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Reactivity of carbonyl oxides generated by the ozonolysis of C_{60} and C_{70} fullerenes: a chemiluminescence study and quantum-topological analysis

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The different reactivity of oxofullerenecarbonyl oxides generated by the ozonolysis of C_{60} and C_{70} fullerenes towards carbonyl oxide traps has been shown by a chemiluminescent study and quantum-topological analysis.

Ozonolysis of fullerenes is one of the simplest ways of fullerenes functionalization to produce water-soluble derivatives.[1] Fullerene epoxides $C_{60}O_x$ and $C_{70}O_x$,[2] polyketones $C_{60}O_z$[1,3–5] and $C_{70}O_z$,[6] polyesters[1,6] and unstable primary[2] and secondary[7] ozonides have been identified as the products of the liquid-phase ozonolysis of C_{60} and C_{70}.

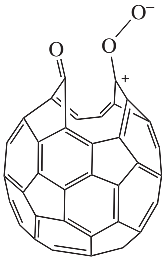
The reaction mechanism of fullerene ozonolysis and the nature of its intermediates are poorly understood. In the first theoretical study of C_{60} ozonolysis, oxofullerenecarbonyl oxide (OFCO) generated upon C–O and O–O bond dissociation in the primary ozonide $C_{60}O_3$ was considered as an intermediate of the reaction.[8] Chemiluminescence (CL) studies have shown that OFCOs take part in the formation of stable products in the liquid-phase ozonolysis of C_{60} and in the generation of the emitters of CL.[9]

The ozonolysis of both C_{60}[4] and C_{70}[6] is accompanied by CL. Recently,[6] it was declared that differences in the CL properties of $C_{60} + O_3$ and $C_{70} + O_3$ systems are brighter than differences in the contents of the stable products of C_{60} and C_{70} ozonolysis and the CL emitters in the case of C_{70} (C_{70} polyketones) are generated in the reactions of carbonyl oxide intermediates (analogously to C_{60} ozonolysis).

Theoretical studies revealed the similar structures of reaction sites in C_{60} (6.6 bond) and C_{70} (*ab* and *cc* bonds) molecules and the same structure of the 1,2,3-trioxolane moiety in the primary ozonides $C_{60}O_3$, *ab*-$C_{70}O_3$ and *cc*-$C_{70}O_3$.[10] However, while $C_{60}O_3$ and *ab*-$C_{70}O_3$ have the same chemical properties, the chemical behaviour of *cc*-$C_{70}O_3$ is different.[2] Consequently, the structure and properties of the unstable products and intermediates of these reactions can differ in spite of the same contents of the stable products of C_{60} and C_{70} ozonolysis.

Here, we studied the influence of the carbonyl oxide traps AcOH, MeOH, EtOH and pyridine (Py) on CL upon C_{70} ozonolysis in CCl_4 to elucidate the nature of the intermediates of C_{70} ozonolysis and performed a quantum-topological analysis of the electronic structure of model intermediates.

There are no significant changes in CL intensity and IR spectra[†] upon C_{70} ozonolysis in the presence of ROH. It demonstrates the lower reactivity of the intermediates of C_{70} ozonolysis towards ROH in comparison with those of C_{60} ozonolysis (Figure 1).



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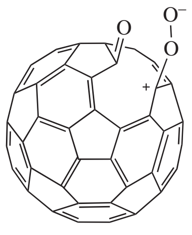

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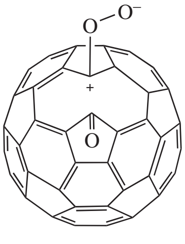

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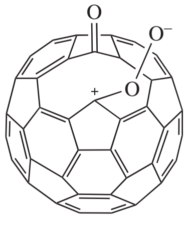

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To explain the reasons of the different reactivity of the intermediates, we have performed a quantum-topological analysis of the electronic structure AIM of several model intermediates with one open 6.6 bond: oxo[60]fullerenon-*O*-oxide **1** (60-OFCO), 9-oxo[70]fulleren-10-on-*O*-oxide **2** (*cc*-70-OFCO) with open *cc* bond, and isomeric 25-oxo[70]fulleren-8-on-*O*-oxide **3** (*ab*-70-OFCO) and 8-oxo[70]fulleren-25-on-*O*-oxide **4** (*ba*-70-OFCO) with open *ab* bond.[‡] A comparative analysis showed that the C=O group in **2** is located closer to the carbonyl oxide fragment, and their interaction is stronger than that in intermediates **1**, **3** and **4** (Figure 2). The interaction $C^+–OO^-\cdots O=C$ in *cc*-70-OFCO leads to the occurrence of a bond critical point between the terminal oxygens of these groups (this bond critical point is absent from other intermediates).

[†] The rate of ozone supply was 1.5 mmol h^{-1}. CL was detected with a FEU-79 photomultiplier. Precipitates of products have been prepared as previously.[9] General bonds in IR spectra for products of C_{70} and C_{70}/ROH ozonolysis are the following: 1736 (vs, C=O), 3400 (s, O–H), 1629 (w, O–H), 1380 (w, $C_{70}–O_2$), 1150 (s, C–O–C).

[‡] The AIM analysis[11] and calculation of the heats of reactions have been performed by PBE/3z method (Priroda 2.02+ program),[12] which correctly reproduces the structures and the energetic properties of C_{60}, C_{70} and their oxy derivatives.[10]

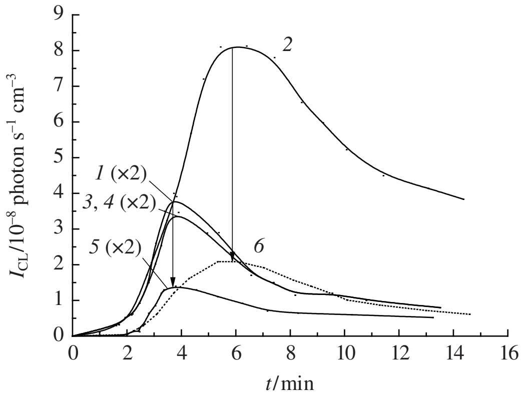
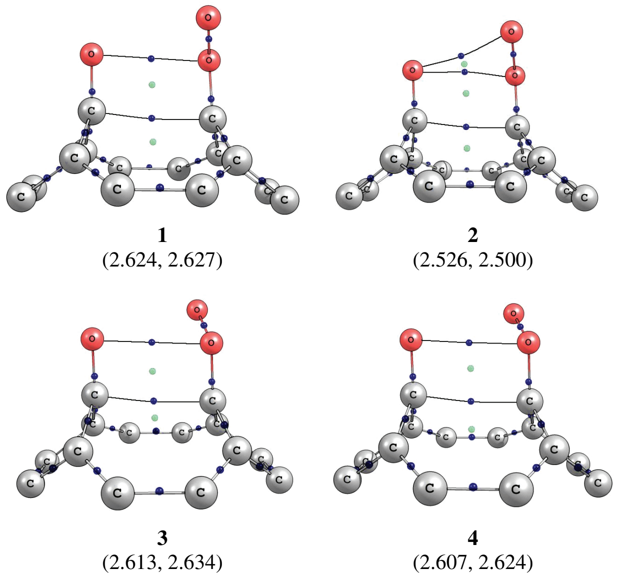


Figure 1 CL kinetics upon ozonolysis of solutions: (*1*) C_{70}, (*2*) C_{60}, (*3*) C_{70}/MeOH, (*4*) C_{70}/EtOH, (*5*) C_{70}/Py, (*6*) C_{60}/Py; [Py] = [ROH] = 0.48 mol dm^{-3}. Solvent, CCl_4; $[C_{70}]_0 = [C_{60}]_0 = 1.6\times10^{-4}$ mol dm^{-3}.

Probably, this interaction makes an obstacle for the two-centre coordination of ROH and *cc*-70-OFCO molecules in the transition state, which is required[13] for reaction (1).

Note that the number of critical points of electronic density in the carbonyl oxide fragments of **3** and **4** with functionalized *ab* bond of C_{70} fullerene is the same as in that of 60-OFCO **1**. Thus, *ab*-70-OFCO, *ba*-70-OFCO and 60-OFCO should be characterized with the same reactivity towards ROH. The absence of a significant decrease in CL intensity upon C_{70}/ROH ozonolysis and the low reactivity of *cc*-70-OFCO towards ROH predicted by AIM analysis allow us to conclude that the electronically excited states of C_{70} fullerene polyketones (CL emitters) with open *cc* bonds make a defining contribution to the CL upon C_{70} ozonolysis.

OFCOs are characterized by different reactivities towards substrates that require two-centre coordination, but the nature of the carbonyl oxide fragment in them is the same. Thus, they should elucidate the similar chemical activity towards substrates that react through a one-centre transition state. To confirm this supposition, we have performed fullerene ozonolysis in the presence of Py. The oxidation of Py by various oxidants leads to pyridine *N*-oxide and needs one-centre coordination of reactants [reaction (2)].[14] Moreover, Py is oxidized by ozone much slower than fullerenes.[§]



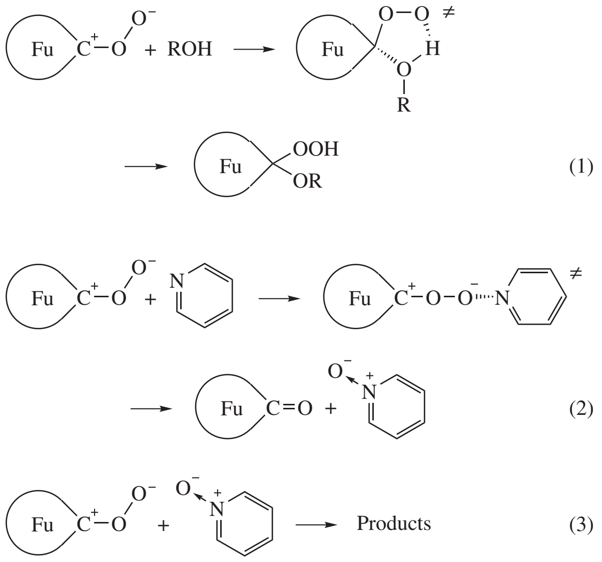
1
(2.624, 2.627)

2
(2.526, 2.500)

3
(2.613, 2.634)

4
(2.607, 2.624)

Figure 2 Quantum-topological analysis of the electronic structure of OFCOs (only carbonyl oxide fragments are shown for clarity): bond critical points are dark, cycle critical points are light; distances (Å) between the carbons of open C–C bond (the first number) and between terminal oxygens of carbonyl oxide fragment and carbonyl group (the second number) are given in parentheses.



Fu is transformed fullerene moiety

Table 1 Heats of reactions of OFCOs with carbonyl oxide traps ($-\Delta H_r^\circ$/kJ mol^{-1}).[‡]

Reaction	OFCO			
	1	**2**	**3**	**4**
(1), R = Me	47.7	21.9	53.2	43.5
(2)	205.1	198.4	203.7	204.8

The CL intensity upon C_{60} and C_{70} ozonolysis in the presence of Py is decreased by ~80% in both cases (Figure 3).[¶] Thus, Py (or/and the product of its oxidation, pyridine *N*-oxide) reacts with OFCOs according to equations (2) and (3). The heats of reactions of model OFCOs **1**–**4** with Py (Table 1) do not differ significantly while the heat of reaction **2** + MeOH is twice lower than the heats of analogous reactions of the other OFCOs with MeOH.

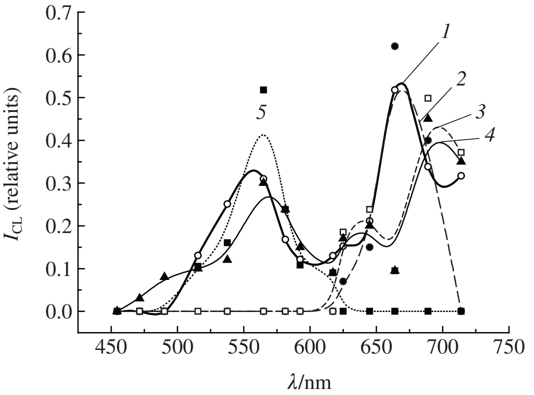


Figure 3 CL spectra upon liquid-phase ozonolysis: (*1*) C_{60}/Py, (*2*) C_{60}, (*3*) C_{70}, (*4*) C_{70}/Py, (*5*) Py. Solvent, CCl_4. $[C_{70}]_0 = [C_{60}]_0 = 1.6\times10^{-4}$ mol dm^{-3}, [Py] = 0.48 mol dm^{-3}.

[§] $k_{ef}(\text{Py} + O_3) = 4.32$ (H_2O, $T = 298$ K);[14] $k_{ef}(C_{60} + O_3) = 8.8\times10^3$ and $k_{ef}(C_{70} + O_3) = 5.0\times10^4$ dm^3 mol^{-1} s^{-1} (CCl_4, $T = 298$ K).[15]

[¶] CL spectra upon C_{60}/Py and C_{70}/Py ozonolysis are characterized by a new maximum at 560 nm (in addition to maxima corresponding to electronically excited polyketones: 660 nm in the case of C_{60} or 630 and 685 nm in the case of C_{70}) that corresponds to excited products of pyridine oxidation. IR spectra of precipitates obtained by C_{60}/Py and C_{70}/Py ozonolysis contain the 1736 cm^{-1} band of much lower intensity than the products of C_{60} and C_{70} ozonolysis without Py (their treatment by 0.1 M pyridine *N*-oxide/CCl_4 solution does not change the IR spectra).

Thus, OFCOs generated by the ozonolysis of fullerenes having different structures (C_{60} and C_{70}) are characterized by the same reactivity in the reactions that require one-centre coordination of reactants and the different reactivity in the reactions that proceed according to the mechanism of two-centre coordination of reactants.

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