Chemiluminescent probing of relaxation transitions in PVC films

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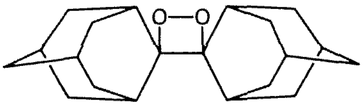
It is known that the mechanical deformation in solid matrices promotes the decomposition of 1,2-dioxetane (**1**) accompanied by chemiluminescence (CL).[1]



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The sensitivity of the dioxetane cycle to intermolecular interactions increases upon coordination with lanthanide ions.[2] In this connection, we assumed that complexes of the [**1** · Eu^{III}] type can be used for studying relaxation transitions in polymers, which are widely studied by luminescent methods.[3]

In fact, the character of CL upon the thermolysis of dioxetane **1** ($8 \cdot 10^{-4}$ mol L^{-1}) in the presence of Eu(fod)$_3$ ($6 \cdot 10^{-3}$ mol L^{-1}) in PVC films (d = 100 mm, dinonyl phthalate 25 %) is explained by the relaxation of the polymeric matrix. The kinetic curve of CL of dioxetane in the freshly cast PVC film in the presence of Eu^{III} consists of two regions with $k_1 = 5.3 \cdot 10^{-3}$ s^{-1} and $k_2 = 1.3 \cdot 10^{-4}$ s^{-1} (T = 363 K) (Fig. 1, curve *1*). It can be considered that the initial region reflects the kinetics of thermal relaxation of PVC, and the second one reflects the decomposition of the complex [**1** · Eu^{III}] in the equilibrium polymeric matrix. This is confirmed by the following observations. The extension of the film after thermal relaxation again results in the biexponential character of the kinetics of the decomposition of **1** (Fig. 1, curve *2*). The kinetics of CL of **1** in the freshly prepared sample is reproduced upon dissolution of the thermally treated film in THF and its repeated casting (Fig. 1, curve *3*). It is noteworthy that the k_1 values, unlike k_2, are not identical in different samples, although the radiation emitter is the same: Eu^{III} (boundary light filters, $\Delta\lambda$ = 20 nm); this testifies to the single mechanism of the chemiexcitation. Special attention should be given to the fact that the kinetics of CL of **1** in the absence of Eu^{III} is exponential (Fig. 1, curve *4*) and does not reflect structural changes in the PVC matrix. Thus, dioxetane is insensitive to the relaxation transitions, and chemiluminescent "response" to them is possible only with the participation of the "mediator," Eu(fod)$_3$.

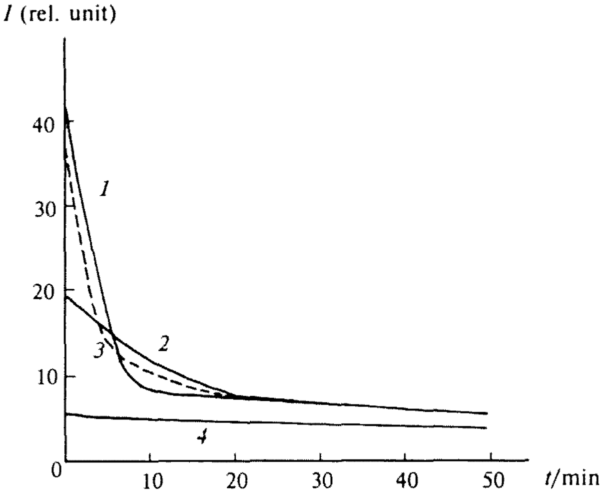
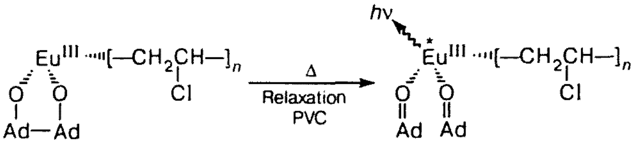


Fig. 1. Kinetic curves of CL of dioxetane **1** ($8 \cdot 10^{-4}$ mol L^{-1}) in the presence of Eu(fod)$_3$ ($6 \cdot 10^{-3}$ mol L^{-1}) in PVC films: freshly prepared (*1*), stretched after the thermal treatment (*2*), repeatedly cast after the thermal treatment (*3*), and freshly prepared in the absence of Eu(fod)$_3$ (*4*) (T = 263 K).



It is evident that it is the complex [**1** · Eu^{III}] that is the probe for the relaxation transitions in the PVC matrix, and these transitions likely favor the formation of the structure of the complex [**1** · Eu^{III}] close to the transition state of the decomposition of dioxetane **1** accompanied by CL.

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Thermal aromatizational rearrangements of 4,4-dimethyl-1-(4-trichloromethyl-4-methylcyclohexa-2,5-dienylidene)cyclohexane-2,6-dione

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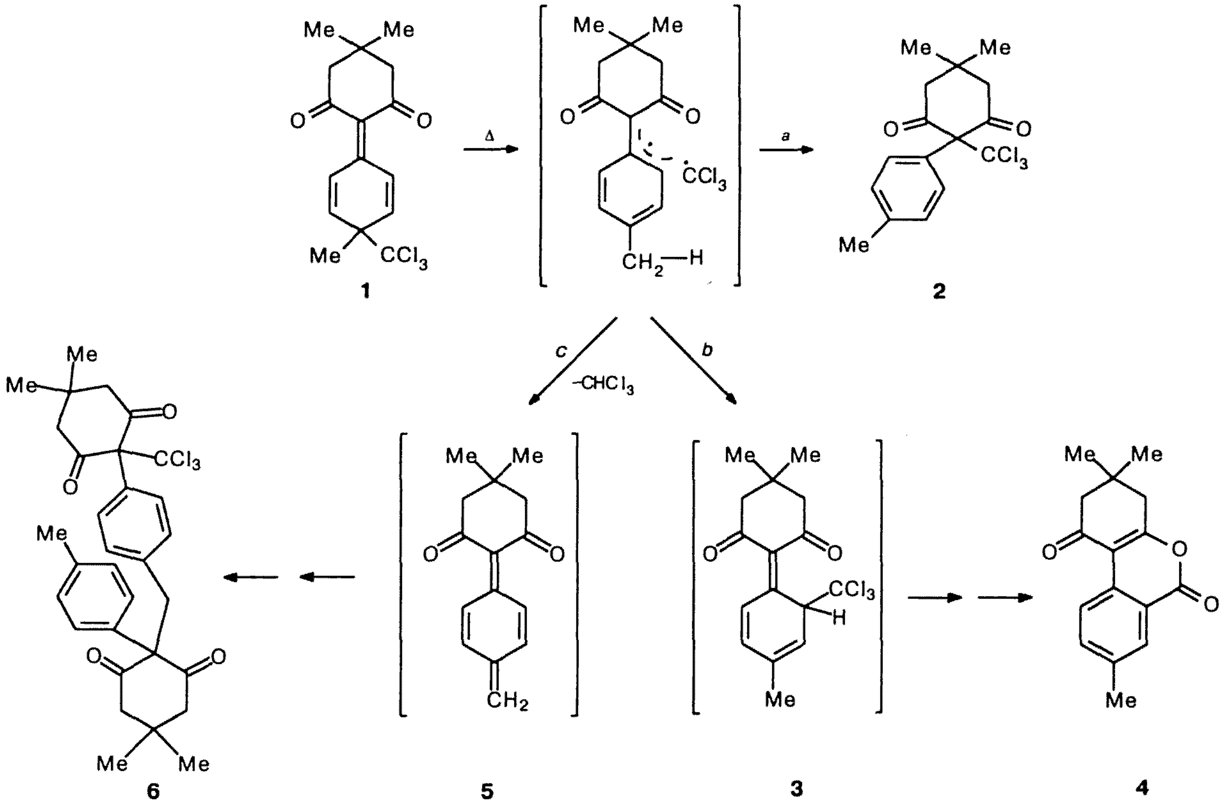
Thermal transformations constitute an important branch of organic chemistry.[1] We discovered new aromatizational rearrangements of trienedione (**1**)[2] (Scheme 1) that occur under thermolysis conditions at 180—185 °C

Scheme 1



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† Deceased.

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