Chemiluminescence and catalysis of decomposition of dispiro(diadamantane-1,2-dioxetane) in solutions of lanthanide perchlorates

2.* Chemiluminescence of Eu^{III}, Tb^{III}, and Pr^{III}

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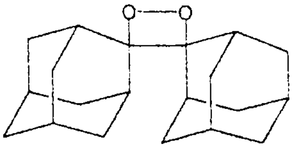
Chemiluminescence (CL) accompanying the decomposition of dispiro(diadamantane-1,2-dioxetane) (1) in acetonitrile solutions of Eu^{III}, Gd^{III}, Tb^{III}, Pr^{III}, and Ce^{III} perchlorates was studied. In the presence of Eu^{III}, Tb^{III}, and Pr^{III} ions, the chemiluminescence spectra contain the luminescence bands of these ions. In the case of Gd^{III} and Ce^{III}, the chemiluminescence is caused by deactivation of singlet-excited adamantanone (2). The excitation of the lanthanide ion depends on the existence of suitable energy levels at which intracomplex excitation transfer from the ^{3}n,π*-state of ketone is possible. Chemiluminescence of 1 increases in solutions of Eu^{III} and Tb^{III}. The yields of CL and excitation of the lanthanide ions in the decomposition of 1 in the 1 · Eu^{III} and 1 · Tb^{III} complexes were determined: $\phi_{Eu^*} = 0.013 \pm 0.003$ and $\phi_{Tb^*} = 0.08 \pm 0.02$. The fact that the efficiency for the population of the $^5D_4$-level of Tb^{III} is higher than that for the $^5D_1$ and $^5D_0$-levels of Eu^{III} is related to the difference in the energy gap between the triplet level of 2 and the excited levels of the lanthanides.

Key words: chemiluminescence, dispiro(diadamantane-1,2-dioxetane), lanthanides, excitation yields, energy transfer.

Thermal decomposition of 1,2-dioxetanes results in the formation of carbonyl compounds in the excited state. Their deactivation is accompanied by light emission. In the presence of coordinationally unsaturated chelates and lanthanide complexes with a labile coordination sphere, for example, Eu^{III} and Tb^{III}, the decomposition of 1,2-dioxetanes occurs much more rapidly. This is associated with the formation of a complex between the lanthanide and peroxide and is accompanied by the enhancement of chemiluminescence (CL) due to charge transfer from the excited carbonyl donor to the efficiently luminescent lanthanide ion.[1–3] When a metal-catalyst does not luminesce in solution under the conditions of thermolysis of dioxetane, no enhancement of CL is observed.[4,5]

We have previously studied the catalysis of the decomposition of dioxetane and substantiated the mechanism of chemiexcitation of an activator using the dispiro(diadamantane-1,2-dioxetane) system (1)—Eu(fod)$_3$ as an example (fod is 1,1,1,2,2,3,3-heptafluorodimethyloctanedione).[6]

In the present work, the chemiluminescence of dioxetane 1 was studied in acetonitrile solutions of luminescent lanthanide perchlorates.



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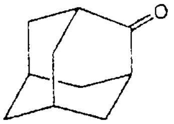

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Experimental

Preparation of lanthanide perchlorates Ln(ClO$_4$)$_3$ (Ln = Tb, Gd, Eu, Pr, and Ce) and a procedure for detecting the CL intensity have been described previously.[1] The spectral sensitivity α of the photocathode of a FEU-140 photomultiplier was determined by a SIRSh-6-100 strip-type tungsten lamp and a set of interference light filters: in the region of fluorescence and phosphorescence of adamantanone 2 ($\alpha_1 = 1$), terbium ($\alpha_2 = 0.8$), and europium ($\alpha_2 = 0.1$). Chemiluminescence spectra were recorded on a photometric installation with an MZD-2M high-power monochromator and a FEU-119 photomultiplier. Photoluminescence (PL) and optical absorption spectra were recorded on a Hitachi MPF-4 spectrofluorimeter and a Specord M-40 spectrophotometer, respectively. Lifetimes of excited states of lanthanides were measured on an LIF-200 laser pulse fluorimeter. The activation energy of chemiluminescence (E_a^{CL}) was determined from the temperature dependence of the quasi-steady-state intensity of CL (I_{CL})

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*For Part 1, see Ref. 1.

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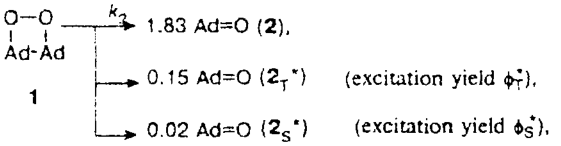
in the range from 50 to 80 °C (during measurements of I_{CL} at these temperatures, the decomposition of **1** is negligible). Emission yields of $Eu(ClO_4)_3$ and $Tb(ClO_4)_3$ in acetonitrile were determined by a known procedure.[7]

Results and Discussion

The chemiluminescence accompanying the thermal decomposition of dioxetane **1** is caused by irradiative deactivation of singlet-excited adamantanone (**2**).[8] Triplet-excited 2_T^* makes almost no contribution to the CL intensity; the phosphorescence quantum yield is $\phi_P = 4 \cdot 10^5$ due to spin forbiddance (see Ref. 3). According to the published data,[8] the regularities of the CL observed are described by the following kinetic scheme.



$$\text{Ad-Ad (O—O)}\ \mathbf{1} \xrightarrow{k_3} 1.83\ \text{Ad=O}\ (\mathbf{2}),\quad 0.15\ \text{Ad=O}\ (2_T^*)\ \text{(excitation yield } \phi_T^*),\quad 0.02\ \text{Ad=O}\ (2_S^*)\ \text{(excitation yield } \phi_S^*) \qquad (1)$$

$$2_S^* \longrightarrow 2 + h\nu\ \text{(fluorescence yield } \phi_F), \qquad (2)$$

$$2_T^* \longrightarrow 2 + h\nu,\ \Delta\ \text{(phosphorescence yield } \phi_P). \qquad (3)$$

In the presence of lanthanide perchlorates, the rate of decomposition of **1** and the spectrum of CL change. Based on the results obtained previously,[6,9,10] it can be assumed that the appearance of CL will be described by the following scheme:

$$\text{Ln}^{III} + \mathbf{1} \overset{K_1}{\rightleftharpoons} \mathbf{1} \cdot \text{Ln}^{III}, \qquad (4)$$

$$\mathbf{1} \cdot \text{Ln}^{III} \longrightarrow (1 - \phi_{Ln^*})[\mathbf{2} \cdot \text{Ln}^{III} + \mathbf{2}], \qquad (5)$$

$$\longrightarrow \phi_{Ln^*}[\mathbf{2} \cdot \text{Ln}^{III*} + \mathbf{2}] \qquad (5a)$$

(excitation yield ϕ_{Ln^*})

$$\mathbf{2} \cdot \text{Ln}^{III*} \longrightarrow \mathbf{2} \cdot \text{Ln}^{III} + h\nu\ \text{(emission yield } \phi_{Ln}'), \qquad (6)$$

$$\mathbf{2} + \text{Ln}^{III} \rightleftharpoons \mathbf{2} \cdot \text{Ln}^{III}, \qquad (7)$$

$$2_T^* + \text{Ln}^{III} \overset{k_{en}}{\rightleftharpoons} \text{Ln}^{III*} + \mathbf{2}, \qquad (8)$$

$$\text{Ln}^{III*} \longrightarrow \text{Ln}^{III} + h\nu\ \text{(emission yield } \phi_{Ln}). \qquad (9)$$

The suggested scheme of reactions (1)—(9) takes into account the ability of lanthanide to accept the energy of the excited adamantanone formed in the decomposition of dioxetane (thermal or catalytic) and thus explains the fact that the luminescence bands of the lanthanides appear in the CL spectrum in the presence of Tb^{III}, Eu^{III}, and Pr^{III} perchlorates (Fig. 1). In the presence of Gd^{III} and Ce^{III}, the CL spectrum is similar to that of **1**, *i.e.*, in these cases, reactions (6) and (9) are insignificant. This is related to the fact that the energy of the triplet level of adamantanone (E_T = 72 kcal mol^{-1})[11] is lower than the energies of the lower luminescence levels of Gd^{III} ($E(^6P_{7/2})$ = 93 kcal mol^{-1})[12] and Ce^{III} ($E(^2D)$ = 78 kcal mol^{-1}).[13]

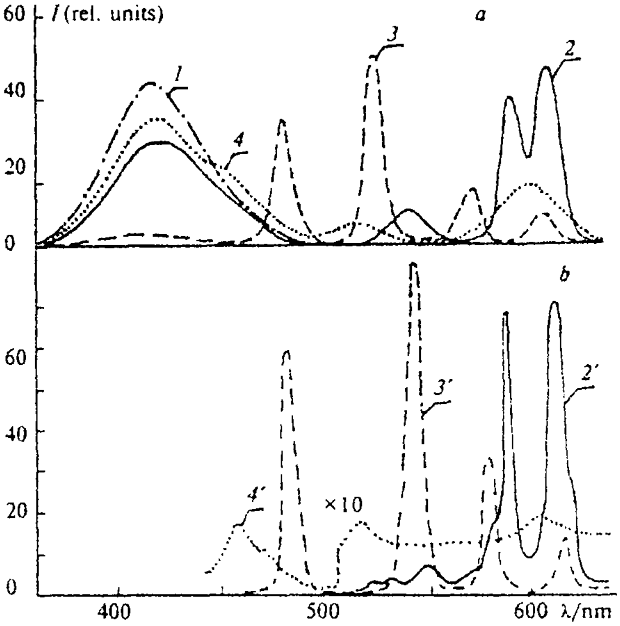


Fig. 1. *a*. Chemiluminescence spectra (*1*—*4*) in MeCN at 353 K: [**1**] = $5 \cdot 10^{-2}$ (*1*); [**1**] = $5 \cdot 10^{-2}$ and [Eu^{III}] = 0.1 mol L^{-1} (*2*); [**1**] = $5 \cdot 10^{-2}$ and [Tb^{III}] = 0.1 mol L^{-1} (*3*); [**1**] = $5 \cdot 10^{-2}$ and [Pr^{III}] = 0.1 mol L^{-1} (*4*); Δλ = 10 nm. *b*. Photoluminescence spectra (*2'*—*4'*) in MeCN at 295 K: [Eu^{III}] = 10^{-2} mol L^{-1}, Δλ = 4 nm, λ_{exc} = 350 nm (*2'*); [Tb^{III}] = 10^{-2} mol L^{-1}, Δλ = 2 nm, λ_{exc} = 365 nm (*3'*); [Pr^{III}] = 10^{-2} mol L^{-1}, Δλ = 6 nm, λ_{exc} = 350 nm (*3'*).

The effective activation energy of emission E_a^{CL} is an important parameter. Analysis of this parameter allows one to draw some conclusions about the mechanism of the process.[14] The values of E_a^{CL} are presented in Table 1. It follows from the data in Table 1, taking into account the temperature dependence of the emission yield of lanthanide, that in the absence of Ln^{III} or in the presence of its coordinationally unsaturated chelates, which do not catalyze the decomposition of **1**, E_a^{CL} is equal to E_a of the thermal decomposition of **1**. In the presence of Tb^{III}, Eu^{III}, and Pr^{III} perchlorates, which do catalyze the decomposition of **1**, $E_a^{CL} > E_a$. For Gd^{III} and Ce^{III}, the values of E_a^{CL} are close to E_a.

The enhancement of CL in the presence of lanthanides is determined by the emission yield of Ln^{III} (ϕ_{Ln}), the excitation yield of Ln^{III} ($\phi_{Ln}{}^*$), the efficiency

Table 1. Activation energies of CL in the decomposition of **1** in the presence of Ln^{III} (system **1**—$Ln(ClO_4)_3$)

$Ln(ClO_4)_3$	$[Ln^{III}]$ /mol L^{-1}	$E_a^{CL}\pm0.2$ /kcal mol^{-1}
—	0	35.0
$Tb(ClO_4)_3$	0.1	28.1
$Gd(ClO_4)_3$	0.1	34.1
$Eu(ClO_4)_3$	0.1	28.6
$Pr(ClO_4)_3$	0.1	31.0
$Ce(ClO_4)_3$	0.1	33.8

of the energy transfer from the donor to the Ln^{III} ion (k_{en}), and the rate of decomposition of **1** in the **1** · Ln^{III} complex. As can be seen from Fig. 2, the enhancement of CL is observed only in the presence of Eu^{III} and Tb^{III}.

The following equation can be written for the CL intensity in terms of the accepted scheme under the condition that the decomposition of **1** in the **1** · Ln^{III} complex is negligible:

$$I_{CL} = \alpha(\phi_S{}^{*}\phi_F + \phi_T{}^{*}\phi_P)k_1[\mathbf{1}] + \alpha_1\phi_T{}^{*}\phi_{Ln}k_{en}\tau_P[Ln^{III}]k_1[\mathbf{1}] + \\ + \alpha_1\phi_{Ln^*}\phi_{Ln}k_2[\mathbf{1}\cdot Ln^{III}], \qquad (10)$$

where α and α_1 are the sensitivities of the photocathodes of the photomultiplier in the region of luminescence of adamantanone and lanthanide, respectively, and τ_P is the lifetime of $\mathbf{2}_T{}^*$ in the excited state.

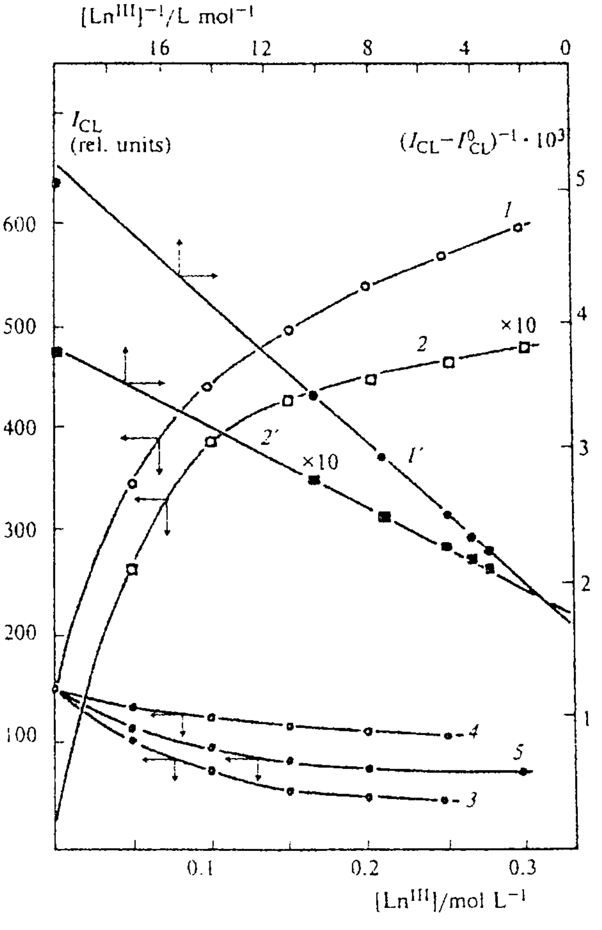


Fig. 2. Dependences of the intensity of CL on the concentration of Eu^{III} (*1*), Tb^{III} (*2*), Gd^{III} (*3*), Pr^{III} (*4*), and Ce^{III} (*5*). Dependences for Eu^{III} and Tb^{III} in the coordinates $1/(I_{CL}-I^0{}_{CL})-1/[Ln^{III}]_0$ (*1′* and *2′*, respectively). $[\mathbf{1}]_0 = 5\cdot10^{-3}$ mol L^{-1}, T = 348 K.

When $[Ln^{III}]_0 > [\mathbf{1}]_0$, the current concentrations of **1** and **1** · Ln^{III} are the following: $[\mathbf{1}] = [\mathbf{1}]_0(1 + K_1[Ln^{III}]_0)^{-1}$ and $[\mathbf{1}\cdot Ln^{III}] = K_1[Ln^{III}]_0[\mathbf{1}]_0(1 + K_1[Ln^{III}]_0)^{-1}$, and Eq. (10) can be rewritten in the form:

$$I_{CL} = \{\alpha(\phi_S{}^{*}\phi_F + \phi_T{}^{*}\phi_P)k_1[\mathbf{1}]_0 + \alpha_1\phi_T{}^{*}\phi_{Ln}k_{en}\tau_P[Ln^{III}]_0k_1[\mathbf{1}]_0 + \\ + \alpha_1\phi_{Ln^*}\phi_{Ln}k_2K_1[\mathbf{1}]_0\cdot[Ln^{III}]_0\}/(1 + K_1[Ln^{III}]_0). \qquad (11)$$

It is evident that at $[Ln^{III}]_0 \to \infty$ and taking into account that $\tau_P = \tau_P{}^0(1 + k_{en}\tau_P{}^0[Ln^{III}])^{-1}$, the channel of the noncatalyzed decomposition of **1** is absent, because all dioxetane is bound in the **1** · Ln^{III} complex. Therefore, the excitation of Ln^{III} and intensity of CL will be determined by reaction (5), *i.e.*,

$$I_{CL}{}^{m} = \alpha_1\phi_{Ln^*}\phi_{Ln}k_2[\mathbf{1}]_0. \qquad (12)$$

Taking into account quenching of $\mathbf{2}_T{}^*$, the intensity of CL appearing due to the noncatalyzed and Ln^{III}-nonactivated reaction of decomposition of **1** can be written in the following form:

$$I^0_{CL} = \frac{[\alpha\phi^*_S\phi_F + \alpha\phi^*_T\phi_P(1 + k_{en}\tau^0_P[Ln^{III}]_0)]k_1[\mathbf{1}]_0}{1 + K_1[Ln^{III}]_0}. \qquad (13)$$

A linear equation relating the kinetic parameters and intensity of CL with the photophysical parameters of the system can be obtained from Eqs. (11)—(13):

$$\left\{\frac{k_2}{k_1}\left[\frac{I_{CL} - I^0_{CL}}{I^m_{CL}}(1 + K_1[Ln^{III}]_0) - K_1[Ln^{III}]_0\right]\right\}^{-1} = \\ = \frac{\alpha_1\phi_{Ln^*}\phi_{Ln}}{\phi^*_T\phi^0_P(\alpha_1\phi_{Ln}/\alpha\phi^0_P - 1)} + \\ + \frac{\alpha_1\phi_{Ln^*}\phi_{Ln}}{\phi^*_T\phi^0_P(\alpha_1\phi_{Ln}/\alpha\phi^0_P - 1)}\cdot\frac{1}{k_{en}\tau^0_P[Ln^{III}]_0}, \qquad (14)$$

where $\phi_P{}^0$ and $\tau_P{}^0$ are the emission yield and lifetime of triplet-excited adamantanone in the absence of Ln^{III}.

In Eq. (14), the rate constants k_2 for the decomposition of **1** in the **1** · Ln^{III} complex were calculated from the Arrhenius parameters: E_a = 26.1±0.4 kcal mol^{-1}, log A = 11.6±0.6 for **1** · Tb^{III} and E_a = 27.3±0.4 kcal mol^{-1}, log A = 12.0±0.6 for **1** · Eu^{III}, and the stability constants were calculated from the thermodynamic parameters of complex formation: $-\Delta H$ = 3.7 kcal mol^{-1}, $-\Delta S$ = 5.8 e.u. for **1** · Tb^{III} and $-\Delta H$ = 3.4 kcal mol^{-1}, $-\Delta S$ = 5.1 e.u. for **1** · Eu^{III} (see Ref. 1). The rate constant of the decomposition of **1** was calculated from the known[15] parameters: E_a = 35.1 kcal mol^{-1} and log A =

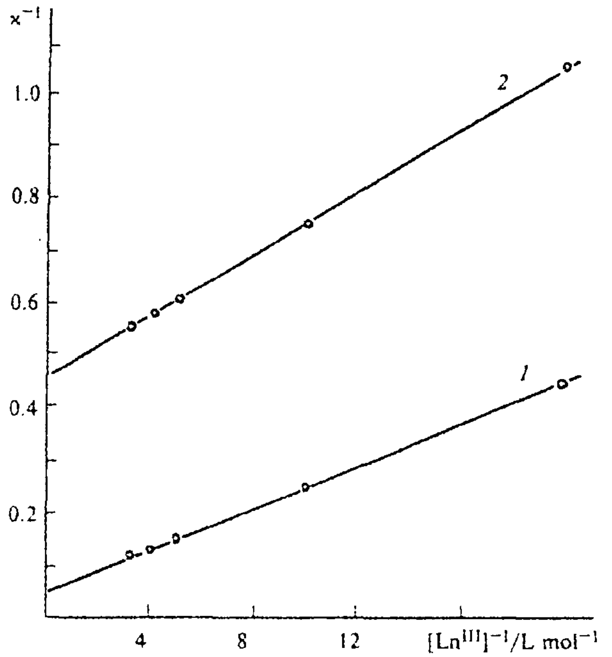


Fig. 3. Dependence of the intensity of CL on the concentration of Eu^{III} (*1*) and Tb^{III} (*2*) in the coordinates of Eq. (14) at 348 K,

$$x = \frac{k_2}{k_1} \cdot \left[\frac{I_{CL} - I_{CL}^0}{I_{CL}^m} (1 + K_1[Ln^{III}]_0) - K_1[Ln^{III}]_0 \right].$$

14.1. Parameters $\phi_P{}^0$ and $\tau_P{}^0$ are equal to $4 \cdot 10^{-5}$ and $4 \cdot 10^{-9}$ s, respectively (see Ref. 3). The $I_{CL}{}^m$ value was determined from the dependence of I_{CL} on $[Ln^{III}]_0$ in the coordinates $(I_{CL} - I_{CL}{}^0)^{-1}$ *vs.* $[Ln^{III}]_0{}^{-1}$ by extrapolation to $[Ln^{III}]_0{}^{-1} = 0$ (see Fig. 2).

As can be seen from Fig. 3, Eq. (14) is well fulfilled. The yields of CL in reaction (5a) $\phi_{Ln^*}\phi_{Ln}$ and the energy transfer constants k_{en} for the decomposition of **1** in solutions of Eu^{III} and Tb^{III} were calculated at different temperatures from the slope of the line and its intersection of the *y* axis. The known values $\phi_S = 0.02$, $\phi_T = 0.15$, and $\phi_F = 0.015$ [8,16] and the values of the relative sensitivity of the photocathode of the photomultiplier in the region of luminescence of Eu^{III} and Tb^{III} were used for the calculation. The results of the calculations are presented in Table 2.

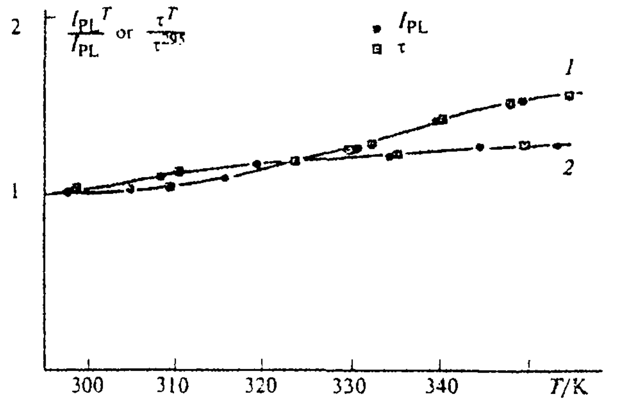


Fig. 4. Relative changes in the intensity of photoluminescence (I_{PL}) and lifetimes (τ) of Eu^{III} (*1*) and Tb^{III} (*2*) in the excited state on temperature (τ_{Eu} = 155 μs, τ_{Tb} = 1.23 μs).

To determine the excitation yields ϕ_{Ln^*} at different temperatures, we estimated changes in the emission yields of Eu^{III} and Tb^{III} as the temperature increased. As has been shown previously,[17] the emission yields of these ions increase as the temperature increases due to a change in the solvate surroundings of the Eu^{III} and Tb^{III} ions and replacement of water by acetonitrile molecules. The change in the relative efficiency is presented in Fig. 4. It was obtained from the temperature dependences of both the intensity of photoluminescence and the lifetimes of Tb^{III} and Eu^{III} perchlorates in the excited states (the lifetimes of Eu^{III*} and Tb^{III*} are 155 and 1220 μs, respectively, at 293 K). Using the ϕ_{Ln} values obtained at room temperature (ϕ_{Eu} = 0.034 and ϕ_{Tb} = 0.09), we determined the values of the emission yields at other temperatures (see Table 2). As can be seen from the data presented in Table 2, as the temperature increases, a tendency for the yields of excited Eu^{III} and Tb^{III} in reaction (5a) and the rate constant of energy transfer k_{en} to decrease is observed. The comparison of these parameters for Eu^{III} and Tb^{III} indicates a more efficient excitation of Tb^{III} in the decomposition of **1** in the **1** · Ln^{III} complex and a more efficient energy transfer

Table 2. Yields of CL, emission and excitation of Ln^{III}, and rate constants of energy transfer at different temperatures

T/K	Eu(ClO$_4$)$_3$				Tb(ClO$_4$)$_3$			
	$\phi_{Eu}\phi_{Eu^*} \cdot 10^4$	ϕ_{Eu}	ϕ_{Eu^*}	$k_{en} \cdot 10^8$/L mol^{-1} s^{-1}	$\phi_{Tb}\phi_{Tb^*} \cdot 10^3$	ϕ_{Tb}	ϕ_{Tb^*}	$k_{en} \cdot 10^9$/L mol^{-1} s^{-1}
328	5.5	0.042	0.013	8.6	8.0	0.1	0.08	4.5
333	6.0	0.046	0.013	8.5	8.1	0.1	0.081	4.1
338	5.3	0.048	0.011	7.0	8.3	0.11	0.075	3.8
343	4.5	0.050	0.009	7.5	7.8	0.11	0.071	3.3
348	4.1	0.051	0.008	8.6	7.2	0.11	0.065	3.1

Note. The average error of measurement of emission yields is ±7%, those of excitation yields and rate constants of energy transfer are ±30%.

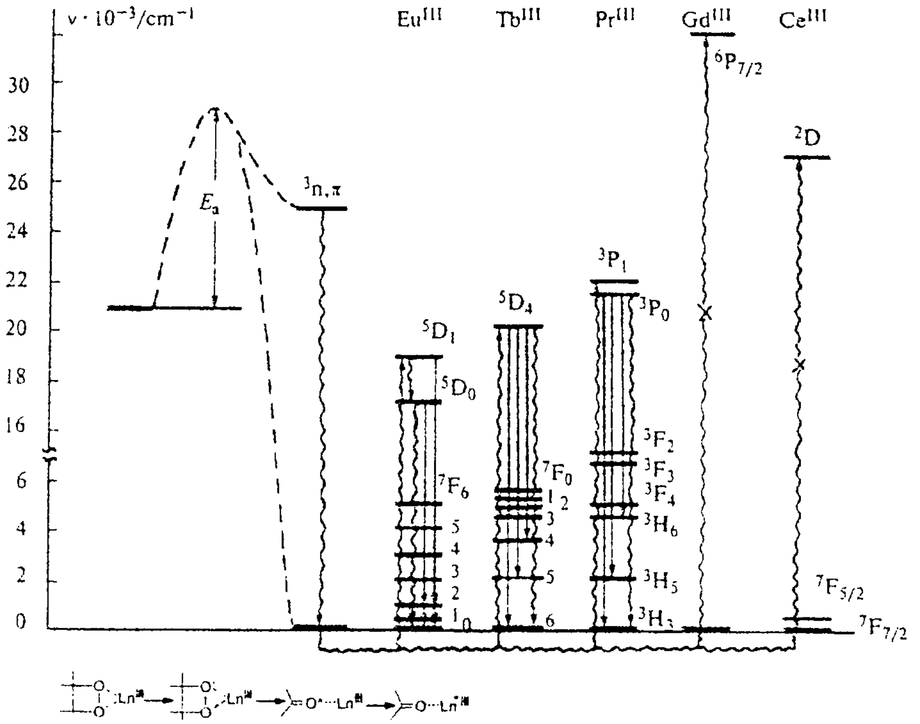


Fig. 5. Energy diagram illustrating the decomposition of **1** in the **1** · Ln^{III} complex and energy transfer to luminescence levels of Ln^{III}. Radiative transitions are shown by straight arrows, nonradiative transitions are shown by waved arrows.

from 2_T*. At the same time, the excitation yield ϕ_{Ln^*} is smaller than the yield of triplet-excited adamantanone in the decomposition of **1**. Since **1** decomposes in a complex with Ln^{III}, the decrease in the excitation yield can be related to a decrease in the activation energy compared to E_a of the decomposition of free dioxetane, which reflects the efficiency of the population of the excited state of ketone. The correlation between the excitation yield and E_a of the thermal decomposition of dioxetanes has been mentioned previously,[18] and the more stable the peroxide, the higher the excitation yield. Probably for this reason, ϕ_T in the decomposition of free **1** is higher than ϕ_{Ln^*} in the decomposition of **1** in the **1** · Ln^{III} complex.

It is likely that the chemiexcitation of Ln^{III} occurs *via* intracomplex and intermolecular transfer of energy from the excited ketone. The ratio of the contributions of these two routes of chemiexcitation to the total intensity of activated CL was estimated using the parameters that characterize reactions (5) and (8). In Eq. (11), the second and third terms represent the intensity of CL excited in the reaction of the catalyzed decomposition of **1** and, as a result, the energy transfer from 2_S* to Ln^{III}. From Eq. (11) we have:

$$\frac{I_{CL}^{cat}}{I_{CL}^{en}} = \frac{\phi_{Ln^*} K_1 k_2 (1 + k_{en} \tau_P^0)}{\phi_T^{\bullet} k_{en} \tau_P^0 k_1}. \qquad (15)$$

When the chemiluminescence of dioxetane **1** is enhanced by the Tb^{III} ions, this ratio is equal to ~500, and for Eu^{III} it is ~60 at $[Ln^{III}]$ = 0.1 mol L^{-1}. Thus, the contribution of the catalytic route to the intensity of CL is ~100 and 98%, respectively.

Since the presence of lanthanides does not result in the enhancement of the luminescence of singlet-excited **2** and, conversely, results in quenching due to the formation of a complex between **1** and Ln^{III}, it is evident that in the catalytic act of decomposition of **1**, *i.e.*, in the **1** · Ln^{III} complex, the excitation is localized only at the ^{3}n,π-level of adamantanone in the coordination sphere of the metal and then it is nonradiatively transferred to the luminescence levels of the lanthanides:

$$\mathbf{1} \cdot Ln^{III} \rightarrow \mathbf{2}_T^* \cdot Ln^{III} \rightarrow \mathbf{2} \cdot Ln^{III*} \rightarrow \mathbf{2} \cdot Ln^{III} + h\nu. \qquad (16)$$

A comparison of ϕ_{Ln} for Eu^{III} with that for Tb^{III} testifies that the efficiencies of the population of the luminescent levels of the lanthanides during energy transfer are different. For the Eu^{III} and Tb^{III} ions, the first luminescence level is lower than the triplet level of adamantanone (for Eu^{III}, $E(^5D_1)$ = 54.3 kcal mol^{-1}; for Tb^{III}, $E(^5D_4)$ = 58.7 kcal mol^{-1}), which results in isothermal energy transfer. For the Eu^{III} ion, the excitation energy is transferred from 2_S* to the $^5D_1$-level of Eu^{III} and then it is emitted (see Fig. 1) or nonradiatively transferred to the $^5D_0$-level. Since the degradation of energy occurs at all stages of the transfer of energy, it is evident that the transfer of energy from $\mathbf{2}_S^*$ to the excited level of the lanthanide and degradation of the energy in the $T_1 \rightarrow S_0$ process compete. It follows from the data obtained that the transfer of energy to the excited levels is more efficient for Tb^{III} than for Eu^{III} and, perhaps, this is related to a lower energy gap between T_1—$^5D_4$ of Tb^{III} and T_1—$^5D_1$ of Eu^{III} and, hence, to smaller internal energy losses resulting in a higher excitation yield of Tb^{III}. The scheme illustrating the processes of the decomposition of **1** in the **1** · Ln^{III} complex and the populations of the excited levels of the lanthanides is presented in Fig. 5.

The ratio of the emission yields of the carbonyl products and the catalyst ion is also significant for the catalyzed decomposition of dioxetane accompanied by luminescence of the metal ion. For example, in the presence of praseodymium perchlorate, CL is quenched, because the CL yield for the decomposition of **1** in the **1** · Pr^{III} complex is lower than the CL yield for the decomposition of **1** (reaction (1)). This is related to the fact that the yield of the luminescence of Pr^{III} ($\phi_{Pr} \le 0.001$) is lower than the emission yield of $\mathbf{2}_S^*$ ($\phi_F = 0.015$). The lower value of ϕ_{Pr} is not compensated for by a greater value of the rate of the decomposition of **1** in the **1** · Pr^{III} complex, which results in the overall quenching of CL despite the evident excitation of Pr^{III} in the reaction with **1** (see Fig. 1).

Thus, the following conditions for enhancement of CL in the catalysis of **1** accompanied by the luminescence of lanthanide are necessary: a) the existence of the appropriate luminescence levels of lanthanide to allow for exothermal energy transfer; b) the emission yield of lanthanide must be higher than the efficiency of fluorescence of the carbonyl compound formed in the decomposition of dioxetane; c) the yield of excited lanthanide must be higher than the yield of the singlet-excited states in the decomposition of dioxetane. The efficiency of the population of the luminescence levels of lanthanide, *i.e.*, excitation yield, depends on the factors that determine the transfer of the excitation energy from the donor.

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