Brief Communications

Chemiluminescence upon isomerization of dimethyldioxirane in the gas phase and on a sorbent surface

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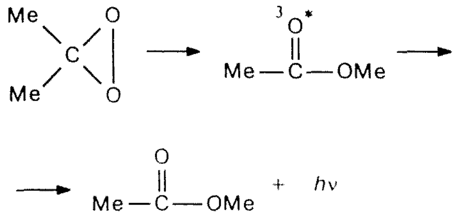
Chemiluminescence (CL) was found upon the isomerization of dimethyldioxirane in the gas phase under argon atmosphere. The intensity of CL increases as temperature increases and decreases with time at constant temperature. If Silipor is placed in a cell containing the dimethyldioxirane vapor in argon, the intensity of CL sharply increases (more than 10 times) and then decreases following the exponential law. In all cases tripletly excited methyl acetate is the emitter of chemiluminescence.

Key words: isomerization, dimethyldioxirane; chemiluminescence; gas phase.

Isomerization of dioxiranes to corresponding esters is known to be an intense exothermic process ($\Delta H > 80$ kcal mol^{-1}) resulting, as was assumed previously,[1] in the possible formation of a tripletly excited product. Actually, as we have shown recently,[2] chemiluminescence (CL), which was observed upon the isomerization of dimethyldioxirane (DMD) in the presence of 9,10-dibromoanthracene (DBA), is due to the transfer of energy from the triplet methyl acetate (^{3}MA$^•$) to DBA. However, no linear dependence of CL was observed in solutions, presumably due to effective quenching processes. We assumed that the quenching processes are not too effective in the gas phase and on the sorbent surface, and CL could be recorded due to emissive deactivation of ^{3}MA$^•$.

This assumption was confirmed by our study. In this work we report on CL upon the decomposition of DMD in the gas phase and after its sorption from the gas phase on the Silipor surface.



Experimental

DMD was obtained and analyzed according to the known procedure.[3] The luminescence was recorded as follows: a solution of DMD in acetone (0.5 mL, $[\mathrm{DMD}]_0 = 0.08$ mol L^{-1}) was placed in one of the cells thermostated at 90 °C and connected to another cell placed above the photocathode of a FEU-140 photomultiplier. An argon flow entering the first cell captured the acetone vapor with DMD that entered the second

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cell. The recording of CL upon the isomerization of DMD absorbed from the gas phase on the sorbent surface was carried out analogously, placing Silipor (50 mg, Silipor 400, Chemapol, 0.125—0.160 mm, 400 $m^2 g^{-1}$) in the second cell. The phosphorescence spectrum of $^3MA^*$ (λ_{max} = 390 nm) was recorded on a Hitachi MPF-4 spectrofluorimeter at 77 K.

Results and Discussion

The intensity of CL observed upon the decomposition of DMD in the gas phase (90 °C) is equal to $\approx 5 \cdot 10^5$ photon s^{-1} mL^{-1} per angle of 4π. The spectral composition of this luminescence, estimated with the aid of light filters, corresponds to the phosphorescence spectrum of $^3MA^*$. The CL intensity increases as temperature increases and decreases when the argon supply is stopped.

A much more bright CL (more than 10 times) was recorded upon the isomerization of DMD absorbed from the gas phase on the Silipor surface. The emission efficiency of triplet molecules on the sorbent surface is known to increase;[4] the rate of chemical transformation of labile molecules (such as 1,2-dioxethanes) also increases.[5] It is likely that the isomerization of DMD and favorable conditions for phosphorescence of $^3MA^*$ on the silipor surface result in increasing the CL intensity. If the argon flow through the cell is constant, the intensity of CL rapidly increases and then decreases following the exponential law. This behavior of CL is most likely associated with the establishment of the adsorption-desorption equilibrium of DMD and MA and a decrease in the activity of the adsorption centers. When the argon flow is stopped, CL drops more rapidly, which is due to isomerization of the adsorbed DMD. In the successive cycles of switching on—switching off the argon supply changes in the luminescence are repeated. It should be noted that the effective rate constant of quenching of CL for adsorbed DMD (k_{eff} = $(1.1\pm0.1)\cdot10^{-2}$ s^{-1}) at 90 °C is nearly an order of magnitude lower than the rate constant of the decomposition of DMD in solution, obtained by the extrapolation of the Arrhenius dependence to T = 90 °C (k_{sol} = 0.13 s^{-1}). A decrease in the rate of decomposition of DMD adsorbed from the gas phase on the Silipor surface apparently is associated with the absence of processes (interaction with the solvent, catalysis by impurities, the chain decomposition, *etc.*) favoring the transformation of DMD in solution.

References

1. W. Adam, R. Curci, and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205.
2. D. V. Kazakov, N. N. Kabal'nova, A. I. Voloshin, V. V. Shereshovets, and V. P. Kazakov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2286 [*Russ. Chem. Bull.*, 1995, **44**, 2193 (Engl. Transl.)].
3. W. Adam, Y.-Y.Chan, D. Cremer, J. Gauss, D. Scheutzow, and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800.
4. N. J. Turro, *Tetrahedron Lett.*, 1987, **28**, 1589.
5. V. P. Kazakov, A. I. Voloshin, S. S. Ostakhov, and N. Sh. Ableeva, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 447 [*Russ. Chem. Bull.*, 1995, **44**, 432 (Engl. Transl.)].

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On the [4+2]-cycloaddition reaction of levoglucosenone with piperylene

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The Diels—Alder reaction of levoglucosenone with piperylene catalyzed by $ZnCl_2$ proceeds regio- and stereoselectively to give the *sin—cis*-adduct **3**; the thermal reaction yields an epimeric mixture of compound **3** with *sin—trans*-adduct **4** in the ratio of 4 : 1.

Key words: levoglucosenone, piperylene, cycloaddition, regio- and stereoselectivity.

Alicyclic 1,3-dienes of different types: butadiene, 1-acetoxy- and 1-trimethylsiloxybutadienes, and 1-benzyloxymethyl-3-methoxybutadiene, readily enter the thermal Diels—Alder reaction with levoglucosenone (**1**)[1,2] to yield the corresponding [4+2]-cycloadducts of type **2**.[3—6] The reactions proceed according to an unam-

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