Chemiluminescence and catalysis of decomposition of dispiro(diadamantane-1,2-dioxetane) in the presence of Eu^{III} and Tb^{III} tris(benzoyltrifluoroacetonate) complexes

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Catalysis of decomposition of dispiro(diadamantane-1,2-dioxetane) (**1**) in the presence of Eu^{III} and Tb^{III} tris(benzoyltrifluoroacetonate) complexes ($Ln(btfa)_3$) accompanied by the formation of adamantanone (**2**) and chemiluminescence (CL) was studied. The rate constants (k_2) of decomposition of compound **1** in the $\mathbf{1} \cdot Ln(btfa)_3$ complexes and their stability constants (K_1) have been determined. The Arrhenius parameters of decomposition of **1** (E_a = 22.4±0.7 kcal mol^{-1}, $\log A$ = 10.2±0.8 for $\mathbf{1} \cdot Tb(btfa)_3$ and E_a = 23.4±0.6 kcal mol^{-1}, $\log A$ = 10.6±0.8 for $\mathbf{1} \cdot Eu(btfa)_3$) and thermodynamic parameters of complex formation (ΔH = −5.5±0.5 kcal mol^{-1}, ΔS = −10.4±0.7 e.u. for $\mathbf{1} \cdot Tb(btfa)_3$ and ΔH = −5.8±0.5 kcal mol^{-1}, ΔS = −10.9±0.7 e.u. for $\mathbf{1} \cdot Eu(btfa)_3$) have been calculated from the temperature dependences of k_2 and K_1. The yields of excitation of the $Ln(btfa)_3$ chelates ϕ^*_{Eu} = 0.021±0.006 and ϕ^*_{Tb} = 0.12±0.04 have been determined. A higher efficiency of the occupation of the $^5D_4$-level of Tb^{3+} compared to those of the $^5D_1$- and $^5D_0$-levels of Eu^{3+} is caused by different efficiencies of the non-radiative energy dissipation in the Ln^{3+} ion after the intracomplex energy transfer from the $^3n,\pi^*$-state of **2** to the resonance excited levels of lanthanides.

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

The Eu^{III} and Tb^{III} β-diketonates are known to accept well the energy of triplet-excited molecules.[1] Due to this property, they are efficient activators of chemiluminescence (CL) of 1,2-dioxetanes, whose thermal decomposition gives triplet-excited carbonyl compounds in high (up to 30%) yields.[2,3] To enhance CL of dioxetanes, coordinationally saturated Eu^{III} chelates are used along with 9,10-substituted anthracene derivatives. The presence of the Eu^{III} chelates has no effect on the rate of decomposition of dioxetanes, and excitation of the chelates occurs due to the energy transfer from triplet-excited carbonyl compounds.[4] Coordinationally unsaturated chelates of lanthanides (Ln^{III}), such as $Eu(fod)_3$, $Pr(fod)_3$, and $Dy(fod)_3$ (Hfod is heptafluorodimethyloctanedione), catalyze the decomposition of peroxide.[5] The decomposition of dioxetane is catalyzed most likely due to weakening of the O—O bond as a result of the formation of a complex with the chelate.[6] In this case, the lanthanide is electron-excited due to the intracomplex energy transfer from the triplet-excited ketone in the coordination sphere of the lanthanide ion:[7]

$$\text{Donor(T)} \xrightarrow{i} \text{Ln}^*(\text{fod})_3 \qquad (1)$$

i. Intracomplex energy transfer.

The mechanism of chemiluminescence in the coordinationally unsaturated Ln^{III} chelate—dioxetane differs from that of excitation of coordinationally saturated lanthanide chelates during activation of CL of peroxides.[4] According to this mechanism, excited levels of the Ln^{3+} ion are occupied due to the triplet-triplet energy transfer from the donor to the ligand and then from the ligand to the lanthanide ion:

$$\text{Donor(T)} \xrightarrow{ii} \text{Ligand(T)} \longrightarrow \text{Ln}^*(\text{fod})_3 \qquad (2)$$

ii. Intermolecular energy transfer.

The difference between these mechanisms is the following: the chemical reaction resulting in the formation of a product in the electron-excited state occurs in the coordination sphere of lanthanide, and this fact affects substantially subsequent photophysical processes (dissipation of the electron excitation energy, efficiency of radiative deactivation, removal of prohibition of radiative deactivation, *etc.*).[8] Lanthanide also affects the chemical stability of dioxetane. This mutual effect has been observed previously for the $Eu(fod)_3$—dioxetane system.[6] In this system, the decomposition of peroxide in a complex with the Eu^{III} chelate results in the formation of a complex of Eu^{3+*} with the nonequilibrium

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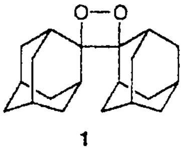
coordination sphere and luminescence from the $^5D_1$-level of Eu^{3+}.

In this work, we studied the decomposition of dispiro(diadamantane-1,2-dioxetane) (**1**)* catalyzed by $Ln(btfa)_3$ chelates (Ln = Eu and Tb; Hbtfa is benzoyltrifluoroacetone) and accompanied by luminescence of lanthanide. The kinetics of CL was studied. The activation parameters of decomposition of **1** in a complex with Ln^{III}, the thermodynamic parameters of complex formation, and the parameters of CL (yield of CL, yield of excitation of Ln^{3+} during decomposition of **1** in the $\mathbf{1} \cdot Ln(btfa)_3$ complex) were determined. The comparative analysis of the effect of the spectral luminescence properties of the Eu^{III} and Tb^{III} complexes on CL was performed.



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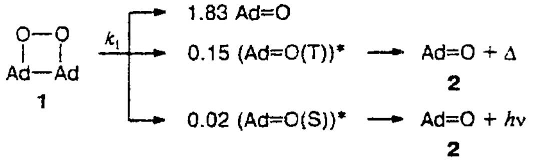
Experimental

Chelates $Eu(btfa)_3 \cdot 2H_2O$ and $Tb(btfa)_3 \cdot 2H_2O$ were obtained from the corresponding chlorides (chemically pure) and trifluorobenzoylacetone (4-phenyl-1,1,1-trifluorobutane-1,3-dione) (pure) by the known procedure.[9] Dioxetane **1** was synthesized by the photosensitized oxidation of adamantylideneadamantane by singlet oxygen.[10] The intensity of CL was detected on a photometric installation described previously.[11] The spectral sensitivity of the photocathode (α) of an FEU-140 photomultiplier was determined by a strip tungsten SIRSh-6-100 lamp and a set of interference light filters in the regions of fluorescence and phosphorescence of adamantanone (λ_{max} = 420 and 440 nm, α_1 = 1) and luminescence of terbium (α_2 = 0.8) and europium (α_3 = 0.1). The measured intensity of CL was corrected in accordance with the photomultiplier sensitivity. Chemiluminescence spectra were recorded on a photometric installation with an aperture MZD-2M monochromator and an FEU-119 photomultiplier. Photoluminescence (PL) spectra were recorded on a Hitachi MPF-4 spectrofluorimeter. Lifetimes of lanthanides in the excited state were measured by a laser pulse LIF-200 fluorimeter. The quantum yields of PL of $Eu(btfa)_3$ and $Tb(btfa)_3$ in toluene were determined by the known procedure.[12]

Results and Discussion

The thermolysis of **1** in toluene results in its decomposition to adamantanone (**2**), a portion of which is formed in the triplet (**2**(T)*, in a yield ϕ^*_T = 0.15) and singlet (**2**(S)*, ϕ^*_S = 0.02) excited states.[10] The chemiluminescence observed during thermolysis of **1** is due to fluorescence of **2**, and phosphorescence is not detected because of the efficient non-radiative deactivation of **2**(T)* (reaction (3), Fig. 1).



$$\underset{\mathbf{1}}{\text{Ad—Ad (O—O)}} \xrightarrow{k_1} \begin{cases} 1.83\ \text{Ad=O} \\ 0.15\ (\text{Ad=O(T)})^* \longrightarrow \underset{\mathbf{2}}{\text{Ad=O}} + \Delta \\ 0.02\ (\text{Ad=O(S)})^* \longrightarrow \underset{\mathbf{2}}{\text{Ad=O}} + h\nu \end{cases}$$

(3)

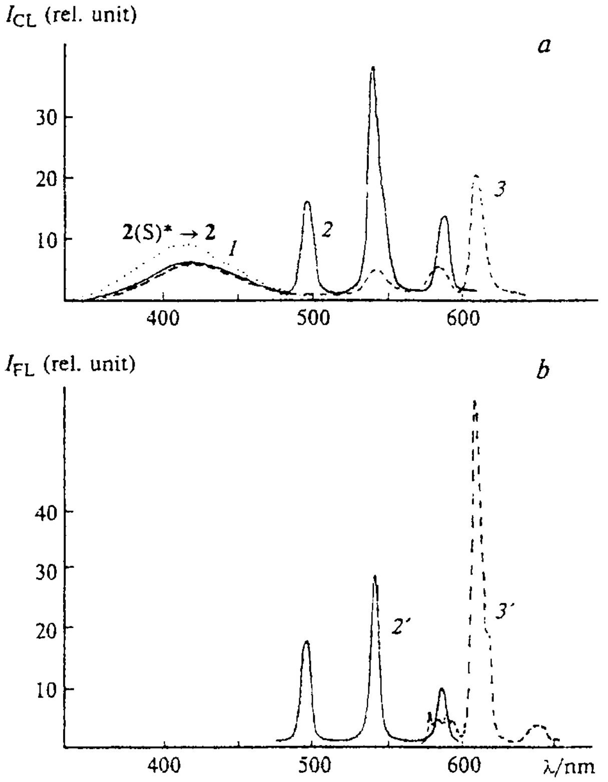
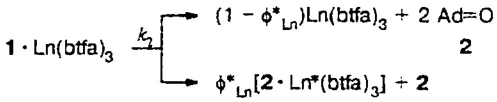


Fig. 1. *a.* Chemiluminescence spectra (*1*—*3*) in the absence (*1*) and presence of $Tb(btfa)_3$ (*2*) and $Eu(btfa)_3$ (*3*): [**1**] = 10^{-2} mol L^{-1} (*1*—*3*); [$Tb(btfa)_3$] = $1.5 \cdot 10^{-2}$ mol L^{-1} (*2*); [$Eu(btfa)_3$] = $1.5 \cdot 10^{-2}$ mol L^{-1} (*3*), resolution 15 nm, toluene, 370 K. *b.* Photoluminescence spectra of $Tb(btfa)_3$ (*2′*) and $Eu(btfa)_3$ (*3′*), [$Ln(btfa)_3$] = $1.5 \cdot 10^{-2}$ mol L^{-1}, resolution 2 nm, toluene, excitation with light with λ_{ex} = 390 nm, 295 K.

The spectral composition of luminescence changes in the presence of $Eu(btfa)_3$ and $Tb(btfa)_3$: bands due to radiative deactivation (f—f-transitions) of Eu^{3+} and Tb^{3+} appear (see Fig. 1), which coincide with the spectra of their PL. The CL spectrum of the Eu^{III} chelate exhibits radiation from the $^5D_1$-level, whose nature is similar to luminescence in the $Eu(fod)_3$—**1** system, *i.e.*, chemiexcitation of Eu^{III} occurs during decomposition of **1** in the $\mathbf{1} \cdot Eu(btfa)_3$ complex. According to the data obtained previously,[6] the observed CL and the scheme of processes responsible for the kinetics of the decomposition of **1** catalyzed by the lanthanide chelate can be presented as follows.

$$Ln(btfa)_3 + \mathbf{1} \xrightleftharpoons{K_1} \mathbf{1} \cdot Ln(btfa)_3 \qquad (4)$$



$$\mathbf{1} \cdot Ln(btfa)_3 \xrightarrow{k_2} \begin{cases} (1 - \phi^*_{Ln})Ln(btfa)_3 + 2\ \underset{\mathbf{2}}{\text{Ad=O}} \\ \phi^*_{Ln}[\mathbf{2} \cdot Ln^*(btfa)_3] + \mathbf{2} \end{cases}$$

(ϕ^*_{Ln} — yield of excitation) (5)

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* The systematic name of this compound is dispiro(adamantane-2,3′-1′,2′-dioxetane-4′,2″-adamantane).

$$\mathrm{Ln(btfa)_3} + \mathbf{2} \overset{K_2}{\rightleftharpoons} \mathbf{2}\cdot\mathrm{Ln(btfa)_3} \quad (6)$$

$$\mathbf{2}\mathrm{(T)^*} + \mathrm{Ln(btfa)_3} \xrightarrow{k_{en}} \mathbf{2} + \mathrm{Ln^*(btfa)_3} \quad (7)$$

$$\mathbf{2}\mathrm{(T)^*} \xrightarrow{k_d} \mathbf{2} \quad (8)$$

$$\mathrm{Ln^*(btfa)_3} \longrightarrow \mathrm{Ln(btfa)_3} + h\nu$$
$$(\phi_{\mathrm{Ln}} \text{ — yield of luminescence}) \quad (9)$$

$$[\mathbf{2}\cdot\mathrm{Ln^*(btfa)_3}] \longrightarrow [\mathbf{2}\cdot\mathrm{Ln(btfa)_3}] + h\nu$$
$$(\phi_{\mathbf{2}\cdot\mathrm{Ln}} \text{ — yield of luminescence}) \quad (10)$$

Here k_{en} and k_d are the rate constants of energy transfer and deactivation, respectively.

Kinetics of decomposition of 1 in the presence of Ln(btfa)$_3$

The CL spectrum of dioxetane **1** in the presence of the Ln^{III} complexes consists of a band caused by radiative deactivation of **2**(S)* and bands of luminescence of Ln^{3+}. The latter are well separated spectrally, which makes it possible to follow their change during thermolysis. The intensity of CL (I_{CL}) in the spectral region of luminescence is proportional to the concentration of **1**, and the rate of its decay is proportional to the rate of consumption of **1**, *i.e.*,

$$I_{CL} \sim \mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_{obs}[\mathbf{1}], \quad (11)$$

where k_{obs} is the observed rate constant of CL decay.

Under conditions of $[\mathrm{Ln(btfa)_3}]_0 > [\mathbf{1}]_0$ and low (not higher than 30%) degrees of consumption of **1**, the reaction of complex formation (6) has no effect on the rate of decomposition of **1**. In this case, we can write:

$$I_{CL} \sim \frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{k_1 + K_1 k_2 [\mathrm{Ln(btfa)_3}]_0}{1 + K_1[\mathrm{Ln(btfa)_3}]_0} \cdot [\mathbf{1}], \quad (12)$$

where [**1**] is the current concentration of dioxetane, and $[\mathrm{Ln(btfa)_3}]_0$ is the initial concentration of the Ln^{III} chelate. In Eq. (12),

$$\frac{k_1 + K_1 k_2 [\mathrm{Ln(btfa)_3}]_0}{1 + K_1[\mathrm{Ln(btfa)_3}]_0} = k_{obs}. \quad (13)$$

To determine the k_2 and K_1 constants, it is convenient to present Eq. (13) in the following form:

$$(k_{obs} - k_1)^{-1} = (k_2 - k_1)^{-1} + \{(k_2 - k_1)K_1[\mathrm{Ln(btfa)_3}]_0\}^{-1}. \quad (14)$$

As can be seen from Eq. (13), k_{obs} depends on the concentration of Ln(btfa)$_3$, and as the latter increases, k_{obs} approaches k_2 in magnitude.

In addition to the dependence of [Ln(btfa)$_3$], k_{obs} also depends on the CL yield in reaction (5), the efficiency of the energy transfer from **2**(T)* to Ln(btfa)$_3$, and the efficiency of luminescence of Ln^{3+*} in the whole spectral range. In addition, the luminescence of Ln^{3+*} is quenched by dioxetane **1**.[13] The transfer of the excitation energy to vibrational levels of **1** results in its decomposition. The energy released due to the decomposition leads[13,14] to the partial regeneration of excited Ln^{3+*} and, as a consequence, to the quantum-chain decomposition of **1**. However, under conditions of our experiments, the fraction of decomposition of **1** *via* the quantum-chain route is negligible. Nevertheless, the rate constant of CL decay in the whole spectral range is not determined by Eq. (14).

The dependences of k_{obs} on the concentrations of Eu(btfa)$_3$ and Tb(btfa)$_3$ are presented in Fig. 2. They fit Eq. (14) (the following Arrhenius parameters of decomposition of **1** were used for the calculation of k_1:[15] E_a =

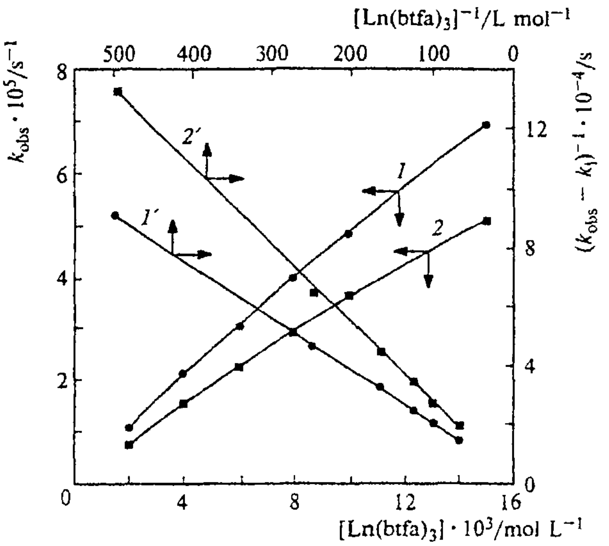

Fig. 2. Dependences of the observed rate constant of CL of dioxetane **1** in the region of luminescence of **2** (380—440 nm) on the concentrations of Tb(btfa)$_3$ (*1*) and Eu(btfa)$_3$ (*2*) at [**1**] = 10^{-3} mol L^{-1} and 370 K; *1'*, *2'* the same dependences in the coordinates of Eq. (14).

Table 1. Rate constants of decomposition of **1** in the **1** · Ln(btfa)$_3$ complex (k_2) and stability constants of the **1** · Ln(btfa)$_3$ complexes (K_1) determined from the rate of CL decay (see Fig. 2) at different temperatures*

T/K	$k_2 \cdot 10^4$/s^{-1}		K_1/L mol^{-1}	
	Eu	Tb	Eu	Tb
353	1.26	2.10	16.7	13.5
359	2.20	3.52	14.8	12.0
363	3.13	5.00	13.2	11.0
368	4.85	7.60	11.8	10.0
370	5.75	9.00	11.3	9.5

* The average errors of determination of k_2 and K_1 are ±4%.

35.1 kcal mol^{-1}, log*A* = 14.2). The rate constants of decomposition of **1** in the **1** · $Ln(btfa)_3$ complex were determined from the intercept cut by the line on the *y* axis, and the stability constants of these complexes were determined from the tangent of the slope. The results are presented in Table 1. Based on these values, we calculated the Arrhenius parameters of decomposition of **1** in the **1** · $Ln(btfa)_3$ complex: E_a = 23.4±0.6 kcal mol^{-1}, log*A* = 10.6±0.8 for $Eu(btfa)_3$ and E_a = 22.4±0.7 kcal mol^{-1}, log*A* = 10.2±0.8 for $Tb(btfa)_3$.

The data obtained indicate that the activation barrier for the decomposition of **1** in the complex with lanthanide is lower than that for the decomposition of the free dioxetane. The comparison of these results with the activation parameters obtained previously[16] for the decomposition of **1** in the **1** · $Eu(fod)_3$ complex (E_a = 24.2 kcal mol^{-1}, log*A* = 10.6) indicates that $Tb(btfa)_3$ possesses a higher catalytic activity. This is likely related to the fact that the ligand of the chelates considered is less bulky than fod, which results in less steric hindrances for the formation of the **1** · $Ln(btfa)_3$ complex. The data on the rate constants of decomposition of **1** in the **1** · $Eu(btfa)_3$ and **1** · $Tb(btfa)_3$ complexes are consistent with the results[5] on the decomposition of 9-(2-adamantylidene)-*N*-methylacrydane-1,2-dioxetane in the presence of $Ln(fod)_3$ (Ln = Eu, Pr, Dy, and Yb). The relative rates of decomposition of this dioxetane correlate with the ionic radii of lanthanides: the greater the ionic radius, the higher the rate of decomposition. This tendency is most likely related to more favorable conditions for the interaction of peroxide with $Ln(btfa)_3$ due to a decrease in steric hindrances from the ligands.

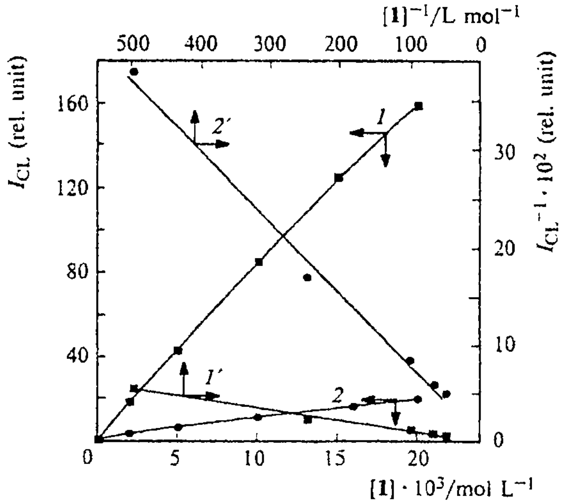

Fig. 3. Dependences of the intensity of CL on the concentration of **1** in the presence of $Tb(btfa)_3$ (*1*) and $Eu(btfa)_3$ (*2*) at 353 K, $[Ln(btfa)_3]$ = 10^{-3} mol L^{-1}; *1'* and *2'*, the same dependences in the coordinates of Eq. (17).

Chemiluminescence of Eu(btfa)₃ and Tb(btfa)₃ in toluene during thermal decomposition of 1

Two emitters luminesce in the **1**—$Ln(btfa)_3$ system: $Ln^*(btfa)_3$ and $[2 \cdot Ln^*(btfa)_3]$, which are formed in reactions (7) and (5), respectively. This conclusion follows from the fact that the CL and PL spectra are not identical, which is especially pronounced in the case of activation by the $Eu(btfa)_3$ chelate (see Fig. 1). The yields of luminescence of these emitters are different, because both the intensity of PL and the lifetimes of $Eu(btfa)_3$ and $Tb(btfa)_3$ in the excited state increase as the concentration of **2** increases. The yields of luminescence $\phi_{2 \cdot Ln}$ of the **2** · $Ln(btfa)_3$ complexes were determined from the dependence of the intensity of PL on the concentration of **2** by extrapolation to the infinite concentration of **2**. The $\phi_{2 \cdot Ln}$ values thus obtained and ϕ_{Ln} of the chelates are presented in Table 2.

The dependences of the intensity of PL on the concentrations of **1** (Fig. 3) (when $[Ln(btfa)_3]$ = const) and $Ln(btfa)_3$ (when [**1**] = const) (Fig. 4) are determined by the reactions of complex formation (reaction (4)), the yield of $Ln^*(btfa)_3$ in the decomposition of **1** in the **1** · $Ln(btfa)_3$ complex, the efficiency of the energy transfer from $2(T)^*$ to $Ln(btfa)_3$, and the yield of luminescence of Ln^{3+*}. The dependence of the quasi-stationary intensity of CL on the concentration of **1** in the

Table 2. Yields of excitation (ϕ^*_{Ln}) and luminescence (ϕ) and rate constants of electron transfer (k_{en}) in the **1**—$Ln(btfa)_3$ system

T/K	ϕ^*_{Ln}		ϕ_{Ln}		$\phi_{2 \cdot Ln}$		$k_{en} \cdot 10^{-9}$/L mol^{-1} s^{-1}	
	Eu	Tb	Eu	Tb	Eu	Tb	Eu	Tb
333	0.025	0.115	0.031	0.013	0.047	0.039	8.4	8.8
338	0.019	0.12	0.027	0.012	0.038	0.036	7.6	9.0
343	0.017	0.128	0.025	0.011	0.033	0.032	7.7	9.0
347.6	0.022	0.105	0.023	0.010	0.030	0.028	8.4	9.5
353	0.020	0.126	0.020	0.0095	0.026	0.027	8.5	9.3
357	0.025	0.120	0.019	0.008	0.024	0.023	8.3	9.5
362	0.021	0.130	0.017	0.008	0.021	0.022	8.0	9.8

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

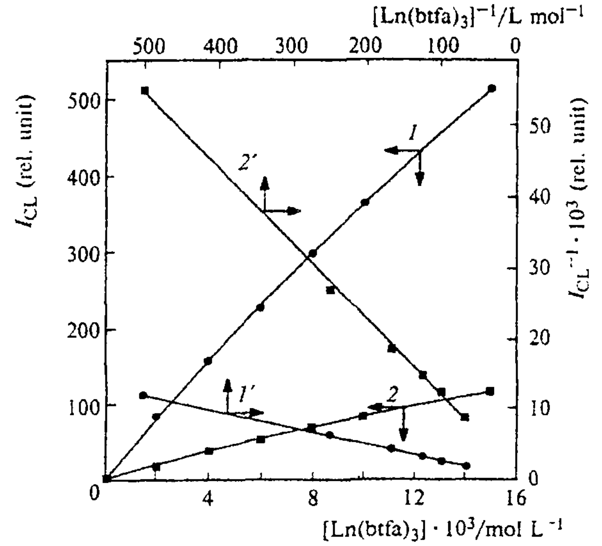

Fig. 4. Dependences of the intensity of CL on the concentrations of $Tb(btfa)_3$ (*1*) and $Eu(btfa)_3$ (*2*) in the presence of **1** (10^{-3} mol L^{-1}) at 353 K. *1'* and *2'*, the same dependences in the I_{CL}^{-1}—$[Ln(btfa)_3]^{-1}$ coordinates.

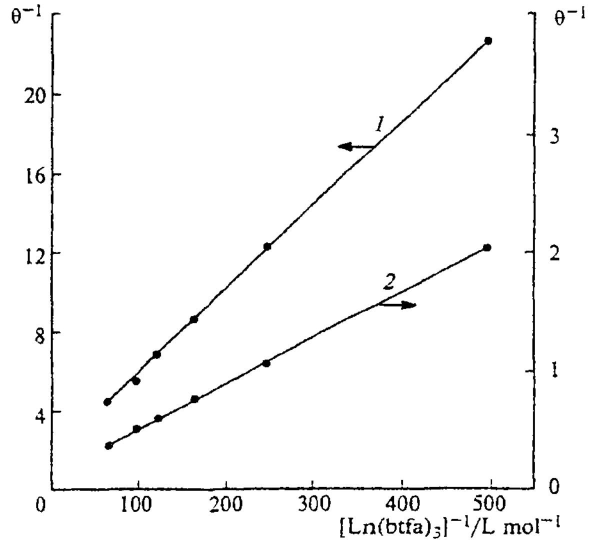

Fig. 5. Dependences of the intensity of CL on the concentrations of $Tb(btfa)_3$ (*1*) and $Eu(btfa)_3$ (*2*) in the presence of **1** (10^{-3} mol L^{-1}) at 353 K in the coordinates of Eq. (21). $\theta = k_2k_1^{-1}[I_{CL}(I_{CL}^{m})^{-1}(1 + K_1[Ln(btfa)_3]_0) - K_1[Ln(btfa)_3]_0]$.

spectral range of luminescence of Ln^{3+} under the condition that $[\mathbf{1}]_0 > [Ln(btfa)_3]_0$, hence, $[\mathbf{1}]_0 = [\mathbf{1}]$, $[Ln(btfa)_3] = [Ln(btfa)_3]_0(1 + K_1[\mathbf{1}]_0)^{-1})$, and $[\mathbf{1} \cdot Ln(btfa)_3] = K_1[\mathbf{1}]_0[Ln(btfa)_3]_0(1 + K_1[\mathbf{1}]_0)^{-1}$, can be described by the following equation:

$$I_{CL} = \frac{\phi^*{}_T\,\phi_{Ln}k_{en}k_1[\mathbf{1}]_0[Ln(btfa)_3]_0}{\{k_d + k_{en}[Ln(btfa)_3]_0(1 + K_1[\mathbf{1}]_0)^{-1}\}(1 + K_1[\mathbf{1}]_0)} + \\ + \frac{\phi^*{}_{Ln}\,\phi_{2\cdot Ln}k_2K_1[\mathbf{1}]_0[Ln(btfa)_3]_0}{1 + K_1[\mathbf{1}]_0}. \qquad (15)$$

The maximum value of the intensity of CL ($I_{CL}{}^m$) in this system at $[\mathbf{1}]_0 \to \infty$ can be expressed by the following expression:

$$I_{CL}^{m} = \left(\frac{\phi^*{}_T\,k_{en}k_1}{\phi^*{}_{Ln}\,k_dk_2K_1} + 1\right) \cdot \phi^*{}_{Ln}\phi_{2\cdot Ln}k_2K_1[Ln(btfa)_3]_0. \qquad (16)$$

From Eqs. (15) and (16) we obtain:

$$\frac{I_{CL}^{m}}{I_{CL}} = 1 + \frac{1 + \phi_{Ln}k_{en}(\phi_{2\cdot Ln}k_d)^{-1}[Ln(btfa)_3]_0}{K_1[\mathbf{1}]_0}. \qquad (17)$$

The rate constant of energy transfer k_{en}, which was determined from the dependence of I_{CL} $[Ln(btfa)_3]_0$, is an unknown value in Eq. (17). In this case, the following equation can be written for the intensity of CL:

$$I_{CL} = \phi^*{}_T\phi_{Ln}k_{en}[Ln(btfa)_3]_0k_1[\mathbf{1}](k_d + k_{en}[Ln(btfa)_3]_0)^{-1} + \\ + \phi^*{}_{Ln}\phi_{2\cdot Ln}k_2[\mathbf{1} \cdot Ln(btfa)_3]. \qquad (18)$$

At $[Ln(btfa)_3]_0 > [\mathbf{1}]_0$, unbound dioxetane and the complex have the following concentrations: $[\mathbf{1}] = [\mathbf{1}]_0\{1 + K_1[Ln(btfa)_3]_0\}^{-1}$ and $[\mathbf{1} \cdot Ln(btfa)_3] = K_1[Ln(btfa)_3]_0[\mathbf{1}]_0\{1 + K_1[Ln(btfa)_3]_0\}^{-1}$.

Taking into account this fact, Eq. (18) can be rewritten in the following form:

$$I_{CL} = \frac{\phi^*{}_T\,\phi_{Ln}k_{en}[Ln(btfa)_3]_0k_1[\mathbf{1}]_0}{(k_d + k_{en}[Ln(btfa)_3]_0)(1 + K_1[Ln(btfa)_3]_0)} + \\ + \frac{\phi^*{}_{Ln}\,\phi_{2\cdot Ln}k_2K_1[Ln(btfa)_3]_0[\mathbf{1}]_0}{1 + K_1[Ln(btfa)_3]_0}. \qquad (19)$$

The terms in Eqs. (15) and (19) are the contribution to the total intensity of CL of the emission of Ln^{3+*} formed due to the energy transfer and decomposition of **1** in the complex with lanthanide.

The maximum intensity of luminescence in this system at $[\mathbf{1}]_0 = \mathrm{const}$ and $[Ln(btfa)_3] \to \infty$ can be expressed by the following equation:

$$I_{CL}^{m} = \phi^*{}_{Ln}\phi_{2\cdot Ln}k_2[\mathbf{1}]_0. \qquad (20)$$

From Eqs. (19) and (20) we obtain:

$$\frac{k_1}{k_2} \cdot \frac{1}{I_{CL}(I_{CL}^{m})^{-1}(1 + K_1[Ln(btfa)_3]_0) - K_1[Ln(btfa)_3]_0} = \\ = \frac{\phi^*{}_{Ln}\,\phi_{Ln}}{\phi^*{}_T\,\phi_{2\cdot Ln}} + \frac{k_d\phi^*{}_{Ln}\,\phi_{Ln}}{k_{en}\phi^*{}_T\,\phi_{2\cdot Ln}[Ln(btfa)_3]_0}. \qquad (21)$$

Equation (21) relates the kinetic and photophysical parameters of the processes that occur in the dioxetane—$Ln(btfa)_3$ system. The kinetic parameters in the left part of the equation have been obtained above. The maximum value of the intensity of CL was determined from the dependence of the intensity of CL on $[Ln(btfa)_3]$. As can be seen from Fig. 5, Eq. (21) is well fulfilled. The

Table 3. Stability constants of the **1** · Ln(btfa)$_3$ complexes determined from the dependence of CL on the concentration of **1** (see Fig. 3)

T/K	K_1/L mol^{-1}		T/K	K_1/L mol^{-1}	
	Eu	Tb		Eu	Tb
333	—	21.8	353	17.1	13.6
338	24.3	19.3	357	14.9	12.3
343	21.5	17.3	362	13.9	—
348	17.8	14.9			

Note. The average error of determination of the stability constant is ±4%.

yield of excitation ϕ^*_{Ln} and the rate constant of energy transfer k_{en} were calculated from the tangent of the slope of the line and from the intercept cut by the line on the y axis. For this purpose, the rate constant of deactivation of **2** was set as $k_d = \tau^{-1} = 2.5 \cdot 10^8$ s^{-1} (see Ref. 17). The results are presented in Table 2.

The stability constants of the **1** · Ln(btfa)$_3$ complexes were calculated from the dependence determined by Eq. (17) (see Fig. 3) using the k_{en} values obtained (Table 3).

Based on the data in Tables 1 and 3, from the temperature dependences of the stability constants of the **1** · Eu(btfa)$_3$ complex (Fig. 6), we calculated the thermodynamic parameters of complex formation with dioxetane: $\Delta H = -5.8 \pm 0.5$ kcal mol^{-1}, $\Delta S = -10.9 \pm 0.7$ e.u. for Eu(btfa)$_3$ and $\Delta H = -5.5 \pm 0.5$ kcal mol^{-1}, $\Delta S = -10.4 \pm 0.7$ e.u. for Tb(btfa)$_3$. As can be seen in Fig. 6, the values of the stability constants obtained from both the kinetics of decay of the intensity of CL (see Table 1) and the dependence of the quasi-stationary CL on the concentration of peroxide (see Table 3) are in good accordance. The temperature dependence of K_1 in the appropriate coordinates (see Fig. 6) is linear. This indicates that the mechanism of complex formation remains unchanged in the temperature interval studied.[18]

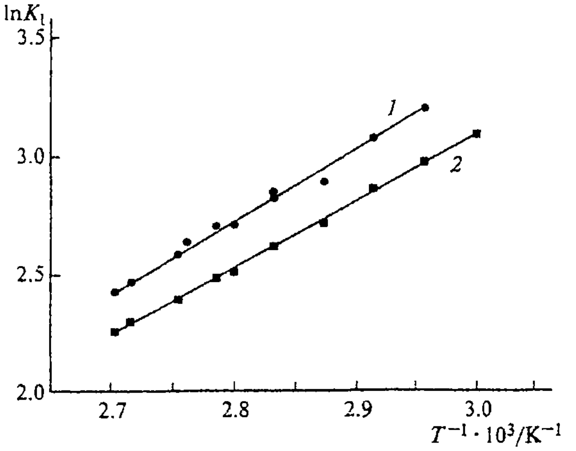

Fig. 6. Temperature dependences of the stability constants of the **1** · Eu(btfa)$_3$ (*1*) and **1** · Tb(btfa)$_3$ (*2*) complexes (data in Tables 1 and 3 are used).

The **1** · Ln(btfa)$_3$ complexes are formed in the exothermic reaction with a negative entropy factor. A change in the enthalpy is determined by the energy of desolvation of the complex and the enthalpy of the interaction between the chelate and peroxide. Toluene is most likely present in the first coordination sphere of the Eu^{III} and Tb^{III} chelates, since at temperatures higher than 40 °C water, which is present as traces in a solvent or introduced to the solution with the chelate, is substituted by solvent molecules.[19,20] Evidently, dioxetane is also inserted into the inner coordination sphere of lanthanides. This is confirmed by the fact that the CL spectrum exhibits luminescence from the $^5D_1$-level of Eu^{3+}. This luminescence is due to a change in the probability of radiative transitions. A similar situation is possible only when peroxide decomposes in the inner coordination sphere.[20]

Thus, when the **1** · Ln(btfa)$_3$ complex is formed, solvent molecules do not leave the sphere of reacting species and do not compensate a decrease in the entropy:

$$[\mathrm{LnL_3} \cdot n\mathrm{Solv}] + \mathbf{1} \rightleftharpoons [\mathrm{LnL_3} \cdot \mathbf{1} \cdot n\mathrm{Solv}]. \qquad (22)$$

As a whole, the establishment of equilibrium (22) in the 333—370 K temperature range is energetically favorable, since $\Delta G < 0$.

The data in Table 2 show that both the excitation yield and k_{en} are temperature independent. The comparison of these parameters indicates a more efficient excitation of the Tb^{3+} ion at close values of the efficiency of energy transfer from **2**(T)*. The yields of CL for the decomposition of free dioxetane ($\phi_{CL} = \phi^*_T\phi_F$, ϕ_F (yield of fluorescence) = 0.015 [10]), Eu(btfa)$_3$, and Tb(btfa)$_3$ during decomposition of **1** in the **1** · Eu(btfa)$_3$ and **1** · Tb(btfa)$_3$ complexes are equal to $3 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, and $10 \cdot 10^{-4}$, respectively. When the rates of the corresponding reactions are comparable, these values are the coefficients of enhancement of CL.

As mentioned previously, CL in the presence of chelates in the spectral range of their luminescence is the sum of the components of radiation appearing due to the catalyzed decomposition of **1** ($I_{CL}{}^{cat}$) and luminescence of Ln^{3+*}, which is formed by the intermolecular energy transfer ($I_{CL}{}^{en}$). From Eq. (19) we obtain:

$$\frac{I_{CL}^{cat}}{I_{CL}^{en}} = \frac{\phi^*_{Ln}\,\phi_{2\cdot Ln}k_2K_1\{k_d + k_{en}[\mathrm{Ln(btfa)_3}]_0\}}{\phi^*_T\,\phi_{Ln}k_{en}k_1}. \qquad (23)$$

At [Ln(btfa)$_3$] = 10^{-2} mol L^{-1}, ratio (23) for the activation of CL by the chelate is 2 for Eu^{III} and 20 for Tb^{III}. Thus, the contribution to the total intensity of CL from the radiation of Eu^{3+*} and Tb^{3+*} formed due to the catalyzed decomposition of **1** is 67 and 95%, respectively.

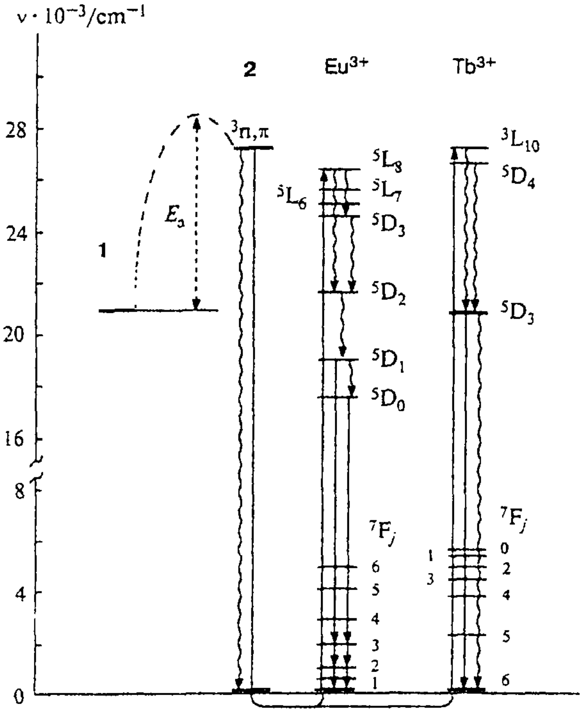

Fig. 7. Energy diagram illustrating the decomposition of **1** in the **1** · Ln(btfa)$_3$ complex, energy transfer to excited levels of Ln^{3+}, and processes of non-radiative energy dissipation.

The presence of lanthanides does not result in enhancement of luminescence of **2**(S)*, but conversely, leads to quenching of CL in the region of 420 nm due to binding of **1** in the complex. Evidently, in the catalytic act of decomposition of **1**, the excitation is localized only on the ^{3}n,π*-level of adamantanone (**2**), whose deactivation occurs in the non-radiative process, by the intersystem crossing $T_1 \rightarrow S_0$, or by the energy transfer to the excited f-levels of Ln^{3+}.

The energy diagram illustrating the formation of the Eu^{III} and Tb^{III} chelates in the excited state is presented in Fig. 7.

The comparison of ϕ^*_{Ln} of Eu(btfa)$_3$ and Tb(btfa)$_3$ indicates the different efficiencies of population of luminescence levels of lanthanides. In the Eu^{3+} and Tb^{3+} ions, the energy of the first luminescence level lies lower than the triplet level of adamantanone (E_T = 75 kcal mol^{-1};[21] for Eu^{3+}, $E(^5D_1)$ = 54.3 kcal mol^{-1}; for Tb^{3+}, $E(^5D_4)$ = 58.7 kcal mol^{-1}). Since the energy dissipation occurs at all stages of energy transfer, it is evident that the energy transfer from **2**(T)* to the excited level of lanthanide competes with the energy dissipation during the $T_1 \rightarrow S_0$ process. Using the ϕ^*_{Ln} values obtained, we can estimate the lower boundary of the rate constant of intracomplex energy transfer (k'_{en}). For example, the constant of deactivation of **2**(T)* k_d = $2.5 \cdot 10^8$ s^{-1}, hence, $k'_{en} = k_d\phi^*_{Ln}(\phi^*_T - \phi^*_{Ln})^{-1}$. For Tb(btfa)$_3$ $k'_{en} \approx 10^9$, and for Eu(btfa)$_3$ it is ~10^8 s^{-1}. The difference of an order of magnitude between the constants is likely explained by the fact that they are effective values that reflect complicated processes of energy transfer in the ketone—Ln^{III} chelate—solvent system. In our opinion, the energy is transferred from the triplet level of ketone to the resonance excited levels of lanthanides. For Eu^{3+}, $^5L_7$, $^5L_6$, and $^5D_3$ with energies of 72.4, 70.1, and 69.9 kcal mol^{-1}, respectively, can be these levels, while for Tb^{3+}, this is $^5D_3$ with an energy of 74.3 kcal mol^{-1}. Dissipation of the excitation energy in the lanthanide ions occurs *via* the mechanism of induction-resonance energy transfer from the excited ion to the surrounding molecular groups with their excitation to high vibrational levels in uni- or multiphonon non-radiative transitions.[20,22] The Eu^{3+} ion can have several such transitions, for example: $^5D_3 \rightarrow {}^5D_2$, $^5D_2 \rightarrow {}^5D_1$, $^5D_1 \rightarrow {}^5D_0$, $^5D_3 \rightarrow {}^5D_1$, *etc.*, whereas the Tb^{3+} ion is characterized by only one transition: $^5D_4 \rightarrow {}^5D_3$. It is reasonable that the probability of energy transfer to the vibrational levels of the surrounding molecular groups in the Eu^{3+} ion is higher than that in Tb^{3+}, since for Tb^{3+} the energy of the quantum of the electron transition is higher and, hence, the probability of its non-radiative deactivation is lower. In our opinion, this fact results in a substantial difference between the yields of excitation. In addition, as the rate constant value shows, in the **2** · Tb(btfa)$_3$ complex, the energy transfer from the donor to lanthanide occurs almost without losses.

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