Letters to the Editor

A new type of a chemiluminescent reaction: hydrolysis of ozonides of fullerenes C_{60} and C_{70}

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A new type of chemiluminescence (CL) was discovered in the hydrolysis of secondary ozonides of fullerenes (FOZ) C_{60} (CL_1) and C_{70} (CL_2) (Fig. 1). The chemiluminescence as a sharp kinetic peak ($I_{max}(CL_1)$ = $2.65 \cdot 10^8$ photon s^{-1} mL^{-1} and $I_{max}(CL_2)$ = $1.63 \cdot 10^8$ photon s^{-1} mL^{-1}) was observed when an aliquot of water (2 mL over 0.5 s) was added through a dosing apparatus into a suspension of FOZ in CCl_4 (20 mL) prepared[1] by ozonolysis of C_{60} and C_{70}. The suspension was completely dissolved in the aqueous phase, while no fullerene derivatives were detected in the organic phase. The FOZ content was determined by iodometry.[2] The CL_1 and CL_2 spectra (Fig. 2) are identical with the CL spectrum recorded in the ozonolysis of C_{60};[3] *i.e.*, fullerene polyketones seem to be CL emitters. The activation energy of the hydrolysis of FOZ C_{60} was determined from the slope of a linear (R = 0.97) plot of $\ln(I_{max})$ of CL_1 *vs.* T^{-1} (E_a = 10.9±1 kcal mol^{-1}). Addition of another portion of water caused no CL; *i.e.*, fullerene ozonolysis products are completely consumed in their reaction with the first portion of water, which induces CL. We believe that these products are FOZ on the following grounds. The intensities of the absorption bands of the ketone and ether groups in the IR spectra of samples prior to (see Ref. 1) and after the hydrolysis are equal. It is known[4] that hydrocarbon ozonides react with water through cleavage of the O—O bond to give compounds containing a >C=O group and the emitting center of CL is an excited >C=O* group. According to iodometric data, the system upon the hydrolysis contains reactive oxygen; taking into account that readdition of water does not induce CL any more, this reactive oxygen does not belong to FOZ.

Chemiluminescence is an essential property of FOZ since organic peroxides, hydroperoxides and bisperoxides are known[4—6] to be virtually inert toward water, in contrast to ozonides. This allows CL in hydrolysis to be used

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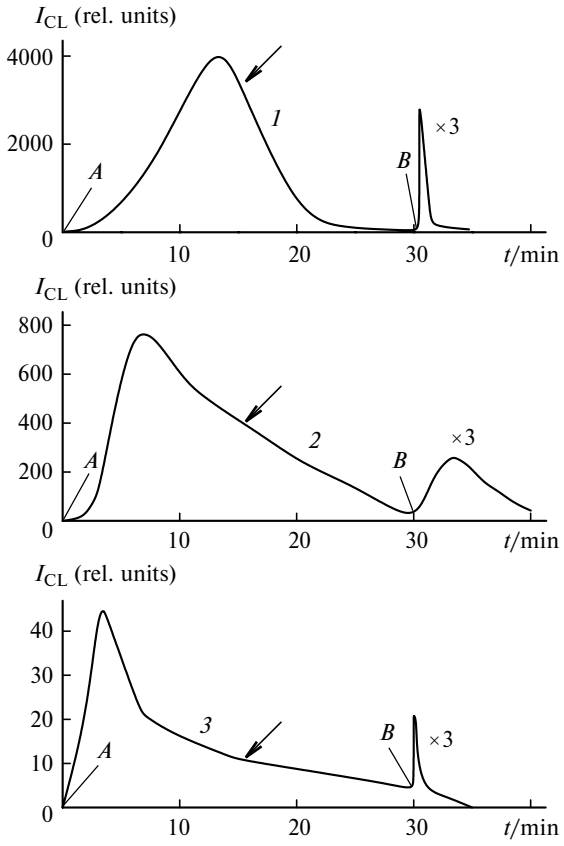


Fig. 1. Kinetics of CL in the hydrolysis of suspensions of FOZ C_{60} (*1*) and C_{70} (*2*) in CCl_4 and benzene ozonide (*3*) (V = 10 mL). Segment *AB* refers to the kinetics of CL during the ozonolysis (1.4 mmol of O_3 h^{-1}); the instants the supply of ozone was stopped with simultaneous start of the argon supply are marked with arrows; *B* is the instant an aliquot of water (V = 1 mL) was added; the scale of the curves is increased three times from point *B*; $[C_{60}]_0 = [C_{70}]_0 = 1.6 \cdot 10^{-4}$ mol L^{-1}; the ozonolysis temperature is 20.8 °C.

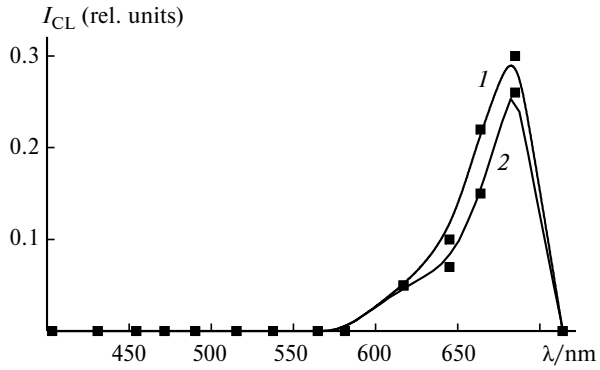
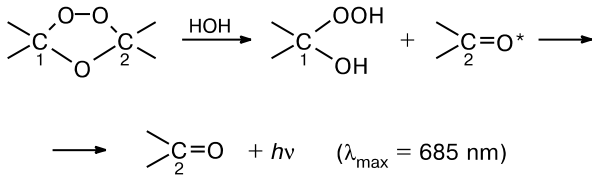


Fig. 2. CL spectra upon the hydrolysis of suspensions of solid products obtained by ozonolysis of solutions of C_{60} (*1*) and C_{70} (*2*) in CCl_4 (the spectra were recorded with the use of a set of light filters with adjacent frequency ranges).

for identification of FOZ in a complex mixture of fullerene ozonolysis products. Since the structures of secondary FOZ have not been determined hitherto,[7,8] the hydrolysis of FOZ and the excitation of CL can be now represented only very generally (Scheme 1).

Scheme 1



In Scheme 1, C_1 and C_2 are the carbon atoms of the same or different fullerene cages transformed during ozonolysis and bearing ketone and ether groups.[1] One can assume that the presence of reactive oxygen detected upon the hydrolysis is due to the formation of hydroxy hydroperoxide (see Scheme 1). The heat effects $\Delta H°$ of this reaction were estimated by the semiempirical AM1/RHF method[9,10] for compounds of the types *A* (C_1 and C_2 are the atoms belonging to the same cage) and *B* (C_1 and C_2 are the atoms of different cages). The average computation error for peroxy compounds[10] was 4.5 kcal mol^{-1}. The energy required for excitation of the CL emitter was determined from the position of λ_{max}(CL) = 685 nm and equals 41.7 kcal mol^{-1}. For hydrolysis of ozonides of the type *A* (see Scheme 1), $\Delta H° = -86.9$ kcal mol^{-1}, which is more than sufficient for excitation of the CL emitter even without considering the activation energy. For hydrolysis of ozonides of the type *B*, the sum of $-\Delta H°$ and E_a is 40.4 kcal mol^{-1}, which is slightly lower than the energy required for excitation of ketone. This can be associated with the error of the AM1 method and makes it quite probable to excite the CL emitter according to Scheme 1 for FOZ of the type *B*.

Presumably, the discovered CL is a more general property of ozonides, which is inherent in not only FOZ but also hydrocarbon ozonides. This was indirectly confirmed by the CL we observed in the hydrolysis of benzene ozonide (see Fig. 1).

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