Mechanically induced chemiluminescence in the dispiro(adamantane-1,2-dioxetane)—Eu(fod)$_3$ system

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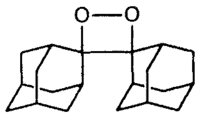
Luminescence accompanying an impact mechanical treatment of solid particles of the complex of Eu(fod)$_3$ (fod is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) with dispiro(adamantane-1,2-dioxetane) (**1**) was discovered and studied. The luminescence has a complex structure, and its spectrum belongs to the excited Eu^{III} ions. The emission of light is observed only in a mechanical mixture of the Eu(fod)$_3$ with dioxetane **1** and in their cocrystallized form, but not in the case of the components taken separately. The mechanism by which the impacts cause the luminescence is considered. It was shown that the luminescence is not triboluminescence, but is chemiluminescence induced by the decomposition of compound **1**.

Key words: chemiluminescence; dispiro(adamantane-1,2-dioxetane)—Eu(fod)$_3$, mechanical deformation.

Mechanical deformation of solids is known to affect the structurally sensitive properties of substances and their reactivities by promoting chemical reactions.[1] Deformation may induce transformations of compounds of various classes, especially labile compounds. Among the latter are four-membered cyclic peroxides, 1,2-dioxetanes, whose decomposition to give two carbonyl compounds involves the formation of electron-excited states and is accompanied by chemiluminescence (CL). The strained and twisted dioxetane ring is sensitive to various kinds of treatment, in particular, to the coordination with lanthanide ions[2] or to adsorption.[3,4] This results in a decrease in the activation barrier to the homolytic cleavage of the O—O bond. A similar effect on the decomposition of dioxetanes is exerted by a freshly formed (juvenile) surface, produced, for example, during crystallization.[5,6]

In this paper we report the results of a study of the luminescence arising on the mechanical destruction of solid particles of the complex of Eu(fod)$_3$ with dispiro(adamantane-1,2-dioxetane) (**1**).



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Experimental

The luminescence was studied on a photometric setup coupled with a PC-controlled Vektor measuring system. The light fluxes were recorded using a FEU-130 instrument by the method of counting photons in the one-electron mode. The time analysis of the light flashes was carried out by the method of pulses at successive time intervals with a maximum resolution of 10 μs per channel. The spectral region of the luminescence was determined using a set of boundary light filters.

The setup for the impact mechanical destruction of samples consisted of a vertical rod with a brass striker in the lower section, which moved inside a fixed guiding tube. In the upper section of the rod, an iron anchor plate was located, which was set in motion by an electromagnet. When a voltage pulse was imposed on the winding of the electromagnet, the rod with the striker hit the sample located in a glass cell over the photoelectric cathode of a photomultiplier. The pulse developed by the striker was $(1.8—2.7) \cdot 10^{-2}$ N s, and the static pressure was $(6.4\pm0.5) \cdot 10^5$ N m^{-2} over a period of 300±50 ms.

Dioxetane **1** was prepared as described previously.[7] The chelate Eu(fod)$_3$ was dried *in vacuo* at 90 °C. Adamantanone (**2**) was purified by column chromatography and by sublimation. The [Eu(fod)$_3 \cdot$ **1**] complex was obtained by evaporating the solvent from a solution containing equimolar amounts of the chelate and dioxetane in CH$_2$Cl$_2$ followed by drying *in vacuo*. Under a microscope, the samples of the [Eu(fod)$_3 \cdot$ **1**] complex looked like glass splinters of size 0.01—0.05 mm, whose shape was similar to that of the solid particles of the chelate. No crystals of dioxetane **1** were detected in the sample. Evidently, under these conditions, dioxetane was virtually completely bound in the complex.

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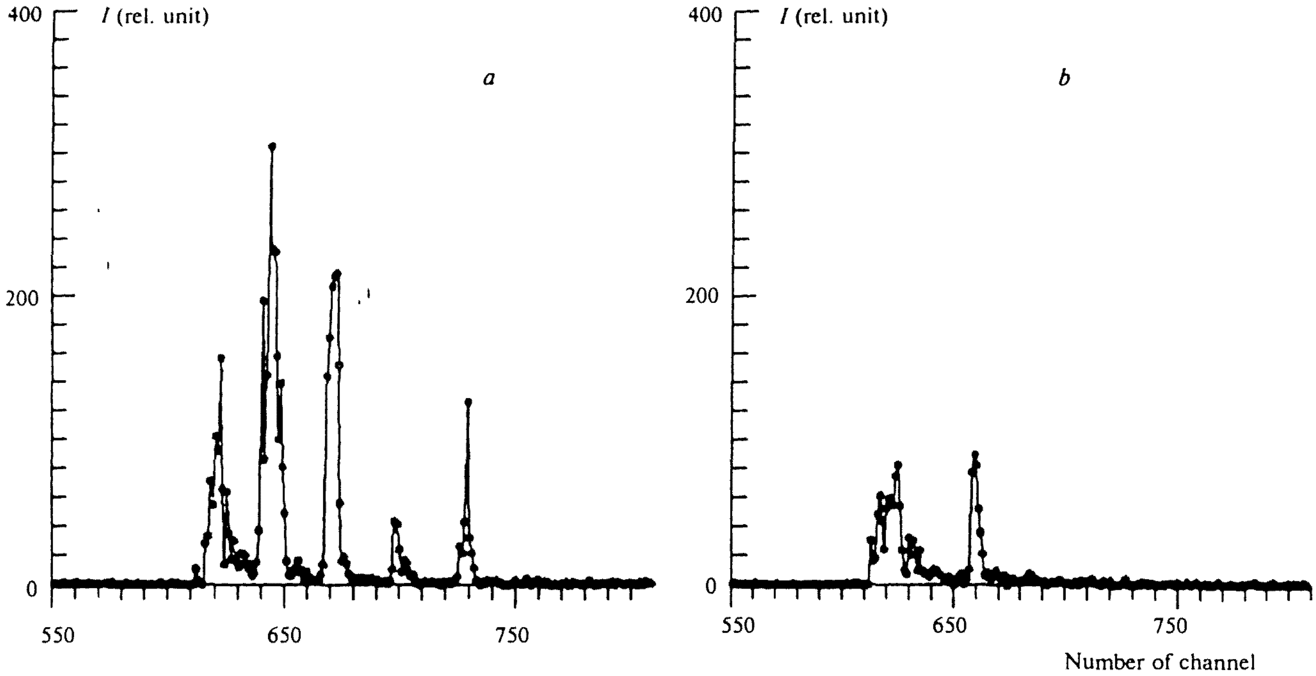
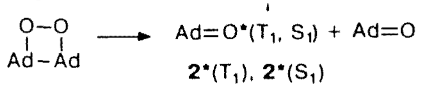


Fig. 1. Light flashes caused by the impact destruction of solid particles of the $[\mathrm{Eu(fod)_3 \cdot 1}]$ complex (*a*) and a mechanical mixture of **1** with $\mathrm{Eu(fod)_3}$ (*b*) recorded by the method of counting the photons at successive time intervals. The window width was 1 ms per channel.

Results and Discussion

We studied the following systems: (a) solid $\mathrm{Eu(fod)_3}$; (b) a mechanical mixture of $\mathrm{Eu(fod)_3}$ with dioxetane **1**; (c) a mechanical mixture of $\mathrm{Eu(fod)_3}$ with adamantanone; and (d) crystals of dioxetane **1** with adamantanone as well as solid complexes: (e) $[\mathrm{Eu(fod)_3 \cdot 1}]$ and (f) $[\mathrm{Eu(fod)_3 \cdot 2}]$. Luminescence was observed only on the impact-induced deformation of the $[\mathrm{Eu(fod)_3 \cdot 1}]$ complex and of the mechanical mixture of $\mathrm{Eu(fod)_3}$ with dioxetane **1**. Figures 1—3 show typical light flashes observed after the impact treatment of $[\mathrm{Eu(fod)_3 \cdot 1}]$ at various time resolutions. A similar pattern differing only in a lower luminescence intensity was observed for the mechanical mixture of $\mathrm{Eu(fod)_3}$ with dioxetane **1** (see Fig. 1, *b*). It can be seen that the emission is a set of light flashes of various amplitudes, which are well resolved at $\Delta t < 2$ ms per channel. The maximum number of pulses for a time resolution of 2 ms per channel reaches 150 pulses per channel (see Fig. 2). It should be noted that upon repeated impacts on the same sample, the light flashes are well reproduced, as regards both the amplitude and the duration of luminescence (see Fig. 3).

To represent more clearly the processes responsible for the emission of light on the deformation, let us consider reactions (1)—(6) occurring in a solution containing the $\mathrm{Eu(fod)_3}$—**1** system.



$$\begin{array}{c}\mathrm{O{-}O}\\ |\quad|\\ \mathrm{Ad{-}Ad}\end{array} \longrightarrow \underset{\mathbf{2}^*(\mathrm{T_1}),\ \mathbf{2}^*(\mathrm{S_1})}{\mathrm{Ad{=}O^*(T_1,\, S_1)}} + \mathrm{Ad{=}O} \qquad (1)$$

$$\mathrm{Eu(fod)_3} + \mathbf{1} \rightleftharpoons [\mathrm{Eu(fod)_3 \cdot \mathbf{1}}] \qquad (2)$$

$$[\mathrm{Eu(fod)_3 \cdot \mathbf{1}}] \longrightarrow \begin{cases} \mathrm{Eu(fod)_3} + \mathbf{2} + \mathbf{2} \\ \mathrm{Eu^*(fod)_3} + \mathbf{2} + \mathbf{2} \longrightarrow \\ \quad \longrightarrow \mathrm{Eu(fod)_3} + \mathbf{2} + \mathbf{2} + h\nu \end{cases} \qquad (3)$$

$$\mathrm{Eu(fod)_3} + \mathbf{2}^*(\mathrm{T_1}) \longrightarrow \mathrm{Eu^*(fod)_3} + \mathbf{2} \qquad (4)$$

$$\mathrm{Eu^*(fod)_3} \longrightarrow \mathrm{Eu(fod)_3} + h\nu \qquad (5)$$

$$\mathbf{2}^*(\mathrm{S_1}) \longrightarrow \mathbf{2}(\mathrm{S_0}) + h\nu \qquad (6)$$

As shown previously,[8] the intensity of the CL in the system under consideration is mostly determined by the decomposition of dioxetane **1** bound in a complex with $\mathrm{Eu(fod)_3}$ (reaction (3)), by the excitation of the $\mathrm{Eu^{III}}$ ion, and by its emissive deactivation (reaction (5)). Complex formation leads to a decrease in the activation barrier to the cleavage of the O—O bond in the dioxetane, which markedly increases the rate of its decomposition. Since the efficiency of the emissive deactivation of $\mathrm{Eu(fod)_3}$ is higher than the emissive efficiency of the triplet- (T) and singlet-excited (S) adamantanone, the intensity of the CL of the $\mathrm{Eu(fod)_3}$—**1** system is greater than that for the dioxetane in the absence of $\mathrm{Eu(fod)_3}$.

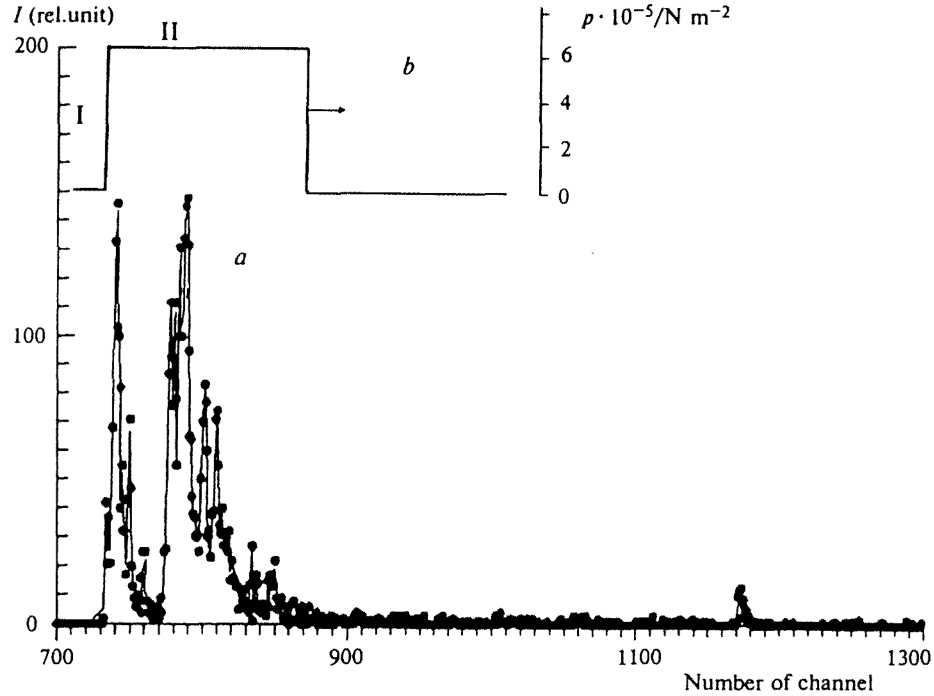


Fig. 2. *a*. Light flashes caused by the impact destruction of solid particles of the [Eu(fod)$_3$ · **1**] complex. The window width was 2 ms per channel. *b*. Pressure distribution during the impact.

The spectral analysis of the light emission arising upon the impact with boundary light filters has shown that the luminescence is concentrated in the red region of the spectrum ($\lambda > 550$ nm), where emissive transitions of the Eu^{III} ion occur. The fact that the luminescence upon the impact is observed only in the systems containing both Eu(fod)$_3$ and dioxetane **1** (as the [Eu(fod)$_3$ · **1**] complexes or as a mechanical mixture) is probably due to chemiluminescent reactions of the chelate with dioxetane similar to those occurring in a solution. The excitation of Eu^{III} occurs most likely during reaction (3) and, probably, during the heterogeneous reaction of sensibilization of **2***(T$_1$) with the chelate (reaction (4)) in the case where the impact causes decomposition of dioxetane **1** (which may be the case with the mechanical mixture of the chelate and dioxetane).

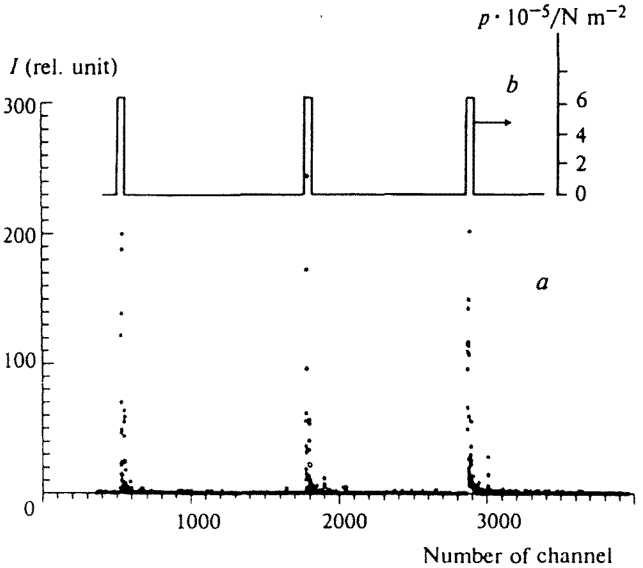


Fig. 3. *a*. Light flashes caused by the impact destruction of solid particles of the [Eu(fod)$_3$ · **1**] complex following successive impact treatments of the same sample. The window width was 10 ms per channel. *b*. Pressure distribution during the impact.

The chemiluminescence nature of the emission is supported qualitatively by the fact that the impact on the individual Eu(fod)$_3$, the [Eu(fod)$_3$ · **2**] complex, mechanical mixture of Eu(fod)$_3$ + **2**, or the crystals of dioxetane **1** cause no luminescence. The absence of emission in the systems with Eu(fod)$_3$ indicates that it is not associated with the processes of exoemission during the mechanical destruction of Eu(fod)$_3$ (see Ref. 9) or triboluminescence,[10] but arises upon the destruction of crystals of dioxetane **1**, possibly due to the low emissive efficiency of **2***(S$_1$) and **2***(T$_1$).

As regards mechanical transformations resulting in the CL observed, the following factors, which act most likely in parallel, are significant: (a) disordering of the structure of the solid particles of [Eu(fod)$_3$ · **1**], the appearance of vacancies and dislocations acting as the centers of topochemical reactions of decomposition of dioxetane **1**, and the appearance of a juvenile surface catalyzing decomposition of dioxetane in the [Eu(fod)$_3$ · **1**] complex;

(b) structural relaxations of the defects accompanied by the evolution of substantial portions of energy, which, in turn, can promote reaction (3), and, probably, reaction (1). An important role is played by the dynamics of the propagation of the defects (cracks, dislocations, intergrain boundaries, *etc.*), favorable for the CL reaction.

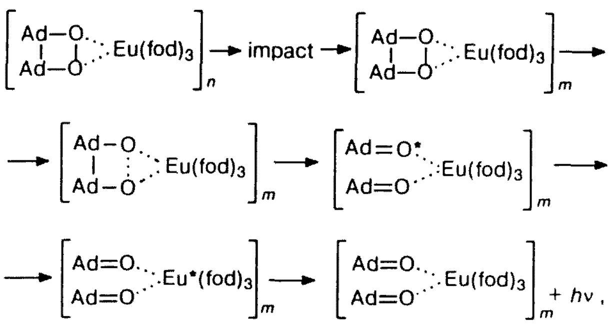
Some conclusions concerning the factors that cause the CL can be drawn on the basis of a consideration of the time dependences of the luminescence intensity. The duration of the dynamic action of the striker was 1—1.5 ms and that of the static pressure was 300±50 ms. It can be seen from Fig. 2, which presents a time-resolved flash of the luminescence caused by a single impact, that the duration of CL is much greater than that of the dynamic effect (see section I in Fig. 2). However, the intensity of the luminescence in this time interval is not the highest, *i.e.*, the disordering of the structure of the $[Eu(fod)_3 \cdot \mathbf{1}]$ complex is an important, although not the crucial factor affecting the decomposition of dioxetane. The fact that the luminescence caused by an impact is a set of flashes of various intensities, the most intense of which lies in the time interval in which the static pressure acts, indicates that the emission of light is probably related to the dynamics of the structural transitions caused by the mechanical action. The role of this factor appreciably increases for the reaction occurring under ordinary conditions (without a mechanical perturbation). In fact, decomposition of dioxetane **1** in the $[Eu(fod)_3 \cdot \mathbf{1}]$ complex proceeds at room temperature, too, and the development of defects caused by the deformation facilitates the occurrence of this reaction. Apparently, this changes the conditions of the coordination of dioxetane with the chelate, and this promotes the formation of a structure similar to the transition state preceding the cleavage of the peroxide bonds and causes the irreversible decomposition of dioxetane **1** with the excitation of adamantanone in the complex with $Eu(fod)_3$. After that, an intramolecular transfer of energy results in the formation of $Eu^*(fod)_3$ (Scheme 1).

The duration of the mechanically induced CL observed is greater than the duration of the impact, which can be easily seen at a time resolution of 10 ms per channel (see Fig. 3). This can be explained, on the one hand, by the prolonged dynamics of the structural transformations and, on the other hand, by the existence in the $[Eu(fod)_3 \cdot \mathbf{1}]$ system of quantum chain reactions similar to those found in a study[11] of the photocatalytic decomposition induced by excited $Eu^*(fod)_3$. Since the molecules of the complex in the solid state are closely packed, the probability of the quantum-chain reaction

$$Eu(fod)_3 + [Eu(fod)_3 \cdot \mathbf{1}] \rightarrow Eu^*(fod)_3 + Eu^*(fod)_3 + \mathbf{2} + \mathbf{2}$$

increases. At the present stage of the study of the mechanically induced CL, we cannot yet decide between the two approaches accounting for the duration of the luminescence observed.

Scheme 1



(*n* and *m* are the numbers of molecules of the complex in a solid particle prior to and after the impact, respectively)

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