Letters to the Editor

Chemiluminescence during thermolysis of fullerene C_{60} derivatives containing reactive oxygen

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Chemiluminescence (CL) of fullerenes was first detected in the ozonolysis of C_{60} solutions[1,2] and later in the oxidation of sodium fullerides with a Ce^{IV} complex.[3] In this work, a new type of the CL of fullerenes was observed during the thermolysis of complex C_{60} oxides (**1**) formed by the ozonolysis of C_{60} solutions and containing reactive oxygen (RO)[4] and epoxide,[5] carbonyl,[6,7] and ester groups.[7] Earlier,[8,9] chemiluminescence in the thermolysis of organic peroxides was reported. Chemiluminescence was measured by a known method.[2] The starting oxide **1** was prepared as a brown precipitate according to a known procedure[7] by the ozonolysis of C_{60} solutions in CCl_4 (1.4 mmol of O_3 h^{-1}, $[C_{60}]_0 = 1.6 \cdot 10^{-4}$ mol L^{-1}, $V = 20$ mL). Heating of the suspension of **1** in CCl_4 (20 mL) results in CL with a kinetic peak at the fifth minute ($I_{max} = 2.5 \cdot 10^9$ photon s^{-1} mL^{-1}) (Fig. 1). From the excitation of CL to its complete disappearance, the content of RO in the sample (determined by iodometric titration[2]) decreases from $1.6 \cdot 10^{-4}$ mol to zero, while the contents of epoxide, carbonyl, and ester groups (determined according to a procedure[7]) do not change noticeably. The energy of activation calculated from the linear plot of $\log I$ *vs.* $1/T$ is 17.3±1.4 kcal mol^{-1}. Thus, CL can be attributed to thermal cleavage of the O—O groups bound to the ozonolysis-transformed framework of C_{60}.[7] The CL spectrum is the same as the known[2] CL spectrum recorded during the ozonolysis of C_{60} solutions (see Fig. 1); *i.e.*, in the thermolysis of **1**, the emitter of CL is also the >C=O* group bound to the framework of C_{60}. The CL excitation scheme can be represented only in the most general form

$$\{O—O\}[C_{60}] \rightarrow \{^*O=C\}[C_{60}] \rightarrow \{O=C\}[C_{60}] + h\nu$$

$$(\lambda_{max} = 680 \text{ nm})$$

($[C_{60}]$ is the ozonolysis-transformed framework of C_{60} also including the epoxide, carbonyl, and ester groups), because the nature of RO in oxide **1** has not yet been specified: ozonide, peroxide, or bisperoxide forms are possible.[4]

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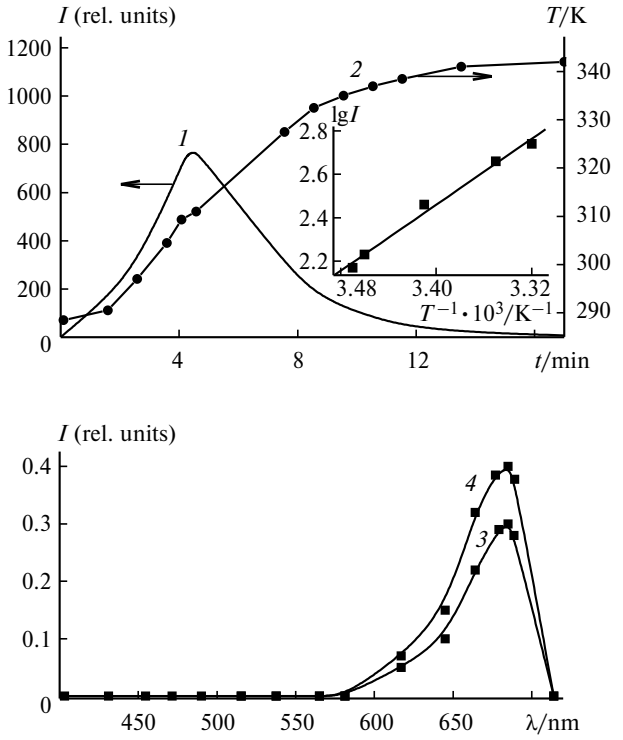

Fig. 1. Kinetic parameters and CL spectra for the thermolysis of a suspension of oxide **1** ($1.6 \cdot 10^{-6}$ mol) in CCl_4 (20 mL): the plots of the CL intensity (*1*) and the temperature (*2*) *vs.* the thermolysis time (inset: linear anamorphism of the temperature dependence of *I* (segment of ascending curve *1* up to a maximum)); CL spectra measured with a set of boundary light filters during the thermolysis of oxide **1** (*3*) and the ozonolysis of a C_{60} solution ($1.6 \cdot 10^{-4}$ mol L^{-1}) in CCl_4 (*4*).

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References

1. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, A. M. Abdrakhmanov, Z. I. Ushakova, and F. M. Sharifullina, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1203 [*Russ. Chem. Bull.*, 1999, **48**, 1190 (Engl. Transl.)].
2. R. G. Bulgakov, A. S. Musavirova, A. M. Abdrakhmanov, E. Yu. Nevyadovskii, S. L. Khursan, and S. D. Razumovskii, *Zh. Prikl. Spektr.*, 2002, **69**, 192 [*J. Appl. Spectr.*, 2002, **69** (Engl. Transl.)].
3. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, and M. T. Golikova, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 702 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 731].
4. F. Cataldo and D. Heymann, *Polymer Degradation and Stability*, 2000, **70**, 237.
5. D. Heymann and L. P. F. Chibante, *Chem. Phys. Lett.*, 1993, **207**, 339.
6. R. Malhotra, S. Kumar, and A. Satyam, *J. Chem. Soc., Chem. Commun.*, 1994, 1339.
7. R. G. Bulgakov, E. Yu. Nevyadovskii, A. S. Belyaeva, M. T. Golikova, Z. I. Ushakova, Yu. G. Ponomareva, U. M. Dzhemilev, S. D. Razumovskii, and F. G. Valyamova, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 144 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 148].
8. R. F. Vasil´ev, O. N. Karpukhin, and V. Ya. Shlyapintokh, *Dokl. Akad. Nauk SSSR*, 1959, **125**, 106 [*Dokl. Chem.*, 1959 (Engl. Transl.)].
9. K.-D. Gunderman and F. McCapra, *Chemiluminescence in Organic Chemistry*, Springer-Verlag, Berlin—Heidelberg, 1987, 217 pp.

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