene derivatives containing active oxygen upon ozonolysis of a solution of C_{60} in CCl_4 has reliably been determined for the first time. The concentration of "fullerenic" active oxygen increases during the whole ozonolysis time (Fig. 2), as well as the content of fullerene polyketones and polyethers.[9]

Chemiluminescence upon hydrolysis of SFOs. We have found[19] the CL arisen upon the hydrolysis of liquid and the solid ozonolysis products of C_{60} solutions. Regardless of the type of methods for mixing reactants, the CL is detected as a narrow (0.3—0.5 min) maximum with I_{max} = $2.65 \cdot 10^8$ photon s^{-1} mL^{-1} at T = 293.8 K (Fig. 3).

In the present work, we performed more thorough measurements of the CL spectra. Unlike the data in Ref. 19, two shorter-wavelength maxima at 608 and 558 nm along with the maximum at 685 nm were detected in the CL spectrum (see Fig. 3). Coincidence of λ_{max} = 685 nm with the wavelength of the maximum of the known[18] CL spectrum observed upon the ozonolysis of C_{60} solutions and the positions of maxima at 608 and 558 nm in a longer-wavelength region (compared to the CL spectra of hydrocarbon ketones[10—12]) indicate that the electron-excited states of fullerene polyketones are the most probable CL emitters.

After water was added to a suspension of the solid ozonolysis products of C_{60} in CCl_4 (the volume ratio is equal to unity, T = 273—338.5 K), they are completely dissolved to form two liquid phases: aqueous (brown-colored) and CCl_4 (colorless). All the oxygen-containing C_{60} derivatives are completely transferred to the aqueous

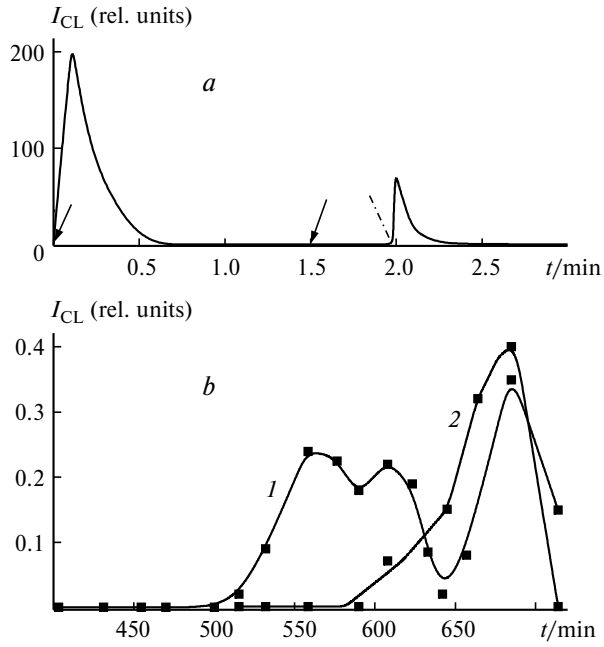


Fig. 3. *a*. Kinetics of the CL during SFO hydrolysis; arrows mark the moments of pouring an aliquot of H_2O (1 mL), and the dash-and-dot line indicates the moment of addition of 1 mL of an aqueous solution of $FeSO_4 \cdot 9H_2O$ ($[Fe^{2+}]_0 = 10^{-2}$ mol L^{-1}); *b*. Spectra of the CL during SFO hydrolysis (*1*) measured in the descent of the curve (see Fig. 3, *a*) and during ozonolysis of a C_{60} solution in CCl_4 (*2*). The CL spectra were measured using boundary light filters.

phase, which is indicated by the absence of the corresponding absorption bands[9] in the UV and IR spectra of the CCl_4 phase and any residues after its evaporation. Unlike published data[20] according to which the absorption spectra of aqueous solutions of the ozonolysis products of solutions of C_{60} contain a series of maxima in the short-wavelength spectral region (at 200—235, 250, 270, 305, and 340 nm), our spectra have no maxima but represent continuums descending from 200 nm. Remind that no spectra are presented and only positions of maxima are given in Ref. 20. After the solvent was removed from the aqueous phase, a brown precipitate remains. In its IR spectrum, positions and intensities of the absorption bands of the ketone (1736 cm^{-1}) and ether (1200 cm^{-1}) groups coincide with similar bands in the IR spectrum[9] of the ozonolysis products of C_{60}. The only distinction between them is somewhat higher intensity of the band at 3340 cm^{-1} (OH) for the precipitate obtained from an aqueous solution, which is caused by the presence of a larger amount of adsorbed water. Other ozonolysis products, namely, $C_{60}O_n$ epoxides, do not enter into the reaction with water (T = 273—338.5 K). For example, according to the HPLC data, the content (%) of epoxides and unreacted C_{60} in the solution (no precipitates are observed at OE = 0.5 min) is the same before and after hydrolysis: C_{60}, 5.26; $C_{60}O$, 90.28; $C_{60}O_2$, 4.19; $C_{60}O_3$, 0.24; $C_{60}O_4$, 0.026. In addition, the CL intensity is minimum when water is added to a solution containing the maximum amount of epoxides (OE = 0.5 min).

These results indicate that fullerene polyketones, polyethers, and epoxides do not react with water and undergo no thermal decomposition under conditions of CL observation (T = 273—338.5 K). Therefore, we relate the appearance of the CL to the reactions of water with fullerene derivatives containing active oxygen.

Organic peroxides, hydroperoxides, and bisperoxides, as a rule, do not react with water,[7,8] whereas hydrocarbon ozonides react with water with the cleavage of the O—O bond and formation of compounds bearing the carbonyl group.[3] Taking into account these data and our results, we can assert that the CL observed is caused by the reaction of water just with SFOs. The detection of CL during hydrolysis is the first unambiguous experimental proof for the fact that the fullerene derivatives containing active oxygen are the SFOs.

The name "fullerene ozonides" are rather conventional. We use this term by analogy to the commonly accepted "benzene ozonide," which is also conventional (taking into account that benzene ozonolysis results in the complete destruction of the aromatic ring).[3]

It should be noted that the CL found by us during hydrolysis was known for neither SFOs nor other classes of ozonides, which follows from analysis of published data.[10—12] Therefore, the emission appeared upon hydrolysis of SFOs is a new type of CL.

The curve of CL descend upon fullerene ozonide hydrolysis can be linearized well in the coordinates of the known[10] first-order equation

$$I = k_1[H_2O][SFO]H_{CL}, \quad (1)$$

where I is the CL intensity during hydrolysis, k_1 is the rate constant of SFO hydrolysis, and H_{CL} is the overall yield of CL.

The k_1 value determined from the slope of the linear (R = 0.99) plot of the I_0/I ratio *vs.* time is equal to $1.8 \cdot 10^{-3}$ s^{-1} (T = 293.8 K). Taking into account that water for hydrolysis is taken in large excess over the SFOs, we can write

$$I = k_2[SFO]H_{CL}, \quad (2)$$

where

$$k_2 = k_1[H_2O]. \quad (3)$$

The water concentration in CCl_4 determined by the Fischer method[16] is 10^{-2} mol L^{-1}. The rate constant of SFO hydrolysis was calculated by Eq. (3) from this value: $k_2 = 1.8 \cdot 10^{-5}$ mol L^{-1} s^{-1} (T = 293.8 K). The activation energy E_a = 10.9±1 kcal mol^{-1} was determined from the slope of the linear (R = 0.97) plot (Fig. 4) obtained in the $\log I_0 - T^{-1}$ coordinates upon the addition of an aliquot

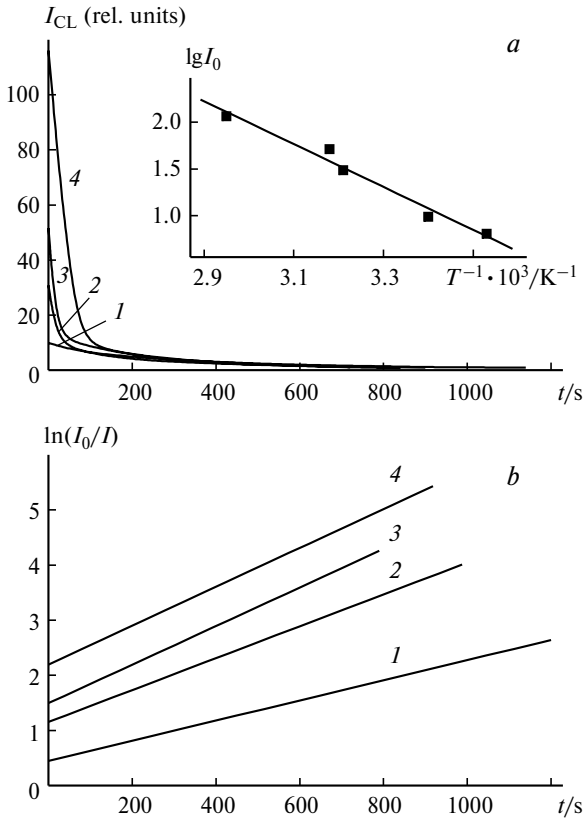


Fig. 4. Time plots of the CL intensity during SFO hydrolysis (*a*) and their linear anamorphoses in the $\ln(I_0/I)$—time coordinates (*b*): 293.8 (*1*), 311.4 (*2*), 317.4 (*3*), and 338.5 K (*4*); I_0 is the maximum CL intensity after addition of 1 mL of a SFO suspension ($T = 293$ K) to 10 mL of a solution of H_2O in CCl_4 ($[H_2O]_0 = 10^{-2}$ mol L^{-1}, $T = 293.8$—338.5 K). Inset: the plot of the maximum CL intensities during SFO hydrolysis in the $\log I_0 - T^{-1} \cdot 10^3$ coordinates.

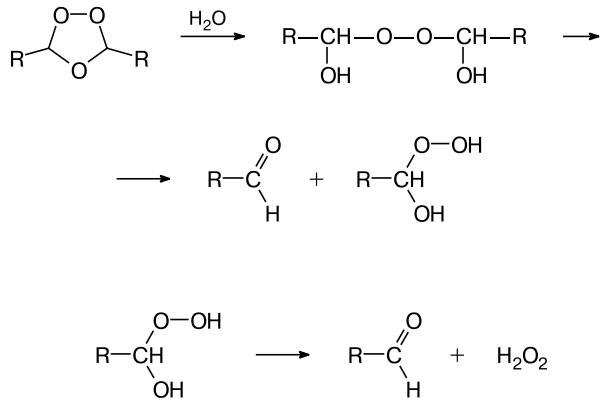
(1 mL) of a SFO suspension in CCl_4 maintained at 293 K to 10 mL of a solution of H_2O in CCl_4 (10^{-2} mol L^{-1}), which can be at different temperatures (273—338.5 K).

After the complete decay of the CL arisen upon water addition to the ozonolysis products of C_{60}, active oxygen in the same amount ($2.5 \cdot 10^{-4}$ mol L^{-1}) as that before hydrolysis is found by spectrophotometry. At the same time, the repeated addition of a water aliquot does not result in CL. These results indicate that the hydrolysis of the SFOs afford compounds also bearing active oxygen but of another (not "ozonide") nature. As known,[3] one of the main products of the reaction of hydrocarbon ozonides with water is presumably H_2O_2 (Scheme 1).

However, the authors[3] found no H_2O_2 after the hydrolysis of hex-1-ene ozonide by the color reaction in which perchromic acid is formed (determination sensitivity is 0.1—0.12% or 2.94—$3.53 \cdot 10^{-2}$ mol L^{-1}).

We tested the hydrolysis products of SFOs to the H_2O_2 content by three methods. First, a more sensitive[17] qualitative color reaction was used. As a result, the characteristic bright red-violet color appeared, indicating H_2O_2 formation after hydrolysis of the ozonolysis products of fullerene. A similar color reaction before hydrolysis does not result in the appearance of this color. Second, ^{1}H NMR spectroscopy can be used. For this purpose, we carried out the ozonolysis of a saturated solution of C_{60} in CCl_4 ($[C_{60}]_0 = 4.4 \cdot 10^{-4}$ mol L^{-1}, $V = 50$ mL, OE = 30 min) followed by dissolution of a suspension of the SFO in 1 mL of D_2O. However, we failed to determine H_2O_2 in this solution, most likely, because of the low content of H_2O_2. This conclusion is confirmed by the results of model experiments in which we detected the ^{1}H signal at 3.35 ppm[21] in the ^{1}H NMR spectra of solutions of commercial H_2O_2 in D_2O only at $[H_2O_2] \geq 0.8 \cdot 10^{-2}$ mol L^{-1}. Third, the CL method is used. It is known[22] that the interaction of aqueous solutions of H_2O_2 and $FeSO_4 \cdot 9H_2O$ is accompanied by CL. As described above, the repeated addition of water to a suspension of the ozonolysis products of C_{60} does not result in the appearance of CL. However, if an aqueous solution of $FeSO_4 \cdot 9H_2O$ is added immediately after repeated water addition, CL arises (see Fig. 3), indicating the formation of H_2O_2 due to the reaction of the SFO with water.

Scheme 1



As shown in the earlier published[9] and present works, the number of added oxygen-containing groups and ozonide cycles (and, perhaps, the degree of fragmentation of the fullerene cages) increases with the elongation of the ozonolysis exposure. Therefore, the CL upon hydrolysis of the products formed at different ozonolysis exposures is caused by the hydrolysis of SFOs of different composition. The results of measuring the CL spectra make it possible to assume the nature of the carbonyl groups in the composition of the substituents. In fact, the CL maxima during SFO hydrolysis lie in a much longer-wavelength region compared with the positions of the diffuse luminescence maxima (420—530 nm) of the carbonyl chromophores of hydrocarbons with different structures.[23—25] Such a large long-wavelength shift of the emis-

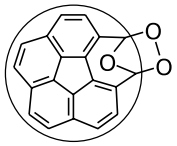
sion maximum for the chromophore in which electron excitation is localized on the C=O* group is caused, most likely, by the fact that at least the C_α and C_β atoms bonded to the carbon atom of the excited carbonyl group, namely, CL-emitting center, contain no hydrogen atoms. In the opposite case, the CL spectra should lie in a much shorter-wavelength spectral region.

It is difficult to propose mechanisms of CL generation upon SFO hydrolysis because published data on the nature and structure of SFOs are ambiguous (see above). In addition, it is unclear from which moment the destruction of the fullerene cage starts (if any) during ozonolysis. The following variants of this degradation can be proposed: cage opening due to the cleavage of the C=C bonds, fragmentation, and elimination of the CO and CO_2 groups. Published data on experimental evidence for CO and CO_2 formation during fullerene ozonolysis and the nature of fragments of the fullerene cage are lacking. Therefore, now we can speak only about the transformation of the fullerene cage during ozonolysis, and the degree and nature of this transformation are unknown to a great extent. It is clear that this is precisely the six-membered ring opening with the formation of two terminal C=O groups[9,18] due to the C=C bond cleavage that makes the main contribution to the transformation and possible destruction of the fullerene cage.

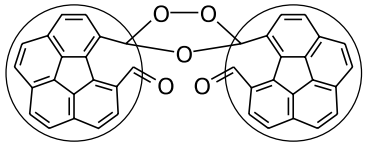
The retention of the transformed fullerene cage upon ozonolysis is confirmed by the results of quantum-chemical calculations,[26] according to which the structure consisting of the transformed C_{60} cage bonded to two ether and four keto groups is stable. Nine peaks have recently been detected[20] by HPLC for aqueous-alcohol solutions of the solid ozonolysis products of C_{60} in CCl_4. No HPLC chromatograms are presented in this work, while it is reported that all the peaks are eluted within the very short time (2.25 min) and are poorly resolved (difference in the retention times of the adjacent peaks is at most 23 s). Based on these results, the authors concluded[20] that ozonolysis decomposes completely the C_{60} cage to fragments linked together through the ozonide, peroxide, ether, and other groups. We believe that this conclusion (made without determination of the number of carbon atoms in the compounds responsible for these peaks) is ambiguous. In fact, several peaks with different retention times can be given from compounds in which different numbers of functional groups (both different and the same) are added to the fullerene cage. For instance, several HPLC peaks with a high difference in retention times (several minutes) were detected for fullerene epoxides and hydrides.[9,27] In addition, the conclusion about the destruction of the fullerene cage[20] contradict the thesis of the same authors[5,6] that the fullerene cage (although open) is retained during ozonolysis.

Thus, the question about the stability of the fullerene cage to ozone remains unanswered. There is a problem concerning assignment of the ozonolysis products to monomers or polymers. For instance, according to published data,[5,6] these products are polymers or oligomers (no exact value of the molecular weight of the products was measured[6] because of experimental difficulties). It is well known[3] that for hydrocarbons the formation of polymeric forms of ozonides does not exclude the presence of monomeric ozonides as well among the products, which is often observed. Perhaps, this situation takes place for fullerene ozonolysis.

Taking into account the above considered problems, one can theoretically propose two main types of simplified model structures of the SFOs: **IV** and **V**. In them the ozonide cycle is bonded to one (structure **IV**) or two (structure **V**) fullerene cages (or their fragments) transformed due to ozonolysis, and different numbers of the epoxide, ketone, or ether groups are added to the latter.



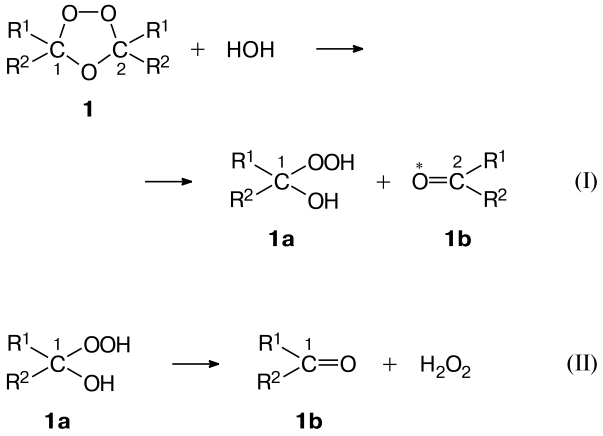
IV



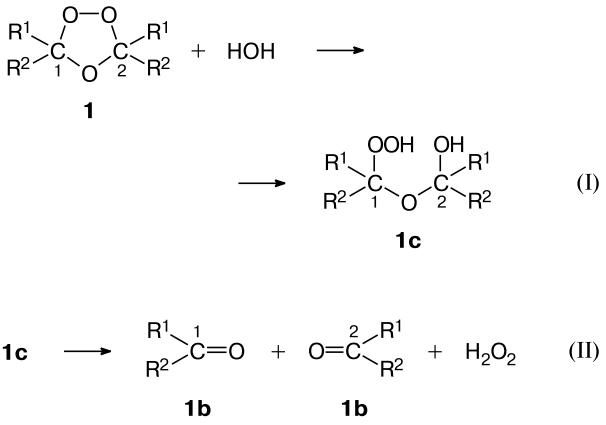
V

The structures of the SFOs in the proposed schemes of hydrolysis (Schemes 2—4) are shown in general. Here C(1) and C(2) are the carbon atoms of the same or different fullerene cages. The cage fragments R^1 and R^2 contain yet unknown[20] number of carbon atoms and above indicated oxygen-containing groups. Probable schemes

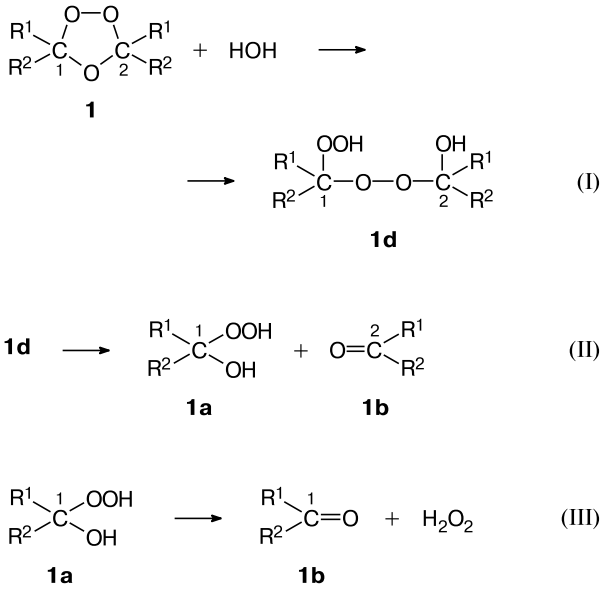
Scheme 2



Scheme 3



Scheme 4



of SFO hydrolysis includes the steps of excitation of the CL emitters and formation of H_2O_2.

According to Scheme 2, oxyhydroperoxide **1a** and ketone **1b** are formed first, and then an H_2O_2 molecule is eliminated from molecule **1a** to form ketone.

According to Scheme 3, hydrolysis proceeds without C—O bond cleavage to form product **1c**, which decomposes to two ketones with H_2O_2 evolution.

Scheme 4 is similar to Scheme 1, which has been assumed earlier[3] for description of the hydrolysis of hydrocarbon ozonides, and leads to the formation of ketone and H_2O_2 through compound **1d** in which the —O—O— bond is retained.

Since data on the structures of complex SFO structures containing different oxygen-containing groups are lacking, we performed quantum chemical calculations for

Table 1. Heat effects of hydrolysis ($\Delta H_h°$) of model ozonides calculated by the AM1 and PM3 methods

Scheme	Reaction	$\Delta H_h°$/kcal mol^{-1}			
		IV		**V**	
		AM1	PM3	AM1	PM3
2	(I)	−86.9	−66.5	−29.5	−22.2
	(II)	−12.1	−15.6	−12.1	−15.6
3	(I)	−118.0	−99.5	−9.2	+3.8
	(II)	+19.0	+17.6	−32.5	−41.6
4	(I)	−90.0	−68.5	−22.1	−7.5
	(II)	+3.1	+2.0	−7.4	−14.7
	(III)	−12.1	−15.6	−12.1	−15.6

structures **IV** and **V** ignoring these groups. The heat effects of the reactions shown in Schemes 2—4 were estimated by the PM3/RHF [28] and AM1/RHF [29,30] semiempirical methods, which reproduce well the geometry of fullerenes and are suitable[28—30] for studying pericyclic reactions. A disadvantage of these methods is the overestimation of the heats of formation of fullerenes and their derivatives; nevertheless, they can be used for comparative estimation of the heat effects. The average error for the heat effects calculated by the AM1 method for the peroxide compounds is[31] 4.5 kcal mol^{-1}. The heat effects of the reactions calculated by the AM1 and PM3 methods (Table 1) were compared with the energy necessary for excitation of a CL emitter (51.2 kcal mol^{-1}), which was estimated from the position of the maximum in the CL spectrum (558 nm).

The results of calculations of the heat effects suggest that SFO hydrolysis can proceed *via* different mechanisms depending on the fact whether the ozonide cycle is a part of one transformed cage (structure **IV**) or a fragment linking two different cages (structure **V**). In the first case, Scheme 2 is preferential, while Scheme 3 should be preferred in the second case. The hydrolysis of fullerene ozonides *via* Scheme 4 is energetically least favorable.

The heat effect of reaction (I) in Scheme 2 calculated by the AM1 and PM3 methods for model structure **IV** is −86.9 and −66.5 kcal mol^{-1}, respectively, which provides (with excess) the excitation of the CL emitter even ignoring the activation energy. In the case of model structure **V**, the heat effect of the same reaction is insufficient for emitter excitation. The heat effect of reaction (II) for the both structures does not either provide the generation of excited ketone **1b**.

The heat effect of reaction (I) in Scheme 3 for model structure **IV** is the highest, being −118.0/−99.5 kcal mol^{-1} (AM1/PM3); however, no luminescent chromophore is formed. The heat effect of reaction (II), taking into account the activation energy (41.6 + 10.9 = 52.5 kcal mol^{-1}), is sufficient for the excitation of ketone only for structure **V**. The heat effects of reactions (II)

and (III) forming ketones in Scheme 4 calculated for structures **IV** and **V** do not provide ketone excitation even taking into account the activation energy.

Thus, reaction (I) in Scheme 2 for the one-cage model and reaction (II) in Scheme 3 for the two-cage model of the SFOs are the most probable steps of CL excitation from the energetic point of view.

The experimental results obtained by us indicate that the SFOs are less stable than it has been reported earlier.[5,6] First, they are not retained during several months, as mentioned in Refs 5 and 6, but decompose completely by moisture traces during ~20 h. In addition, they decompose on heating not at 573 K [5,6] but already at 343—353 K.[32] Second, no SFOs are observed by iodometric titration of the precipitate obtained after CCl_4 removal by evacuation of a suspension of the solid ozonolysis products of C_{60}. No chemiluminescence is either observed upon water addition to this precipitate. We believe that hydrolysis with decomposition of the SFOs occurs during evacuation because of the low stability of the SFOs and very high hygroscopicity of the oxygen-containing ozonolysis products. Therefore, CL upon hydrolysis is observed only upon the treatment with water of precisely the freshly prepared suspension of the solid ozonolysis products in CCl_4 rather than the dried precipitates.

References

1. D. Heymann, S. M. Bachilo, R. B. Weisman, F. Cataldo, R. H. Fokkens, N. M. M. Nibbering, R. D. Vis, and L. P. F. Chibante, *J. Am. Chem. Soc.*, 2000, **122**, 11473.
2. D. Heymann, S. M. Bachilo, and R. B. Weisman, *J. Am. Chem. Soc.*, 2002, **124**, 6317.
3. S. D. Razumovsky and G. E. Zaikov, *Ozon i ego reaktsii s organicheskimi soedineniyami* [*Ozone and Its Reactions with Organic Compounds*], Nauka, Moscow, 1974, 322 pp. (in Russian).
4. S. D. Razumovsky and G. E. Zaikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1971, 2657 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1971, **20**, 2524 (Engl. Transl.)].
5. F. Cataldo and D. Heymann, *Polymer Degradation and Stability*, 2000, **70**, 237.
6. F. Cataldo, *Carbon*, 2002, **40**, 1457.
7. V. L. Antonovskii and M. M. Buzlanova, *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* [*Analytical Chemistry of Organic Peroxide Compounds*], Khimiya, Moscow, 1978, 308 pp. (in Russian).
8. V. L. Antonovskii, *Organicheskie perekisnye initsiatory* [*Organic Peroxide Initiators*], Khimiya, Moscow, 1972, 448 pp. (in Russian).
9. R. G. Bulgakov, E. Yu. Nevyadovsky, A. S. Belyaeva, M. T. Golikova, Z. I. Ushakova, Yu. G. Ponomareva, U. M. Dzhemilev, S. D. Razumovsky, and F. G. Valyamova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 144 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 148].
10. R. F. Vasil´ev, O. N. Karpukhin, and V. Ya. Shlyapintokh, *Dokl. Akad. Nauk SSSR*, 1959, **125**, 106 [*Dokl. Chem.*, 1959 (Engl. Transl.)].
11. K.-D. Gunderman and F. McCapra, *Chemiluminescence in Organic Chemistry*, Springer-Verlag, Berlin—Heidelberg, 1987, 217 p.
12. V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, I. V. Zakharov, A. A. Vichutinskii, and V. F. Tsepalov, *Khemilyuminestsentnye metody issledovaniya medlennykh khimicheskikh protsessov* [*Chemiluminescence Methods for Studying Slow Chemical Processes*], Nauka, Moscow, 1966, 300 pp. (in Russian).
13. D. Wagner, R. H. Smith, and E. D. Peters, *J. Anal. Chem.*, 1947, **19**, 976.
14. P. Altshuller, C. M. Schwab, and M. Bare, *J. Anal. Chem.*, 1959, **31**, 1987.
15. D. K. Banerjee and C. C. Budke, *J. Anal. Chem.*, 1964, **36**, 792.
16. G. Charlot, *Les Methodes de la Chimie Analytique. Analyse Quantitative Minerale*, Masson et C[ie], Ed´iteurs, Paris, 1961.
17. W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold Publishing Corp., New York, 1955.
18. R. G. Bulgakov, A. S. Musavirova, A. M. Abdrakhmanov, E. Yu. Nevyadovsky, S. L. Khursan, and S. D. Razumovsky, *Zh. Prikl. Spektrosk.*, 2002, **69**, 192 [*Russ. J. Appl. Spectr.*, 2002, **69** (Engl. Transl.)].
19. R. G. Bulgakov, E. Yu. Nevyadovsky, Yu. G. Ponomareva, D. Sh. Sabirov, V. P. Budtov, and S. D. Razumovsky, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 2391 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2468].
20. F. Cataldo, *Fullerenes, Nanotubes, and Carbon Nanostructures*, 2003, **11**, 105.
21. M. Anbar, A. Loewenstein, and S. Meiboom, *J. Am. Chem. Soc.*, 1958, **80**, 2630.
22. W. R. Seitz and D. M. Hercules, *Anal. Chem.*, 1972, **44**, 2143.
23. C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam—London—New York, 1968.
24. S. P. McGlynn, T. Azumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1969, 448 pp.
25. B. Ranby and J. F. Rabek, *Photodegradation, Photooxidation and Photostabilization of Polymers*, Wiley-Interscience Publication, J. Wiley and Sons, London—New York—Sydney—Toronto, 1978, 675 pp.
26. D. L. Kepert and B. W. Clare, *Inorg. Chim. Act.*, 2002, **327**, 41.
27. L. Becker, T. P. Evans, and J. L. Bada, *J. Org. Chem.*, 1993, **58**, 7630.
28. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.
29. M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.*, 1986, **108**, 8075.
30. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
31. A. Yu. Shibaev and Yu. V. Puzanov, *Zh. Fiz. Khim.*, 1988, **62**, 600 [*J. Phys. Chem. USSR*, 1988, **62** (Engl. Transl.)].
32. R. G. Bulgakov, E. Yu. Nevyadovsky, A. S. Belyaeva, M. T. Golikova, Yu. G. Ponomareva, S. D. Razumovsky, and U. M. Dzhemilev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 1700 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1768].

Received April 11, 2006;
in revised form June 21, 2006