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The chemiluminescence of dispiro(1,2-dioxetane-diadamantane) sorbed on silipore activated by a phenanthroline complex of Eu(III)

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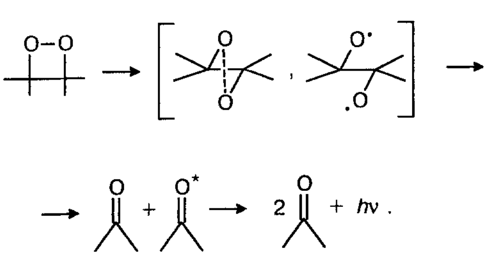
The thermal decomposition of dispiro(1,2-dioxetane-diadamantane) (**1**) sorbed on silipore containing $EuCl_3$ and *o*-phenanthroline was investigated. The observed chemiluminescence is caused by radiative deactivation of Eu*(III) formed according to an energy transfer mechanism. Chemiluminescence decay in the course of the decomposition of **1** is exponential with the rate constant k. The activation parameters of the decomposition of **1** sorbed on silipore were determined from the temperature dependence of k. These parameters are independent of the Eu(III) content. A kinetic compensating effect was found: the dependence of $\log A$ on E_a as a function of the content of **1**. The mechanism of the compensating effect is discussed.

Key words: chemiluminescence, catalysis, kinetic compensating effect, dispiro(1,2-dioxetane-diadamantane), $EuCl_3$, *o*-phenantroline.

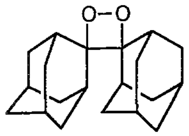
The behavior of excited molecules and their reactions on different solid surfaces and in structured (anisotropic) media have attracted the attention of numerous researchers.[1] The behavior of excited organic and inorganic compounds on solid sorbents, for example, on silica gel,[2,3] is under intense investigation. The adsorption of luminescent compounds substantially changes their photophysical properties.[3,4] Naturally, reactions leading to the formation of products in the excited state, radicals and other reactive species should be the most sensitive to the nature of the surface. Thus, one of the sources of crystallo-luminescence (CRL) is the chemiluminescence (CL) that occures as a result of the decomposition of peroxides catalyzed by the formation of a crystal surface.[5] The decomposition of ozone on silica gel leads to the formation of singlet oxygen,[6] which can be easily identified by its reaction with olefins and by luminescence in the near IR region.[7] It is known that compounds with a developed surface catalyze the decomposition of peroxides including dioxetanes.[8,9] We believe that 1,2-dioxetanes are the most suitable compounds for the investigation of reactions on solid surfaces, since their thermal decomposition into two carbonyl moieties leads directly to excited products (reaction (1)) the properties of which can be sensitive to the nature of surfaces.



(1)

In addition, the formation of excited species in reaction (1) allows one to investigate the transfer of energy to the excitation acceptors, which has been shown to occur rather efficiently in solid media.

In the present paper we report data concerning CL during the decomposition of dispiro(1,2-dioxetane-diadamantane) (**1**) sorbed on silipore, and the activation of CL by a phenanthroline complex of Eu(III).



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Experimental

Preparation of samples of silipore with dioxetane and activator. The appropriate amount of silipore 30 (Chemapol) was introduced into an aqueous solution of $EuCl_3$. The suspension obtained was stirred for 15 min, allowed to settle, and the solution was decanted. $EuCl_3$ was almost completely sorbed onto the carrier. Then the suspension was dried *in vacuo*. A solution of *o*-phenanthroline (Phen) in aqueous ethanol was added to the dried silipore in the amount nesesseary to obtain the proportion Eu(III):Phen=1:3 (this proportion was maintained in all samples excluding those used to study the influ-

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ence of the amount of Phen on the intensity of CL. The mixture obtained was stirred and allowed to settle, and the solution was removed. Then the silipore containing Eu(III) and phenanthroline was dried for a second time and mixed with a solution of **1** in CH_2Cl_2. The suspension obtained was dried at 40—50 °C and at a pressure of 10^{-2} Torr. Under these conditions the samples were freed from water which turned out to effectively quench CL. A comparison of the intensity of CL for two equal portions of the same sample dried *in vacuo* and under atmospheric pressure showed the intensity of CL in the former case to be 2—2.5 times higher. The size of the samples used for measurements of the parameters of CL was 0.1 g. A code was accepted for describing the samples, according to which, for example, SP—3:9:1 (Eu, Phen), means that $3 \cdot 10^{-5}$ mol of $EuCl_3$, $9 \cdot 10^{-5}$ mol of Phen, and $1 \cdot 10^{-5}$ mol of **1** were applied onto 1 g of silipore.

Synthesis and purification of reagents. Chemiluminescent, fluorescent and other measurements. Dioxetane **1** was synthesized according to the procedure described previously.[11] $EuCl_3$ of "chemically pure" grade was recrystallyzed twice from bidistilled water. Solvents were purified by distillation. Silipore 30 was used without additional treament. CL was measured using an FEU—140 photomultiplier with signals recorded on a K—201 recorder. CL spectra were obtained using an installation equipped with a wide—aperture MZD—2M monochromator and an FEU—119 photomultiplier. Photoluminescence (PL) spectra were recorded on a "Hitachi MPF—4" spectrofluorimeter, the lifetime in the excited state was determined on a LIF—200 pulse laser fluorimeter (GDR).

The activation energy of CL of **1** (E_a^{CL}) in the presence of an activator was found from the dependence of the intensity of CL on temperature in the interval 40—50 °C. The observable constant of rate of the decomposition of **1** and the activation parameters E_a and log*A* were determined from the decrease in intensity of CL in the course of thermolysis at 105—130 °C.

Results and Discussion

The samples of silipore containing phenanthroline and dispiro(diadamantane-1,2-dioxetane) give intense CL when heated above 60 °C. The intensity of CL allows one to observe a red luminescence in a slightly darkened room. The CL spectrum of SP—3:9:1 (Eu, Phen) is presented in Fig 1. It almost corresponds to the PL spectrum of the same sample at higher resolution. The spectra consist of lines caused by $^5D_0 \rightarrow ^7F_j$ (j = 0, 1, 2, 3) transitions in Eu^{3+} ions. However, the ratios of the intensities of the bands, for example for the $^5D_0 \rightarrow ^7F_2$ transition, is different for photo- and chemiexcitation. Apparently, the redistribution of the band intensities in CL and PL spectra is caused by the different pathways leading to Eu*(III) in photo- and chemiexcitation.[14]

There is no chemiluminescence in the region 350—500 nm, typical of the fluorescence of adamantanone. This fact suggests essentially complete transfer of energy from excited adamantanone to the europium chelate. It is well known that coordinatively saturated europium chelates, for example Eu(TTA)$_3$Phen (where TTA is thenoyltrifluoroacetone) activate the chemiluminescence of dioxetanes in accord with an energy transfer mechanism.[13] Coordinatively unsaturated chelates of Eu catalyze the decomposition of oxetanes and activate CL through intracomplex energy transfer from the excited carbonyl molecule. In this case the dependence of CL on the concentration of the activator is linear.[14]

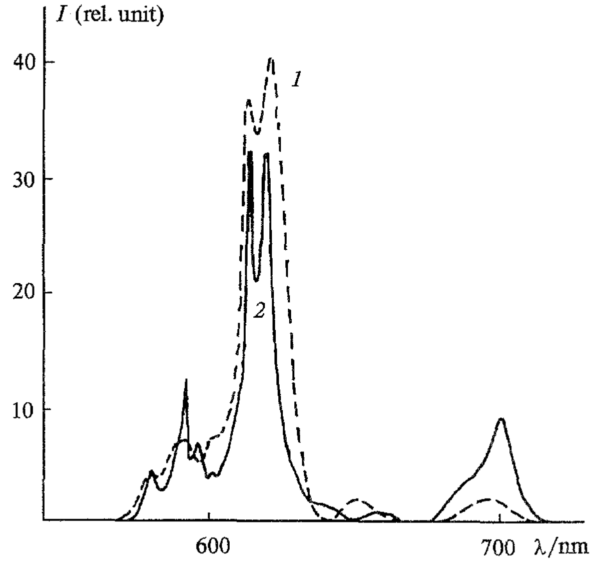

Fig 1. CL (*1*) and PL (*2*) spectra of the sample SP — 10:30:1 (Eu, Phen): *1)* 93 °C, MZD-2M, Δλ = 5 nm; *2)* 22 °C, MPF-4 "Hitachi", registration angle 60°, λ_b = 350 nm, λ = 1 nm.

Apparently, the activation of chemiluminescence by the Eu(III) complex in the course of the decomposition of **1** on silipore proceeds *via* an energy transfer mechanism. Indeed, the dependence of PL on Eu(III) concentration is linear, whereas that of CL (I_{CL}) is described by a curve with a trend towards saturation which characterize energy transfer (Fig. 2). In addition, the activation energy of quasi-steady-state luminescence, E_a^{CL}, is independent of the concentration of europium and coincides with E_a^{CL} for oxetane decomposition on silipore (Table 1) in the absence of europium. This value coincides

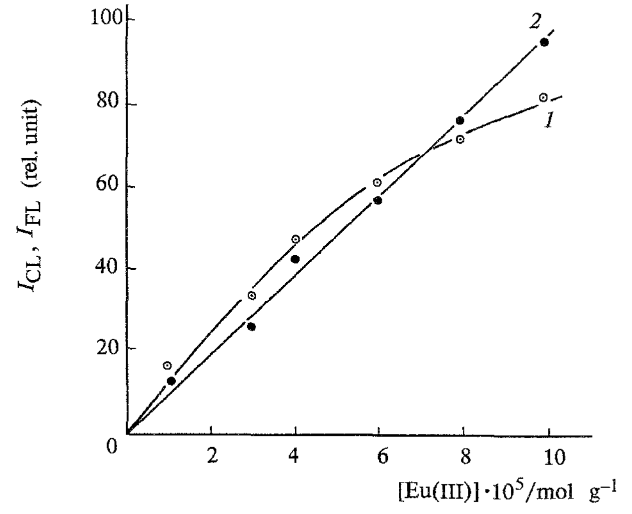

Fig. 2. Dependence of the intensity of CL (*1*) and PL (*2*) on Eu(III) content in silipore samples SP — *n*:3*n*:1 (Eu, Phen).

Table 1. Activation parameters of the decay of **1** on silipore

Sample	$E_a^{CL}\pm0.5$ kcal/mol	$E_a\pm0.5$ kcal/mol	$\log A\pm0.1$
SP — 0:0:1	32.3	32.1	13.2
SP – 1:3:1(Eu, Phen)	32.8	–	–
SP – 3:9:1(Eu, Phen)	32.1	32.1	13.2
SP – 4:12:1(Eu, Phen)	32.8	–	–
SP – 6:18:1(Eu, Phen)	32.3	–	–
SP – 8:24:1(Eu, Phen)	32.5	–	–
SP – 10:30:1(Eu, Phen)	32.6	–	–
SP – 3:9:0.8(Eu, Phen)	–	31.5	13.0
SP – 3:9:0.5(Eu, Phen)	–	30.6	12.8
SP – 3:9:0.2(Eu, Phen)	–	29.2	12.1
SP – 3:9:0.1(Eu, Phen)	–	28.5	11.9

within the limits of experimental error with E_a obtained from measurements of the first order rate constant of CL decay.

Thus, the complex does not catalyze neither chemiluminescent or thermal decay of **1** and plays only the role of an acceptor of excitation energy.

In our case the chloride salt probably contains two phenanthroline ligands in the coordination sphere, *viz.*, $Eu(Phen)_2Cl_3$. An indirect confirmation of this assumption follows from the dependence of CL intensity upon the content of phenanthroline. The intensity of CL reaches the steady-state level when Eu:Phen=1:2 (Fig. 3). Also, the lifetime of the $Eu(Phen)_2Cl_3$ complex sorbed on silipore in the excited state corresponds to that of the europium complex in samples with different amounts of Eu, *viz.*, SP—*n*:3*n*:1 (Eu,Phen) (where *n* = 1, 3, 4, 6, 8, 10), and is equal to 1.18 ms.

CL intensities were measured for the following systems: 1) $0.1\cdot10^{-5}$ mol of dioxetane in acetonitrile; 2) $0.1\cdot10^{-5}$ mol of dioxetane on silipore (concentration 10^{-5} mol g^{-1}); 3) $0.1\cdot10^{-5}$ mol of dioxetane and $0.3\cdot10^{-5}$ mol of $Eu(Phen)_2Cl_3$ in acetonitrile; 4) $0.1\cdot10^{-5}$ mol of dioxetane, $0.3\cdot10^{-5}$ mol of $EuCl_3$ and $0.9\cdot10^{-5}$ mol of phenanthroline on silipore (SP—3:9:1 (Eu, Phen)). These intensities relate to each other as 1:1.3:5:55. This increase in activated luminescence during the decomposition of dioxetane on silipore relative to that in solution cannot be explained by faster degradation of oxetane on silipore. This could provide only a twofold increase in luminescence, assuming constant yields of triplet and singlet excited states in solution and on silipore.

The synergetic effect of the increase in CL is probably related to the increase in the efficiency of the irradiative deactivation of the europium complex on silipore relative to that in solution. Thus, the lifetime of excited $Eu(Phen)_2Cl_3$ in acetonitrile amounts to 0.39 ms, whereas that on silipore is 1.18 ms, *i.e.*, the quantum efficiency of radiation increases 3.03 fold. It is possible that the excitation yields (Φ_s*, Φ_t*) increase during the decomposition of **1** on silipore as well. Apparently, it is the influence of these factors that causes the effect observed.

The intensity of CL is proportional to the amount of dioxetane, which makes it possible to investigate the kinetics of the decomposition of **1** on silipore. The dependence of CL intensity on time is exponential until a 70% decrease in the intensity (Fig. 4). The parameters of the activation of dioxetane decomposition can be

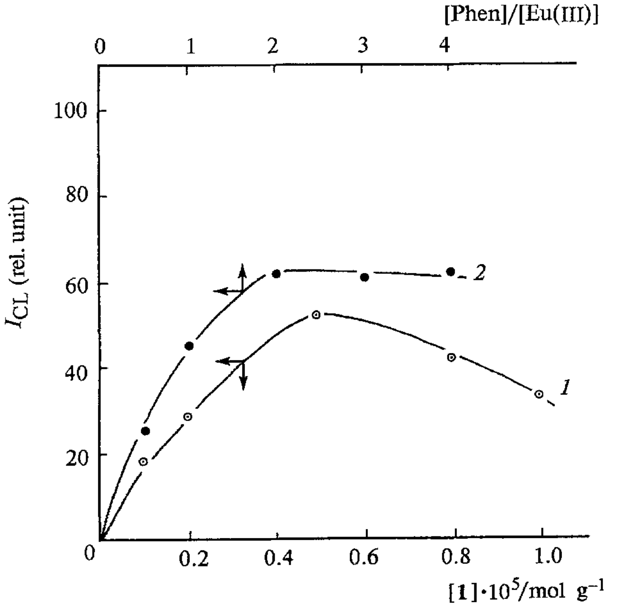

Fig. 3. Dependence of the intensity of CL on the content of **1** for silipore samples SP — 3:9:*m* (Eu, Phen) (*1*) and on the Eu(III) –*o*-phenanthroline ratio in silipore samples SP — 3:*k*:1 (Eu, Phen) (*2*).

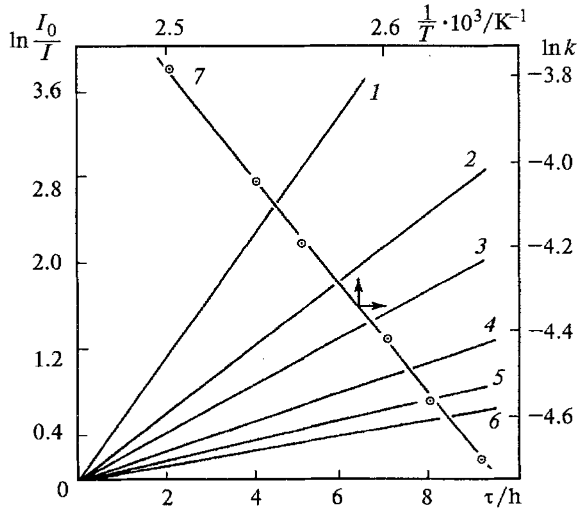

Fig 4. CL kinetics in the course of thermolysis of SP — 3:9:0.1 (Eu, Phen): *1*) 400, *2*) 394; *3*) 390.5; *4*) 384.5; *5*) 382; *6*) 378 K; *7*) dependence of the observed CL attenuation rate constant on temperature in the coordinates of the Arrhenius equation.

easily determined from the temperature dependence of the rate constant k of CL decay using the Arrhenius equation. As shown in Fig. 4, the dependence of log$k$ on T^{-1} is linear in the temperature range under investigation. Similar dependences hold for other samples with different dioxetane concentrations. The values of E_a and log$A$ are given in Table 1. Both E_a and log$A$ increase as the concentration of **1** increases, but to a smaller extent than the activation parameters in solution.[11,15] The dependence of log$A$ on E_a presented in Fig. 5 can be rather well described by the equation log$A$ $= 0.36E_a + 1.45$ (r = 0.99), which points to the existence of a kinetic compensation effect (KCE).[16—20]

There exists a viewpoint that KCE is an artificial phenomenon caused by overreading or underreading kinetic parameters in the course of experimental measurements.[17] However, there are arguments that this relationship is real and that it has at least several causes. Thus, for instance, there is almost no doubt concerning the occurrence of a KCE for the activation parameters of the deactivation of an excited state that is an elementary process.[18,19] Similarly, one can assume that the thermodynamic compensation effect is a consequence of the kinetic one.[20]

The decomposition of dioxetane is characterized by certain steric evolution along the reaction route from the starting compound *via* a transition state into the reaction products. The transition state (see reaction (1)) is a twisted peroxide ring that is transformed into 1,4-diradical in the transoid state.[21]

Obviously, the adsorption of dioxetane on a solid surface can influence the structure of the transition state. This peculiarity of decomposition is general for dioxetanes. It is also valid for compound **1**, but with some peculiarities including the interaction of bulky adamantyl substituents during the formation of the 1,4-diradical.[21] These features explain the abnormally high stability of dioxetanes bearing bulky substituents. The compensation effect is probably based on the scission of the O—O-bond of the dioxetane ring, which determines the reaction rate. We believe that the decrease in E_a in the transition from solution to silipore and its dependence on the content of **1** are related to the loosening action of the silipore surface on the bonding orbitals of the O—O-bond. The degree of this action depends on the adsorption strength of **1**. Perhaps there are adsorption centers with different catalytic activity on the silipore surface. Naturally, dioxetane initially occupies the most active adsorption centers. An increase in peroxide content is accompanied by an increase in the fraction of molecules less strongly bonded and thus less susceptible to catalytic degradation. Apparently, E_a reflects this mixed decomposition on adsorption centers with different activities. The occurrence of this process is expressed in the peculiar dependence of CL intensity on dioxetane content (Fig. 3), represented by a curve with a maximum caused by the influence of two opposite factors: the natural increase in luminescence intensity due to the increase in the total amount of compound **1**, and the drop in the decomposition rate accompaning the decrease in the fraction of molecules that undergo catalytically effective decomposition. Probably, the different efficiency of the transfer of exitation to Eu(III) affects the form of this curve as well. The compensating decrease in log$A$ shows that the transition state in the decomposition becomes more ordered as dioxetane content decreases.

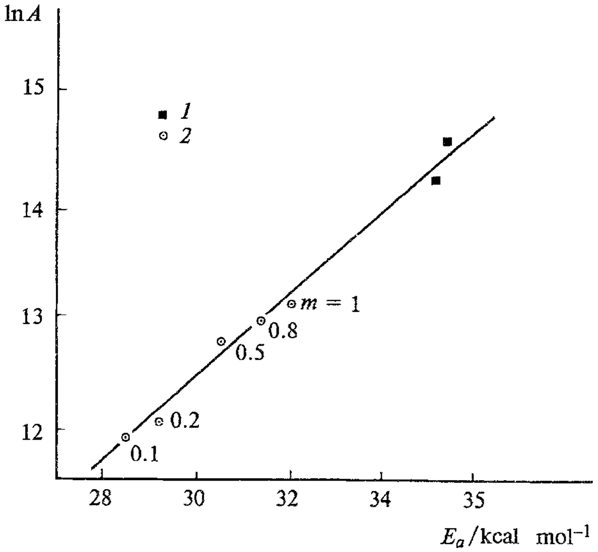

Fig 5. Dependence of the compensatrion of the activation parameters of the thermolysis of **1** in solution (*1*) and in samples of silipore SP — 3:9:m (Eu, Phen) on the content of **1** (*2*).

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