Chemiluminescence initiated by complex formation in solutions of 1,2-dioxetane and lanthanide perchlorates

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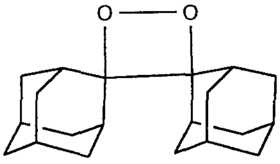
The spectral and activation parameters of chemiluminescence in the thermal decay of 1,2-dioxetane based on adamantylideneadamantane in acetonitrile in the presence of Tb^{III}, Eu^{III}, Pr^{III}, Ce^{III}, and Gd^{III} perchlorates and $UO_2(NO_3)_2$ have been studied. Two types of catalysis by metals, luminescent and nonluminescent, can be distinguished in the framework of one mechanism of dioxetane decay initiated by metal—peroxide complex formation. The mode of catalysis depends both on the presence of suitable energy levels in the metal ion to which the intracomplex transfer of excitation from the $^3n,\pi^*$-state of the ketone that appears in the decay of dioxetane in a catalytic complex can occur and on the ratio of the quantum yields of luminescence of the ketone and the metal ion that is the catalytic activator of luminescence.

Key words: chemiluminescence; 2,2′-biadamantane 2,2′-dioxide, 1,2-dioxetanes, thermal decay; adamantanone; lanthanides, uranyl.

The thermal decomposition of 1,2-dioxetanes to form carbonyl fragments, which are the products of the cleavage of the O—O and C—C bonds of the four-membered cycle, is accelerated in solutions of coordination compounds of transition metals. The catalysis is caused by the formation of a metal—peroxide complex.[1,2] As a rule, metal-catalyzed decomposition is not chemiluminescent, although the formation and luminescence of excited states of carbonyl products is the most typical feature of the noncatalytic thermal decay of 1,2-dioxetanes, except the decay of 1,2-dioxetane in the presence of chelates of some lanthanides:[3,4] a catalytic process involving Ln^{III} ions is accompanied by their excitation and subsequent de-excitation. The mechanism of catalytic lanthanide-activated chemiluminescence (CL) of 1,2-dioxetanes has been studied for the 2,2′-biadamantane 2,2′-dioxide (**1**)—Eu(fod)$_3$ system (fod is 1,1,1,2,2,3,3-heptafluorodimethyloctanedione).[4—6]



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The chemiluminescence of compound **1** in solutions of lanthanide perchlorates and uranyl nitrate has been studied in the present work in order to elucidate the factors that favor luminescent and nonluminescent pathways of decomposition of 1,2-dioxetanes catalyzed by metals.

Experimental

Salts of tervalent lanthanides $Ln(ClO_4)_3$ (Ln = Tb, Eu, Pr, Ce, Gd) were prepared by dissolution of the corresponding oxides or $Ln_2(CO_3)_3$ salts (chemically pure) in 57 % solution of $HClO_4$ (chemically pure) with subsequent recrystallization. The content of water of crystallization in the samples dried *in vacuo* varied from 5 to 6 molecules of H_2O per $Ln(ClO_4)_3$ molecule. Uranyl nitrate (pure) was twice recrystallized from bidistilled water and dried *in vacuo* to obtain $UO_2(NO_3)_2 \cdot 3H_2O$. Acetonitrile was purified by azeotropic distillation with H_2O with subsequent dehydration to spectral purity, which corresponds to 90 % transmission at λ = 200 nm in a 1 cm-long cell. 1,2-Dioxetane **1** was prepared by photosensitized oxidation of adamantylideneadamantane according to the known procedure.[7] Adamantylideneadamantane was prepared from adamantanone (**2**) (see Ref. 8).

The intensity of CL and the CL spectra were recorded on instruments described previously.[9,10] The energy of activation of chemiluminescence (E_a^{cl}) was determined from the analysis of the temperature dependence of the quasi-steady state intensity of luminescence in the 50—85 °C range (the decay of **1**

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during the measurement time may be neglected even under the conditions of catalytic reactions). Photoluminescence spectra (PL) were recorded on a Hitachi MPF-4 spectrofluorimeter. Lifetimes of the excited states of tervalent lanthanides were measured on a LIF-200 laser pulse fluorimeter. Absorption spectra were recorded on a Specord M-40 spectrophotometer.

Results and Discussion

It has been shown in previous works[4—6] that in solutions of lanthanide CL appears both for the catalytic and noncatalytic decay of dioxetane **1** to give adamantanone (**2**), and this may be described by the following scheme:

$$\mathbf{1} \longrightarrow \mathbf{2} + \mathbf{2}\ (\text{or } \mathbf{2}^*) \tag{1}$$

$$\mathbf{2}^* \longrightarrow \mathbf{2} + h\nu(2) \tag{2}$$

$$\mathbf{1} + \mathrm{Ln^{III}} \rightleftharpoons \mathbf{1}\cdot\mathrm{Ln^{III}} \tag{3}$$

$$\mathbf{2} + \mathrm{Ln^{III}} \rightleftharpoons \mathbf{2}\cdot\mathrm{Ln^{III}} \tag{4}$$

$$\mathbf{1}\cdot\mathrm{Ln^{III}} \longrightarrow \mathbf{2}\cdot\mathrm{Ln^{III}}\ (\text{or } \mathbf{2}\cdot\mathrm{Ln^{III*}}) + \mathbf{2} \tag{5}$$

$$\mathbf{2}\cdot\mathrm{Ln^{III*}} \longrightarrow \mathbf{2}\cdot\mathrm{Ln^{III}} + h\nu(\mathrm{Ln}) \tag{6}$$

$$\mathbf{2}^* + \mathrm{Ln^{III}} \rightleftharpoons \mathbf{2}^*\cdot\mathrm{Ln^{III}} \longrightarrow \mathbf{2}\cdot\mathrm{Ln^{III*}} \rightleftharpoons \mathbf{2} + \mathrm{Ln^{III*}} \tag{7}$$

$$\mathrm{Ln^{III*}} \longrightarrow \mathrm{Ln^{III}} + h\nu(\mathrm{Ln}) \tag{8}$$

$$\begin{aligned} \mathrm{Ln^{III*}} + \mathbf{1} \rightleftharpoons \mathbf{1}\cdot\mathrm{Ln^{III*}} \longrightarrow \mathbf{1}'\cdot\mathrm{Ln^{III}} \longrightarrow \\ \longrightarrow \mathbf{2}\cdot\mathrm{Ln^{III}}\ (\text{or } \mathbf{2}\cdot\mathrm{Ln^{III*}}) + \mathbf{2} \end{aligned} \tag{9}$$

The direct CL is caused by the decay of dioxetane (Eq. (1)) and de-excitation of adamantanone (Eq. (2)). The energy of activation of this luminescence ($E_a{}^{cl}$ = 35 kcal mol^{-1}) is almost the same as E_a of reaction (1).[2,7] The energy transfer (Eq. (7)) results in a change in the CL spectrum: the band of compound **2** (420 nm) is quenched, and the bands of the lanthanide appear (Eqs. (6) and (8)). However, $E_a{}^{cl}$ does not change, since the activation energy of reaction (7) is very small and the formation of the excited products is determined by process (1).[9] This "simple" activation of CL is realized for coordinationally saturated lanthanide compounds or at a great excess of adamantanone when the complex formation (Eq. (3)) competing with process (4) is suppressed.

Reactions (3) and (5) determine the catalytic activation of CL. The decay of dioxetane in the $\mathbf{1}\cdot\mathrm{Ln^{III}}$ complex occurs much faster than reaction (1) but first it results in the excitation of the lanthanide.[5] In the catalytic activation, $E_a{}^{cl}$ is determined by the activation energy of reaction (5), which is much lower than E_a of process (1). Thus, a lower $E_a{}^{cl}$ is one of the characteristics of catalytic activation. One may also judge the existence of catalysis by the change in the lifetime (τ) of $\mathrm{Ln^{III*}}$ in the presence of dioxetane (τ was measured in the experiments on PL quenching). Complex formation *via* reaction (9) leads to quenching of $\mathrm{Ln^{III*}}$ due to the conversion of the energy of the electronic excitation of the lanthanide to the vibrational excitation of the dioxetane ligand. Since dioxetane decays in this process and can liberate excess stored chemical energy, partial regeneration of $\mathrm{Ln^{III*}}$ is probable in analogy with Eq. (5), and, hence, quantum-chain decomposition of **1** is also possible (*cf.* Ref. 11). The role of this process may become significant in concentrated dioxetane solutions.

The detailed mechanism of $\mathrm{Ln^{III}}$ excitation in the catalytic complex is of the most interest. It has been suggested[6] that the decay of dioxetane **1** results in localization of the excitation on the triplet ^{3}n,π^*-level of ketone **2** from which the excited states of $\mathrm{Eu^{III}}$ are occupied as a result of intramolecular energy transfer. However, taking into account the interaction and the strong mixing of the electronic states of dioxetane and lanthanide in a complex, one cannot exclude the possibility of nontrivial direct excitation of $\mathrm{Eu^{III}}$ (until localization of the excitation at the carbonyl group). In this case, one should expect the excitation not only of $\mathrm{Eu^{III}}$ or $\mathrm{Tb^{III}}$, but also of virtually all of the lanthanides, because the energy storage of the decay of **1** ($\Delta E = \Delta H^{\neq} - \Delta H_0 \cong 94$ kcal mol^{-1} in the catalytic reaction[6]) is sufficient for occupation of the high-lying levels of $\mathrm{Gd^{III}}$, $\mathrm{Ce^{III}}$, and probably, $\mathrm{Pr^{III}}$. As is known, luminescence from these levels causes UV luminescence in the 310—350 nm range.[12] UV chemiluminescence in the decay of dioxetanes has also been observed previously. The maximum shift in the CL spectrum of the carbonyl products of decay from 400 to 320 nm was observed in the cases when these products formed an intramolecular exiplex.[13]

In order to check the possibility of the catalytic excitation of UV-CL in compound **1** we studied the decay of dioxetane in the presence of $\mathrm{Gd^{III}}$, $\mathrm{Ce^{III}}$, and $\mathrm{Pr^{III}}$ perchlorates, and $\mathrm{Tb^{III}}$ and $\mathrm{Eu^{III}}$ perchlorates for comparison. The perchlorate ion does not absorb in the 300—400 nm range. In addition, its own weak ability to form complexes makes possible the formation of $\mathbf{1}\cdot\mathrm{Ln^{III}}$ complexes and catalysis of the dioxetane decay.

In fact, the addition of these salts to a MeCN solution of compound **1** accelerates the thermal decay of dioxetane. In the visible region of the CL spectrum of $\mathrm{Tb(ClO_4)_3}$, $\mathrm{Eu(ClO_4)_3}$, and $\mathrm{Pr(ClO_4)_3}$ solutions, bands appear that coincide with the de-excitation bands of these lanthanides (Fig. 1). The CL spectrum of the

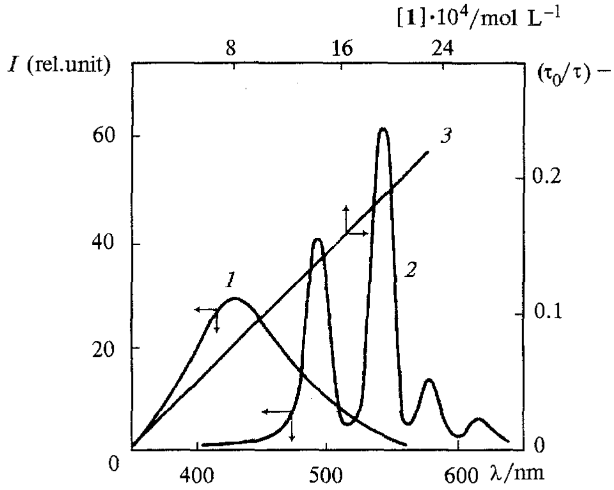

Fig. 1. CL spectra (*1, 2*) in the thermolysis of acetonitrile solutions of **1** and the Stern—Volmer dependence (*3*) for quenching of PL of Tb^{III} (10^{-2} mol L^{-1}) by dioxetane **1** (MeCN, 298 K): (*1*) $1.3 \cdot 10^{-3}$ mol L^{-1} of **1**; (*2*) $9 \cdot 10^{-3}$ mol L^{-1} of **1**; (*3*) $6 \cdot 10^{-2}$ mol L^{-1} of $Tb(ClO_4)_3 \cdot 6H_2O$ (348 K).

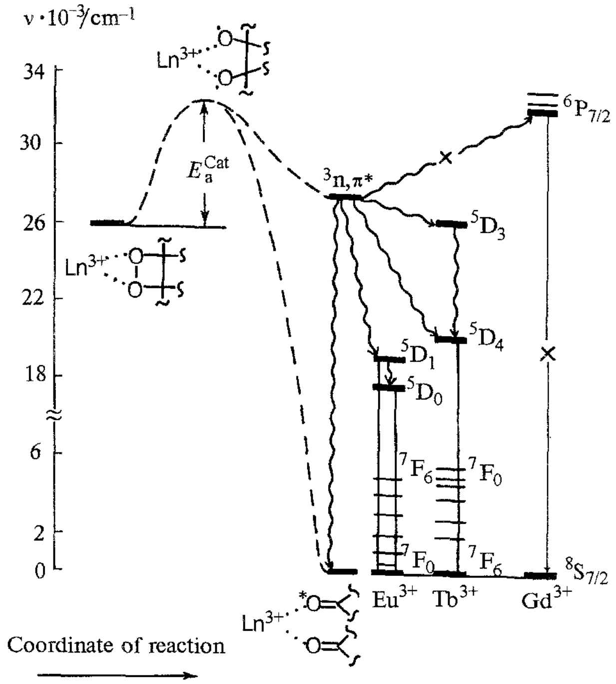

Fig. 2. Scheme of the energy levels and the decay of dioxetane **1** in complexes $\mathbf{1} \cdot Ln^{III}$ and energy transfer to Ln^{III}. Radiative transitions are denoted by straight arrows, nonradiative transitions are denoted by wavy arrows.

solutions with additions of $Ce(ClO_4)_3$ and $Gd(ClO_4)_3$ has only the luminescence band of adamantanone **2**. The band in the UV region of the spectrum that corresponds to luminescence of $Pr(ClO_4)_3$ from the high-lying level of Pr^{III} is also absent. One may judge the existence of catalysis of the decomposition of dioxetane **1** by the decrease in the activation energy of the quasi-steady state luminescence in $Tb(ClO_4)_3$ solutions from 35.4±2.3 kcal mol^{-1} (in the absence of Tb^{III}) to 28.5±2.0 kcal mol^{-1} (0.01 mol L^{-1} of Tb^{III}). The quenching of PL of terbium by dioxetane also takes place (see Fig. 1).

However, this method for identification of catalysis is inapplicable for ions that cause nonluminescent catalysis (CL is caused only by the de-excitation of adamantanone, *i.e.*, by reactions (1) and (2)). In the presence of these ions, E_a^{cl} is not decreased. Therefore, the catalytic action of Ce^{III} and Gd^{III} was established by the direct measurement of the constants of the decay of compound **1** in the presence and in the absence of metals by the method of residual intensities[9] (by the measurement of the quasi-steady state luminescence level at relatively low temperatures after high-temperature thermolysis). The acceleration of the decay of **1** in the presence of metals unambiguously attests to the catalytic effect of $Gd(ClO_4)_3$ and $Ce(ClO_4)_3$ on the decomposition of dioxetane. The absence of UV luminescence proves that the decay of dioxetane in the complexes $\mathbf{1} \cdot Ce^{III}$ and $\mathbf{1} \cdot Gd^{III}$ is not accompanied by the occupation of the excited levels of these ions. Since the presence of these metals also does not cause an increase in the luminescence of singlet-excited adamantanone, it is evident that in the catalytic complex the excitation is localized only at the $^3n,\pi^*$-level of **2**. The presence of a metal in the system initiates the nonradiative deactivation of this level (Fig. 2). Ions of other metals that cause luminescent catalysis, for example, Cu^{II}, Ni^{II}, Co^{II}, *etc.*, apparently act in similar way. The absence of luminescent levels in the metals suitable for occupation results in the nonradiative degradation of the energy liberated by dioxetane during the decay in the catalytic complex.

The ratio of the quantum yields of the luminescence of the carbonyl products of the decay of dioxetane and the metal-catalyst has a significant effect on occurrence of luminescent or nonluminescent routes of catalysis. For example, the effect of uranyl nitrate on CL may be considered to be intermediate between the luminescent catalysis inherent in Tb^{III} and Eu^{III}, on the one hand, and the nonluminescent catalysis typical of Gd^{III} and Ce^{III}, on the other hand.

The UO_2^{2+} ion is known for its luminescence. However, in organic solvents the quantum yield of luminescence $\varphi(UO_2^{2+})$ does not exceed 10^{-3}, while for adamantanone $\varphi(\mathbf{2}) = 1.5 \cdot 10^{-2}$ (*cf.* Ref. 14). Thus, in spite of the possible excitation of uranyl in the catalytic complexes $\mathbf{1} \cdot UO_2^{2+}$, the contribution of the catalytic activation to the luminescence of $\mathbf{1} \cdot UO_2^{2+}$ may become insignificant compared with the fairly bright luminescence in the reaction of catalytic decay. This situation is illustrated by the simplified scheme of direct and uranyl-catalyzed CL given below.

$$\mathbf{1} \longrightarrow \mathbf{2}^* \longrightarrow h\nu(\mathbf{2}) \qquad (10)$$

$$1 \xrightarrow{UO_2^{2+}} 1\cdot UO_2^{2+} \longrightarrow h\nu(UO_2^{2+}) \qquad (11)$$

$$[1] > [1\cdot UO_2^{2+}],\ \varphi(2) > \varphi(UO_2^{2+}),\ I^{cl}(2) \gg I^{cl}(UO_2^{2+})$$

Here $I^{cl}(2)$, $I^{cl}(UO_2^{2+})$ are the intensities of the corresponding components of luminescence.

Indeed, the CL spectrum in the thermolysis of dioxetane **1** in the presence of $UO_2(NO_3)_2$ is almost identical to that of the luminescence of adamantanone (Fig. 3). Only small distortions on the "wings" of the band at 420 nm are noticeable, especially in the long-wave spectral range. These may be a result of the contribution to CL of a spectrally forbidden component caused by the de-excitation of excited UO_2^{2+} ions (the main maximum is at 513 nm). The catalytic effect of uranyl on the decay of **1** is small but noticeable. A decrease in the activation energy of the decay of dioxetane **1** from 35 to 32 kcal mol^{-1} was determined by the method of residual intensities, but there was practically no decrease in E_a^{cl} (Table 1).

However, the analysis of the nature of the lowest electron-excited state of the UO_2^{2+} ion (most likely, the triplet state[15]) testifies that there is a possibility of the excitation of uranyl as the result of the intramolecular energy transfer from the triplet states of ketones, which is similar to lanthanides. This type of transfer has been little studied, but its existence is confirmed by our observation of the radioluminescence of uranyl in acetone, which is more intense than the probable radioluminescence[16] caused by the direct excitation of the UO_2^{2+} ion. Therefore, the small quantum yield of the luminescence of uranyl should be considered as the main factor in the weak "manifestation" of luminescent catalysis.

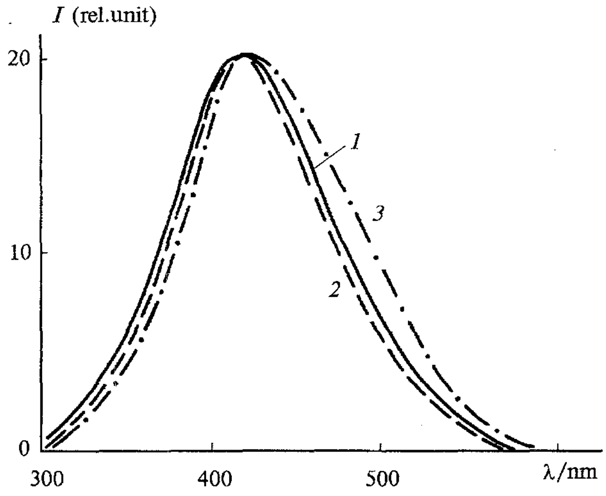

Fig. 3. Luminescence spectra of acetonitrile solutions: (*1*) PL and radioluminescence of adamantanone (0.4 mol L^{-1}, 293 K); (*2*) CL of dioxetane **1** (10^{-2} mol L^{-1}, 353 K); (*3*) CL of dioxetane **1** and $UO_2(NO_3)_2\cdot 3H_2O$ ($5\cdot 10^{-3}$ mol L^{-1}, 353 K). The spectra are normalized by the intensity at the maximum.

Table 1. Activation parameters of the chemiluminescent decay of **1** ($5\cdot 10^{-3}$ mol L^{-1}) in MeCN in the presence of $UO_2(NO_3)_2\cdot 3H_2O$

$[UO_2^{2+}]$/mol L^{-1}	*T*/K	$k\cdot 10^5$/s^{-1}	E_a /kcal mol^{-1}
By the method of quasi-steady state intensities			
—	323—357	—	35.0±0.9
$1\cdot 10^{-3}$	323—357	—	32.9±1.1
$2\cdot 10^{-3}$	323—357	—	31.9±1.9
$4\cdot 10^{-3}$	323—357	—	32.4±1.6
$6\cdot 10^{-3}$	323—357	—	34.2±2.3
By the method of residual intensities			
$5\cdot 10^{-3}$	393	0.8±0.6	—
$5\cdot 10^{-3}$	398	1.4±0.4	31.9±1.0*
$5\cdot 10^{-3}$	403	2.2±0.5	—
$5\cdot 10^{-3}$	408	3.6±0.6	—

* $\Delta S^{\neq}$ = 3.1±0.8 entropy units.

Thus, one mechanism of complex formation, which weakens the O—O bond of peroxide, forms the basis for luminescent and nonluminescent catalyses. The decay of dioxetane in the complex results in the formation of triplet-excited ketone, which deactivates in most cases in a nonradiative mode. The occurrence of the luminescent route is determined by the possibility of the intramolecular transfer of the triplet excitation to a metal ion accompanied by de-excitation with a sufficiently high quantum yield. The considered mechanism of the catalytic activation of CL may be named chemiluminescence initiated by complexation (CLIC), unlike the other known mechanism of catalytic activation based mainly on reactions of reversible electron transfer, chemically initiated electron-exchange luminescence (CIEEL).

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