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Mendeleev Commun., 2008, **18**, 307–308

Mendeleev Communications

Chemiluminescent test for oxofullerenecarbonyl oxides generated *in situ* by C_{60} ozonolysis

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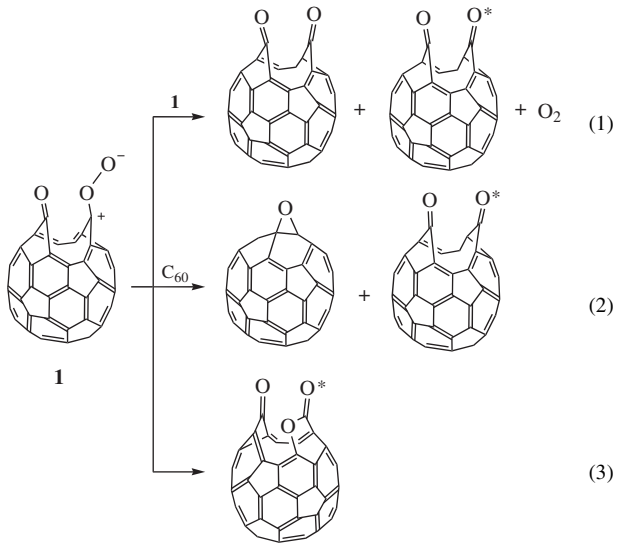
DOI: 10.1016/j.mencom.2008.11.006

A decrease in the intensity of chemiluminescence upon C_{60} ozonolysis in the presence of protic substrates XH (X = MeO, EtO and AcO) suggests the generation of oxofullerenecarbonyl oxides.

The following stable products of C_{60} ozonolysis in solutions have been identified: epoxides $C_{60}O_{n=1-6}$,[1,2] ketones, polyketones,[2–4] polyesters[4] and secondary C_{60} ozonides.[5–7] Note that epoxides can be obtained by C_{60} ozonolysis if conversion of C_{60} is low because they are easily oxidized in ketones and esters.[4] The secondary fullerene ozonides are also unstable and hydrolyzed by atmospheric moisture.[6]

In spite of the great success in identification of the products of C_{60} ozonolysis, the mechanism of their generation and the nature of labile intermediates of fullerene ozonolysis have been poorly understood. According to Malhotra *et al.*,[2] fullerene ketones are produced as a result of transformations of oxofullerenecarbonyl oxide (OFCO), which is a product of C–C and O–O bond dissociation in the primary ozonide $C_{60}O_3$. The carbonyl derivatives of C_{60} are generated by oxygen transfer from OFCO to aromatic solvents (toluene and xylene) that leads to their epoxides, which then convert to phenols (cresols and xylenols, respectively).

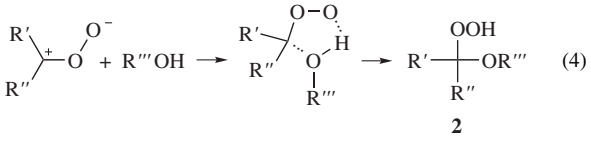


However, the fact that the carbonyl derivatives of C_{60} are also produced by C_{60} ozonolysis in aprotic solvents, which epoxidation is impossible, allows us to propose that ketones result from the bimolecular decay of OFCO **1** [equation (1)].[3] This reaction has been identified as a source of chemiluminescence (CL) upon the C_{60} liquid-phase ozonolysis.[3,7]

Table 1 Concentration of active oxygen [O–O]/mol dm^{-3} in the products of ozonolysis (5 min of O_3 bubbling, 1.5 mmol h^{-1}; [XH] = 0.42 mol dm^{-3}) determined by iodometric titration.

X	$C_{60} + O_3$	C_{60}/XH + O_3	XH/CCl_4	Pure CCl_4
MeO		4.5×10^{-3}	1.0×10^{-4}	
EtO	3.1×10^{-3}	5.3×10^{-3}	2.7×10^{-4}	$<2.5\times10^{-5}$
AcO		4.1×10^{-3}	$<2.5\times10^{-5}$	

It is well known that hydrocarbon carbonyl oxides react with alcohols and carboxylic acids producing alkoxy and acyl hydroperoxides.[8] Moreover, reaction (4) became a classic test for carbonyl oxides generated by unsaturated hydrocarbons ozonolysis.[9]



(4)

2

We studied the influence of carbonyl oxide traps XH (X = MeO, EtO, AcO) on the CL upon C_{60} ozonolysis in CCl_4 to elucidate whether OFCO intermediate takes part in the fullerene ozonolysis.

The products of ozonolysis (O_3 bubbling for 5 or 10 min) are insoluble in non-polar solvents. The IR spectra of the products[†] show chemical binding between the modified fullerene framework and X group according to equation (4). In the case of XH addition, content of active oxygen, *i.e.*, O–O group, in the products of C_{60} ozonolysis increases (Table 1) that is explained by accumulation of hydroperoxides **2**, which are more stable

[†] Precipitates obtained by 10 min ozonolysis of fullerene solutions have been centrifuged and washed with the solvent to move away unreacted XH. General bonds in IR spectra for products of C_{60} and C_{60}/XH ozonolysis are: 1736 (vs, C=O), 3400 (s, O–H), 1629 (w, C–OH), 1382 (w, C_{60}–O_2). In the case of C_{60} ozonolysis in the presence of XH, new bands in addition to the above appeared: (X = MeO) 1440 (m, δ_{as} Me), 1380 (m, δ_s Me), 1080 (w); (X = EtO) 1443 (m, δ_{as} Me), 1380 (m, δ_s Me), 1080 (vw), 747 (w, –CH_2O–); (X = AcO) 1728 (sh, O=C–O), 1100 (w), 1050 (w), 986 (w).

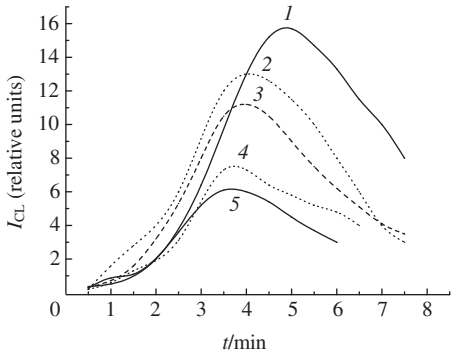


Figure 1 Kinetics of CL in the ozonolysis of solutions of (*1*) C_{60} without addition of XH; (*2*) C_{60}/AcOH; (*3*) C_{60}/EtOH; (*4*) C_{60}/MeOH, [XH] = = 0.48 mol dm^{-3} and (*5*) C_{60}/MeOH, [MeOH] = 0.72 mol dm^{-3}; $[C_{60}]_0$ = 1.6×10^{-4} mol dm^{-3}. Solvent, CCl_4.

than the other active oxygen-containing fullerene derivatives identified previously.[6]

The kinetics of CL in the ozonolysis of C_{60}/XH solutions is presented in Figure 1.‡ CL spectra with the only maximum at λ_{max} = 660 nm are not changed if a carbonyl oxide trap XH is added to the reaction system. The excited carbonyl derivatives of C_{60} are emitters of CL as in the case of C_{60} ozonolysis without XH.

Addition of 0.48 mol dm^{-3} MeOH, EtOH or AcOH to the reaction system leads to the decrease of CL intensity by about 50, 30 or 20%, respectively. The effectiveness of OFCO elimination from the reactions generating emitters of CL in the series MeOH > EtOH > AcOH is in accordance with the relative reaction rates of these compounds with the hydrocarbon carbonyl oxide Me_2COO.[8] The dependence of CL intensity on the concentration of XH (Figure 2) is characterized with the threshold concentration of XH (~0.75 mol dm^{-3}). Addition of larger amounts of XH does not cause the further decrease in I_{max}.

The decrease of CL intensity during C_{60} ozonolysis in the presence of XH, which is not larger than 60%, and absence of the decrease if [XH] > 0.75 mol dm^{-3} allow us to conclude that the CL observed in C_{60} ozonolysis is generated not only in bimolecular OFCO reactions [equations (1) and (2)] but also in unimolecular processes [equation (3)]. Heat effects of these reactions [$\Delta H_r(1) = -203.9$, $\Delta H_r(2) = -237.0$, $\Delta H_r(3) = -402.5$ kJ mol^{-1}]§ are sufficient for excitation of oxy derivatives of C_{60} (the energy of excitation measured previously[3] is 191.6 kJ mol^{-1}).

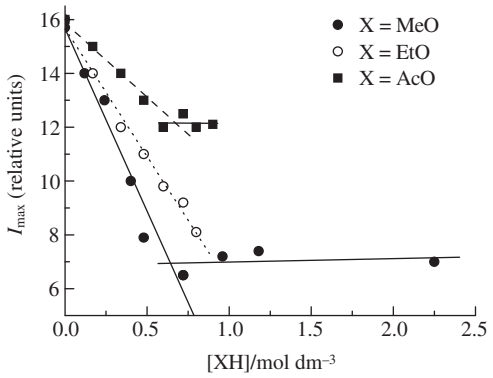


Figure 2 CL intensity I_{max} *vs.* the concentration of XH in the C_{60}/XH/ $CCl_4 + O_3$ system.

‡ The rate of ozone supply was 1.5 mmol h^{-1}. CL kinetics and CL spectra have been detected with a FEU-79 photomultiplier. The ozonation of pure CCl_4 is accompanied by very low background luminescence caused by thermal decay of ozone. Addition of AcOH, MeOH or EtOH to CCl_4 ([XH] = 0.72 mol dm^{-3}) do not influence this background CL.

Thus, the CL emitters upon C_{60} ozonolysis are generated in several parallel reactions of an OFCO intermediate. Addition of a carbonyl oxide trap XH eliminates OFCO from bimolecular channels that is accompanied by decrease of CL intensity but does not influence unimolecular processes because the possibility of the OFCO decay in a unimolecular reaction is higher than that for its bimolecular reaction with XH.

This work was supported by the RF Ministry of Education (project no. DSP 2.2.1.1.6332) and the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (programme no. 1).

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Received: 20th May 2008; Com. 08/3145

§ Heat effects have been estimated by PBE/3z density functional theory method (Priroda 2.02+ program),[10] which correctly reproduces experimental data on the structure and energetic properties of ozone and fullerene derivatives.[11]