

References

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Received January 10, 1995;
in revised form April 26, 1995

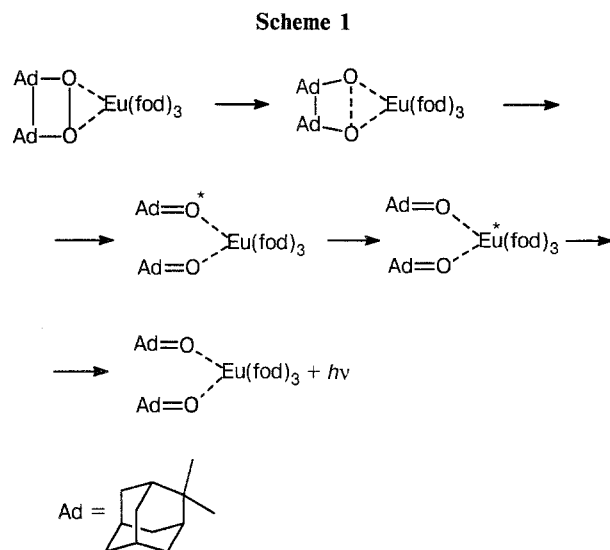
Chemiluminescence during the decomposition of dispiro(adamantane-1,2-dioxetane) cocrystallized with $\text{Eu}(\text{fod})_3$ induced by mechanical destruction of crystals

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It is known that decomposition of 1,2-dioxetanes into two carbonyl fragments results in formation of electron-excited states and is accompanied by chemiluminescence (CL).¹ The strained and twisted peroxide dioxetane cycle is sensitive to effects originating, e.g., from coordination with lanthanide ions or adsorption on the surface,² which accelerate the decomposition of the peroxide. It has previously been shown³ that coordination of the O—O bond in dispiro(adamantane-1,2-dioxetane) (**1**) with $\text{Eu}(\text{fod})_3$ (where "fod" is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) considerably increases the rate of its decomposition into adamantanone. We found that mechanical impact (time of dynamic contact: 1.5–2.5 ms; time of static contact: 0.3 ± 0.05 s; impulse: $5 \cdot 10^2$ g cm s⁻¹) on cocrystallized dioxetane **1** and $\text{Eu}(\text{fod})_3$ (molar ratio 1 : 1) is accompanied by light emission (Fig. 1) in the form of damping, randomly distributed pulses, analogous to those observed during crystalloluminescence.⁴ The emission is predominantly observed in the red spectral region (recording through an OS-14 light filter, $\lambda > 550$ nm). This implies that Eu^{III} serves as the emitter.

The above phenomenon probably has the following origin: crystals of the $[\text{Eu}^{\text{III}} \cdot \mathbf{1}]$ complex undergo destruction under impact, and hence the conditions of coordination of the dioxetane with the chelate change. This may favor the formation of a structure of the complex similar to the transition state, which precedes the cleavage of peroxide bonds, and cause irreversible decomposition of **1** with excitation of adamantanone in the complex with $\text{Eu}(\text{fod})_3$. Subsequently, $\text{Eu}^*(\text{fod})_3$ is formed due to intramolecular transfer of energy (Scheme 1).



When a mechanical mixture of dioxetane **1** with $\text{Eu}(\text{fod})_3$ is affected by impact, light emission also occurs. Its intensity is lower than that of cocrystallized reagents, although the type and structure of pulses remain the same (see Fig. 1). Model systems (crystals of $\text{Eu}(\text{fod})_3$, chelate mechanically mixed or cocrystallized with adamantanone, and 1,2-dioxetane) affected similarly did not display light pulses.

Thus, the luminescence observed in the dioxetane— $\text{Eu}(\text{fod})_3$ system originates from impact-initiated chemiluminescent decomposition of dioxetane **1** in a complex with $\text{Eu}(\text{fod})_3$.

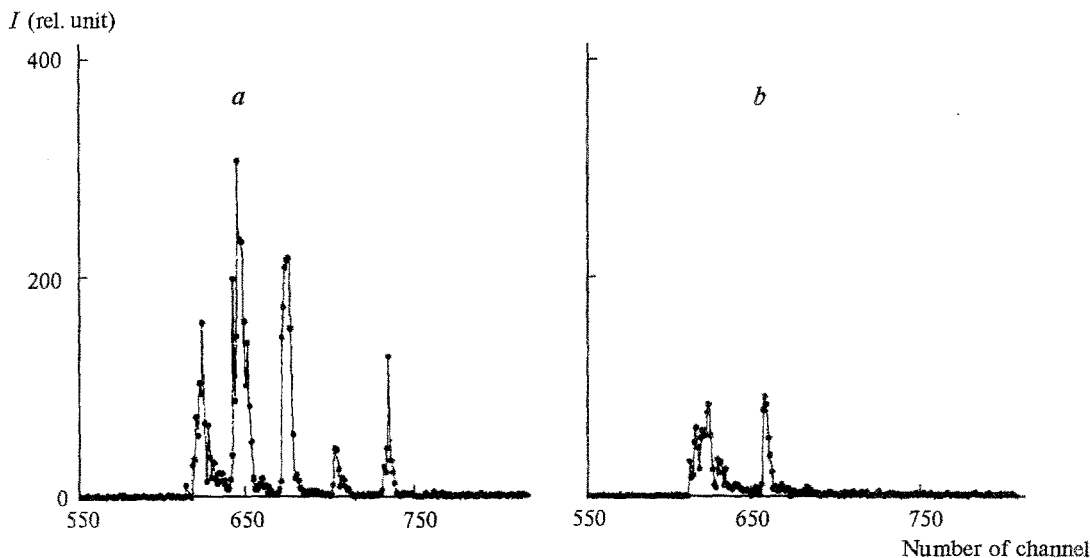


Fig. 1. Light pulses during impact-induced destruction of crystals of the $[1 \cdot \text{Eu}(\text{fod})_3]$ complex (a) and a mixture of 1 with $\text{Eu}(\text{fod})_3$ (b) recorded by photon counting on consecutive time intervals. Window width: 1 ms per channel.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-18165).

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Received March 1, 1995;
in revised form May 15, 1995

Reaction of dithiobisamines with cyclohexene in the presence of phosphorus(v) oxohalides*

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To date there is no information about the use of dithiobisamines as sulfonylating agents. We have investigated the interaction between dithiobismorpholine and cyclohexene in the presence of POCl_3 and POBr_3 . In each case mixtures of the corresponding diastereomeric

β, β' -dihalodisulfides were isolated as the products (Scheme 1).

Thus, for the first time dithiobisamines were successfully involved in electrophilic addition to the $\text{C}=\text{C}$ bond. This method is shown to be more convenient for synthesis of β, β' -dihalodisulfides than the addition of unstable and unpleasantly smelling sulfur dihalides to olefins, which is usually used for this purpose.

* Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).