Letters to the Editor

Chemiluminescence upon the oxidation of fullerene fluorides $C_{60}F_x$ (x = 18, 36, 48) with ozone in solution

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Fullerene fluorides $C_{60}F_x$ (x = 18, 36, 48) are the most studied[1—3] polyfluoro derivatives of C_{60}. Compounds $C_{60}F_x$ are characterized by nucleophilic substitution reactions.[2—4] In addition, higher fluorides ($C_{60}F_{46}$, $C_{60}F_{48}$) manifest oxidation properties,[3,5] and the lower fluorides enter addition reactions.[2,3] At the same time, literature data on the reactivity of fluorides $C_{60}F_x$ with respect to oxidants, including O_2 and O_3, are lacking. It is only known that compounds $C_{60}F_x$ in the solid state are stable in air for a long time.[1—3] It is known[6] that oxygen-containing fluorides $C_{60}F_{18}O$ and $C_{60}F_{18}O_2$ are formed as by-products during the synthesis of $C_{60}F_{18}$.

In the present work, we have found for the first time chemiluminescence (CL) upon the liquid-phase oxidation of fluorides $C_{60}F_x$ (x = 18, 36, 48) by ozone. The chemiluminescence involving $C_{60}F_x$ has not been described earlier, although the photoluminescence of these compounds is known.[7]

Solid samples of fluorides $C_{60}F_x$ (x = 18, 36, 48) (purity more than 95%) were synthesized using known procedures[8—10] at the M. V. Lomonosov Moscow State University. Commercial samples of fullerite C_{60} (99.9% purity) were purchased from the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences. Solvent CCl_4 (reagent grade) and gases (Ar, O_2) were purified according to procedures described previously.[11,12] To study the reactivity of fluorides $C_{60}F_x$ towards O_3 and O_2, an O_3/O_2 mixture ($7 \cdot 10^{-2}$ (mmol of O_3) min^{-1}) or pure O_2, respectively, were bubbled for 40 min at 20 °C through the solutions of $C_{60}F_x$ in CCl_4 ($1.6 \cdot 10^{-4}$ mol L^{-1}). For this purpose, solutions of $C_{60}F_x$ (5 mL) were placed in a Pyrex chemiluminescent cell mounted in the light-proof chamber for CL detection by a known procedure.[12]

No CL is observed upon the action of oxygen on solutions of $C_{60}F_x$ (20 °C), *i.e.*, compounds $C_{60}F_x$ in solution are resistant to O_2. Unlike this, bright CL was observed during bubbling O_3 through the solutions of $C_{60}F_x$. The CL kinetic curves contain one maximum. The CL brightness of all fluorides $C_{60}F_x$ is substantially weaker than that of the known[12,13] CL appeared upon the ozonation of C_{60} solutions under similar conditions (Fig. 1). The changes in the intensities of the kinetic CL maxima (I_{max}) and time (t) of their appearance for compounds $C_{60}F_x$ and C_{60} are shown in Fig. 1. It is seen that the brightness of CL, and the time of its

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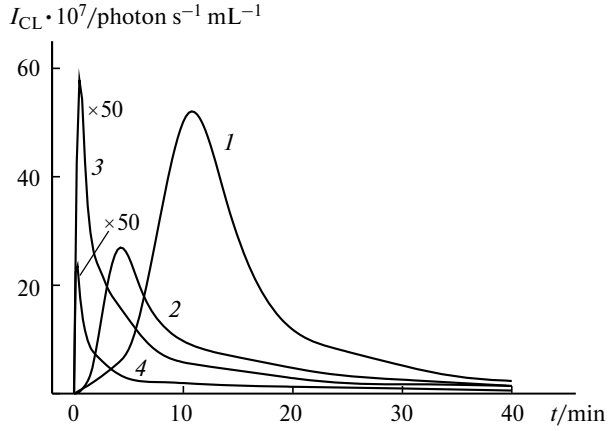

Fig. 1. Chemiluminescence kinetics upon the ozonolysis of fullerene C_{60} (*1*) and fullerene fluorides $C_{60}F_{18}$ (*2*), $C_{60}F_{36}$ (*3*), and $C_{60}F_{48}$ (*4*) (CCl_4, 20 °C, $[C]_0 = 1.6 \cdot 10^{-4}$ mol L^{-1}; the abscissa is shifted to the right relative to the point of origin for clarity of representation of the rapidly formed maxima).

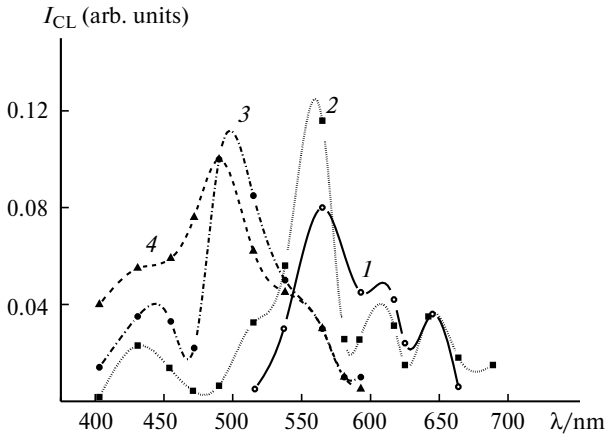

Fig. 2. Chemiluminescence kinetics upon the ozonolysis of fullerene C_{60} (*1*) and fullerene fluorides $C_{60}F_{18}$ (*2*), $C_{60}F_{36}$ (*3*), and $C_{60}F_{48}$ (*4*) (the spectra of C_{60} and $C_{60}F_{18}$ were recorded on a FEU-79 photomultiplier, and those of $C_{60}F_{36}$ and $C_{60}F_{48}$ were detected on FEU-39; obtained using boundary light filters after the maxima of kinetic curves *1*—*4* in Fig. 1 were achieved; corrected with allowance for the FEU sensitivity).

inflaming, and hence, the reactivity, are inversely proportional to the degree of fluorination of the C_{60} cage.

Compound	I_{max}/photon s^{-1} mL^{-1}	t/min
C_{60}	$5.22 \cdot 10^8$	10.5
$C_{60}F_{18}$	$2.69 \cdot 10^8$	4.2
$C_{60}F_{36}$	$1.14 \cdot 10^7$	0.5
$C_{60}F_{48}$	$4.65 \cdot 10^6$	0.3

The maxima in the CL spectra of C_{60} and $C_{60}F_{18}$ lie in a longer-wavelength region than the maxima in the spectra of $C_{60}F_{36}$ and $C_{60}F_{48}$ (Fig. 2). The CL spectrum of fluoride $C_{60}F_{18}$ contains maxima at 430, 560, 610, and 645 nm and a shoulder at 520 nm. The long-wavelength maxima of this CL (at 560, 610, and 645 nm) nearly coincide with the maxima of the CL spectrum detected upon the prolong ozonolysis of fullerene C_{60}. Therefore, taking into account the known data on the CL mechanism[13] during the ozonolysis of C_{60} and the structure[3] of $C_{60}F_{18}$, we may conclude that during the ozonolysis of fluoride $C_{60}F_{18}$ the CL emitters are the excited states of the carbonyl derivatives of $C_{60}F_{18}$ formed due to the attack of ozone to the C=C bond of the "fullerene hemisphere" of the $C_{60}F_{18}$ cage. Correctness of the conclusion about the nature of the CL emitter is confirmed by the absorption band at 1734 cm^{-1} (C=O) in the IR spectrum of the solid products of ozonolysis of $C_{60}F_{18}$. We assume that the CL emitters in the ozonolysis of fluorides $C_{60}F_{36}$ and $C_{60}F_{48}$ have the carbonyl nature as well. At this stage of investigation, the mechanism of CL appeared upon the ozonolysis of compounds $C_{60}F_x$ can be presented in the general form only.

$$C_{60}F_x + O_3 \longrightarrow {}^*[O]{=}C_{60}F_xO_y + [O]{=}C_{60}F_xO_y,$$

$$^*[O]{=}C_{60}F_xO_y \longrightarrow [O]{=}C_{60}F_xO_y + h\nu$$

(x = 18, 36, 48)

The weaker CL intensity of fluorides $C_{60}F_{36}$ and $C_{60}F_{48}$ and the arrangement of the maxima in the CL spectra in the shorter-wavelength region are due to two main factors, first, the known[1—3] shielding of the C=C bonds adjacent to the F atoms and impeding the attack of ozone to the C=C bond of these fluorides; second, the characteristic[14,15] short-wavelength shift of the luminescence maxima of the C_{60} derivatives compared to those in the spectrum of unsubstituted fullerene C_{60}. The mechanism of CL and reaction products of the ozonolysis of fluorides $C_{60}F_x$ will be studied in more detail elsewhere.

References

1. L. N. Sidorov, O. V. Boltalina, *Usp. Khim.*, 2002, **71**, 611 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2002, **71**].
2. R. Taylor, *J. Fluorine Chem.*, 2004, **125**, 359.
3. A. A. Goryunkov, N. S. Ovchinnikova, I. V. Trushkov, M. A. Yurovskaya, *Usp. Khim.*, 2007, **76**, 323 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2007, **76**].
4. A. G. Avent, A. K. Abdul-Sada, B. W. Clare, D. L. Kepert, J. M. Street, R. Taylor, *Org. Biomol. Chem.*, 2003, 1026.
5. A. A. Gakh, A. A. Tuinman, J. L. Adcock, R. N. Compton, *Tetrahedron Lett.*, 1993, **34**, 7167.
6. O. V. Boltalina, B. Vaissiere, A. Yu. Lukonin, P. W. Fowler, A. K. Abdul-Sada, J. M. Street, R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2001, 550.
7. A. M. Lebedev, K. A. Menshikov, V. G. Stankevich, N. Yu. Svechnikov, A. V. Ryzkov, O. V. Boltalina, I. V. Goldt, I. N. Ioffe, I. A. Kamenskikh, L. N. Sidorov, *Nuclear Instruments and Methods in Physics Research A*, 2005, **543**, 221.
8. O. V. Boltalina, V. Yu. Markov, R. Taylor, M. P. Waugh, *Chem. Commun.*, 1996, 2549.
9. O. V. Boltalina, A. Ya. Borschevskiy, L. N. Sidorov, J. M. Street, R. Taylor, *Chem. Commun.*, 1996, 529.

10. V. F. Bagryantsev, A. C. Zapol´skii, O. V. Boltalina, N. A. Galeva, L. N. Sidorov, *Dokl. Akad. Nauk*, 1997, **357**, 487 [*Dokl. Chem.* (*Engl. Transl.*), 1997, **357**].
11. A. Gordon, R. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, Wiley-Interscience, New York, 1972, 443.
12. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, A. M. Abdrakhmanov, Z. I. Ushakova, R. M. Sharifullina, *Izv. Akad. Nauk*, *Ser. Khim.,* 1999, 1203 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1999, **48**, 1190].
13. R. G. Bulgakov, A. S. Musavirova, A. M. Abdrakhmanov, E. Yu. Nevyadovskii, S. L. Khursan, S. D. Razumovskii, *Zh. Prikl. Spektr.*, 2002, **69**, 193 [*J. Appl. Spectr.* (*Engl. Transl.*), 2002, **69**].
14. D. K. Palit, H. Mohan, J. P. Mittal, *J. Phys. Chem. A*, 1998, **24**, 4456.
15. S. V. Amarantov, V. N. Bezmelnitsin, O. V. Boltalina, M. Danailov, P. V. Dudin, A. V. Ryzkov, V. G. Stankevitch, *Nuclear Instruments and Methods in Physics Research A*, 2001, **470**, 318.

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