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

1. Catalysis of the 1,2-dioxetane decomposition

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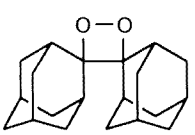
Decomposition of dispiro(diadamantane-1,2-dioxetane) (**1**) in acetonitrile solutions of Eu^{III}, Gd^{III}, Tb^{III}, Pr^{III}, and Ce^{III} perchlorates was studied by the chemiluminescence method. The rate constants of decomposition of **1** in complexes of composition $\mathbf{1} \cdot Ln^{III}$ and stability constants of these complexes, as well as activation parameters of the decomposition of **1** and thermodynamic parameters of the complexation were determined. A correlation between the thermodynamic parameters of complexation and ionic radii of Ln^{III} was found.

Key words: chemiluminescence; catalysis; dispiro(diadamantane-1,2-dioxetane), lanthanides.

Thermal decomposition of 1,2-dioxetanes (cyclic four-membered peroxides) is accompanied by the formation of carbonyl fragments in the excited state and, as a result, by chemiluminescence (CL).[1] The decomposition of dioxetane is accelerated in the solutions of complexes of f- and d-elements. Catalysis is associated with the formation of a coordination complex with peroxide whose formation is accompanied either by the reversible electron transfer or by the oxidative addition of the metal to dioxetane followed by the decomposition of the metallocycle and regeneration of the metal to its initial oxidation state.[2,3]

In addition to the catalyzed decomposition of dioxetane, an increase in CL is observed in the presence of luminescent chelate complexes of metals.[3,4] The occupation of the luminescent levels of the metal occurs due to the intracomplex energy transfer from the excited carbonyl fragment.[4] Thus, complexation of the metal ion with dioxetane affects both the efficiency of catalysis and CL. In this work, the kinetics of CL of dispiro(diadamantane-1,2-dioxetane) (**1**) in acetonitrile solutions of lanthanide perchlorates was studied in order to establish factors on which the catalysis of dioxetane decomposition depends.



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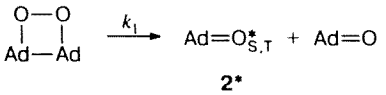
Experimental

Lanthanide salts of composition $Ln(ClO_4)_3$ (Ln = Tb, Gd, Eu, Pr, Ce) were prepared by dissolution of the corresponding oxides or carbonates in $HClO_4$ (of "chemically pure" grade) with subsequent recrystallization and drying *in vacuo* at 80—90 °C. Acetonitrile of "extra pure" grade (95% transmission at λ = 200 nm in a 1 cm cell) was used without additional purification. Dioxetane **1** was synthesized by photosensitized oxidation of adamantylideneadamantane following the known procedure.[5] The intensity of CL was determined using an installation described previously.[6] The kinetics of CL decay at the temperatures above the acetonitrile boiling point were recorded in sealed ampules.

Results and Discussion

Decomposition of dioxetane **1** results in the formation of two molecules of adamantanone (**2**) and is accompanied by CL associated with emissive deactivation of singly excited **2** (triply excited adamantanone is deactivated without emission). The excitation yields in the decomposition of compound **1** are 0.02 and 0.15 for singly and triply excited **2**, respectively:



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(1)

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$$Ad{=}O_S^* \longrightarrow Ad{=}O + h\nu \qquad (2)$$

$$2_S^*$$

Decomposition of **1** in the presence of luminescent lanthanide ions either can be or can not be accompanied by the luminescence. In the first case the lanthanide ion gets excited, in the second case it does not. Catalyzed decomposition of **1**, accompanied by luminescence, can be described by the following scheme:

$$\mathbf{1} + Ln^{III} \overset{K_1}{\rightleftharpoons} \mathbf{1}\cdot Ln^{III}, \qquad (3)$$

$$\mathbf{1}\cdot Ln^{III} \xrightarrow{k_2} \mathbf{2}\cdot Ln^{III} + \mathbf{2}, \qquad (4)$$

$$\mathbf{1}\cdot Ln^{III} \xrightarrow{k_2} \mathbf{2}\cdot Ln^{III*} + \mathbf{2}, \qquad (4a)$$

$$\mathbf{2}\cdot Ln^{III*} \longrightarrow \mathbf{2}\cdot Ln^{III} + h\nu, \qquad (5)$$

$$\mathbf{2} + Ln^{III} \rightleftharpoons \mathbf{2}\cdot Ln^{III}, \qquad (6)$$

$$\mathbf{2}^* + Ln^{III} \longrightarrow \mathbf{2} + Ln^{III*}, \qquad (7)$$

$$Ln^{III*} \longrightarrow Ln^{III} + h\nu, \qquad (8)$$

$$Ln^{III*} + \mathbf{1} \longrightarrow \mathbf{1}\cdot Ln^{III} \longrightarrow \mathbf{2}\cdot Ln^{III} + \mathbf{2}, \qquad (9)$$

$$\mathbf{1}\cdot Ln^{III} \longrightarrow \mathbf{2}\cdot Ln^{III*} + \mathbf{2}, \qquad (9a)$$

which should be supplemented with reactions (1) and (2).

Decomposition of **1** in the presence of Ln^{III}, not accompanied by luminescence, can be described by reactions (1—4) and (6). The CL observed is only due to the dioxetane decomposition and adamantanone luminescence. The intensity (I) of CL is proportional to the consumption rate of **1**, *i.e.*

$$I \sim -d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}],$$

here $[\mathbf{1}]$ is the sum of dioxetane concentrations in the bound and free states.

If $[Ln^{III}]_0 > [\mathbf{1}]_0$ and the conversion degree of **1** is low, one can write:

$$I \sim -d[\mathbf{1}]/dt = \left(\frac{k_1 + K_1k_2[Ln]_0}{1 + K_1[Ln]_0}\right)\cdot[\mathbf{1}], \qquad (10)$$

$$k_{obs} = \frac{k_1 + K_1k_2[Ln]_0}{1 + K_1[Ln]_0}, \qquad (11)$$

where k_{obs} is the observed rate constant for the CL decay, and $[Ln]_0$ is the initial concentration of lanthanide. Expression (11) is easily transformed as follows:

$$1/(k_{obs} - k_1) = 1/(k_2 - k_1) + 1/\{(k_2 - k_1)K_1[Ln]_0\}. \qquad (12)$$

As can be seen from Eq. (11), k_{obs} depends on the concentration of Ln^{III}, and with its increase the value of the observed rate constant for the CL decay k_{obs} approaches k_2.

In the case of catalyzed decomposition of **1** accompanied by luminescence, the observed rate constant of CL decay k_{obs} in the visible region (apart from dependence on $[Ln^{III}]$) is also related with the CL yield in reaction (4), the energy transfer from **2*** to Ln^{III}, and the efficiency of Ln^{III*} emission. In addition, Ln^{III*} is quenched with dioxetane (see Ref. 7). The transfer of the electron excitation energy to the vibrational levels of dioxetane results in its decomposition. The energy released in this process causes a partial regeneration of the excited Ln^{III*} and, as a result, a quantum-chain decomposition of **1** (see Refs. 7, 8). Thus, in this case k_{obs} is related with $[Ln^{III}]$ in a more complex way than determined by Eq. (11). However, if CL is recorded in the spectral region of luminescence of 2_S^* (380—440 nm), kinetic relationships for catalyzed decomposition of **1** are reduced to the above scheme.

The dependences of k_{obs} on the Gd^{III} concentration (for catalysis not accompanied by luminescence) and on concentration of Eu^{III} (for catalysis accompanied by

Table 1. Rate constants of the decomposition of **1** and stability constants of $\mathbf{1}\cdot Ln^{III}$ complexes obtained from the kinetics of CL decay

$Ln(ClO_4)_3$	T/K	$k_2\cdot 10^{-5}$ /s^{-1}	K_1 /L mol^{-1}
$Tb(ClO_4)_3$	348	1.54	11.6
	353	2.64	10.4
	357	4.01	9.7
	360	5.40	9.5
$Gd(ClO_4)_3$	353	1.60	9.6
	358	2.73	9.1
	360	3.37	9.0
	365	5.67	8.3
$Eu(ClO_4)_3$	348	0.69	9.5
	350	0.88	9.3
	353	1.20	8.8
	358	2.11	8.2
	360	2.63	8.0
$Pr(ClO_4)_3$	348	0.29	6.0
	353	0.51	5.8
	358	0.97	5.4
	360	1.09	5.4
	368	2.58	5.1
$Ce(ClO_4)_3$	348	1.77	5.5
	353	2.67	5.4
	357	4.48	5.2
	361	7.09	5.0

Note. Average errors for k_2 and K_1 are ±17%.

luminescence) are shown in Fig. 1. The curves become linear in the coordinates of Eq. (12) (the activation parameters of decomposition of **1**, E_a = 35.1 kcal mol^{-1} and log$A$ = 14.1 (see Ref. 6), were used to calculate k_1). Analogous dependences were also obtained for the other lanthanides. The rate constants of decomposition of **1** in the **1** · Ln^{III} complexes were determined from the intercepts on the ordinate axes, and the stability constants of these complexes were determined from the slope. The results are presented in Table 1.

Chemiluminescence in the region of 380—440 nm, caused by the dioxetane decomposition and emissive deactivation of adamantanone (reactions (1) and (2)), is quenched with increasing concentration of Ln^{III}. If one assumes that the CL quenching is a result of binding compound **1** to a complex, then in the case of negligibly small decomposition of **1** during recording the intensity of CL at temperatures from 323 to 348 K, one can write

$$I^0/I = 1 + K_1[Ln^{III}]_0, \qquad (13)$$

here I^0_{CL} and I_{CL} are the values of the CL intensity in the absence and in the presence of Ln^{III}, respectively.

The dependences of quenching of CL by Eu^{III} and Pr^{III} perchlorates are shown in Fig. 2. Analogously, CL is also quenched by the other lanthanides. The values of the stability constants are listed in Table 2. It can be assumed that the adamantanone luminescence is quenched (apart from binding compound **1** to a complex) also through a reaction of energy transfer:

$$\mathbf{2}_S^* + Ln^{III} \longrightarrow \mathbf{2} + Ln^{III} \text{ (or } Ln^{III*}\text{)} . \qquad (14)$$

However, as can be seen from Table 2 and Fig. 3, quenching (with regard to the temperature dependence and stability constants obtained from the kinetics of the CL decay) is quantitatively described by Eq. (13).

The activation parameters for the decomposition of **1** in complexes **1** · Ln^{III} and thermodynamic parameters of complexation were determined from the corresponding temperature dependences of k_2 and K_1 (Table 3).

Comparative analysis of the data listed in Tables 1—3 shows that the higher the stability constant of the **1** · Ln^{III} complex is, the higher is the rate constant of decomposition, k_2. The only exception is Ce(ClO$_4$)$_3$. It

Table 2. Stability constants of complexes **1** · Ln^{III} (obtained from the CL quenching in the 380—440 nm region) at different temperatures

Ln(ClO$_4$)$_3$	K_1/L mol^{-1}					
	323	328	333	338	343	348
Tb(ClO$_4$)$_3$	17.2	15.8	14.5	13.4	12.3	11.4
Gd(ClO$_4$)$_3$	15.3	14.1	13.0	12.1	11.2	10.4
Eu(ClO$_4$)$_3$	13.8	12.8	11.7	10.9	10.2	9.5
Pr(ClO$_4$)$_3$	7.5	7.2	6.8	6.5	6.3	6.0
Ce(ClO$_4$)$_3$	7.2	6.8	6.5	6.2	5.9	5.7

Note. Average errors for K_1 are ±8%.

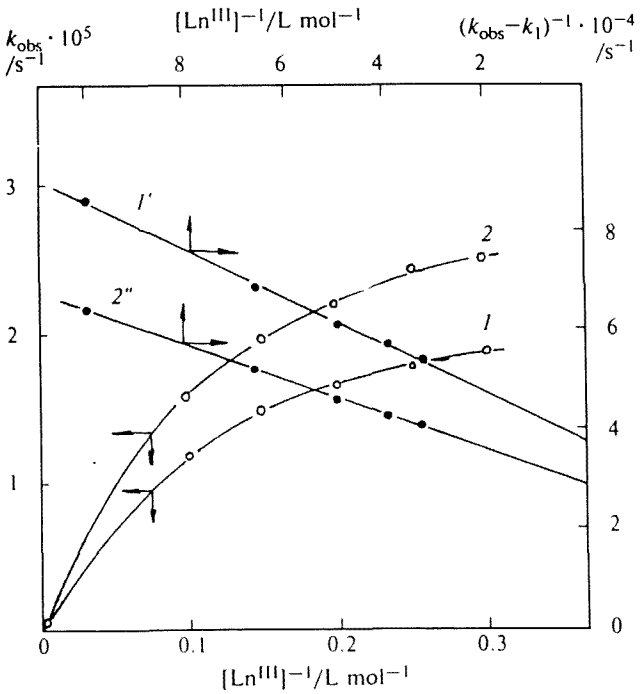


Fig. 1. Dependence of the observed rate constant of CL decay in the region of luminescence of **2** (380—440 nm) on the concentrations of Eu^{III} (curve *1*) and Gd^{III} (curve *2*) at [**1**] = 5 · 10^{-3} mol L^{-1} and T = 360 K, the same dependences in the coordinates of Eq. (12) (curves *1'*, *2'*).

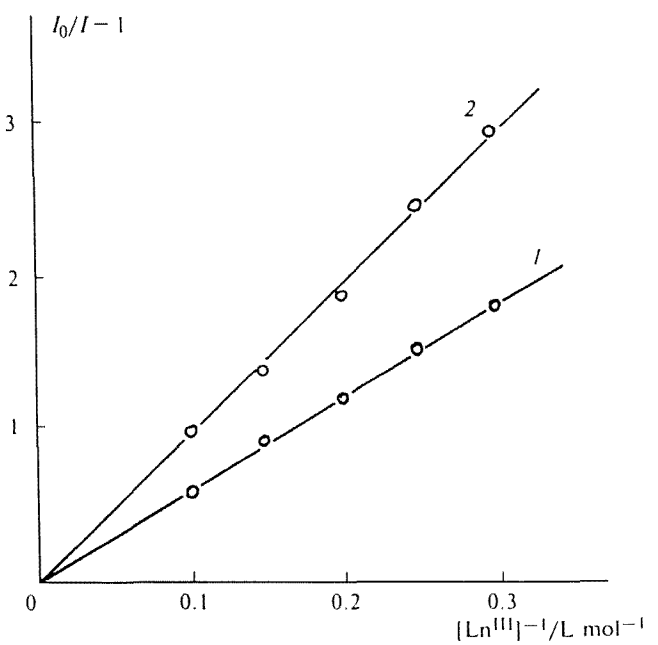


Fig. 2. CL quenching in the region of luminescence of **2** (380—440 nm) by Eu^{III} (curve *1*) and Pr^{III} (curve *2*) at [**1**] = 5 · 10^{-3} mol L^{-1} and T = 348 K.

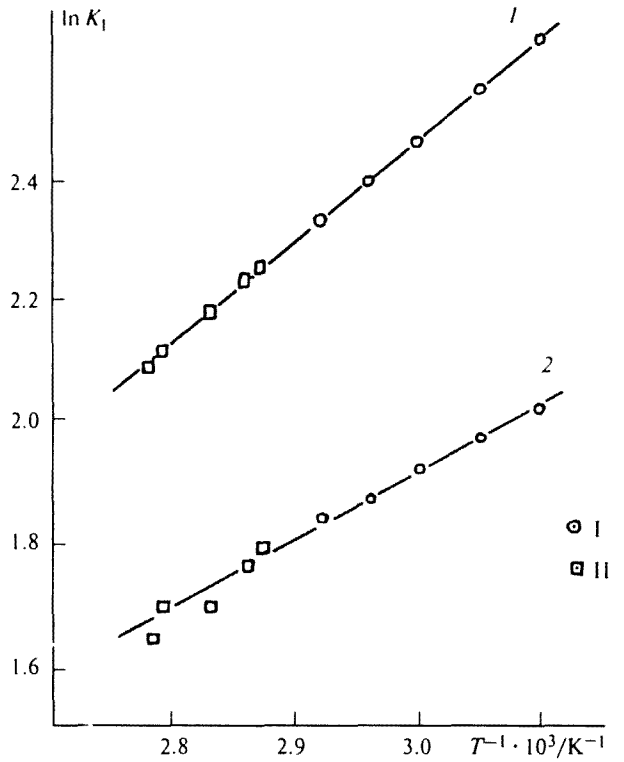


Fig. 3. Temperature dependences of the stability constants for complexes $\mathbf{1} \cdot Eu^{III}$ (curve *1*) and $\mathbf{1} \cdot Pr^{III}$ (curve *2*) (I — obtained from data on CL quenching, II — obtained from kinetic data).

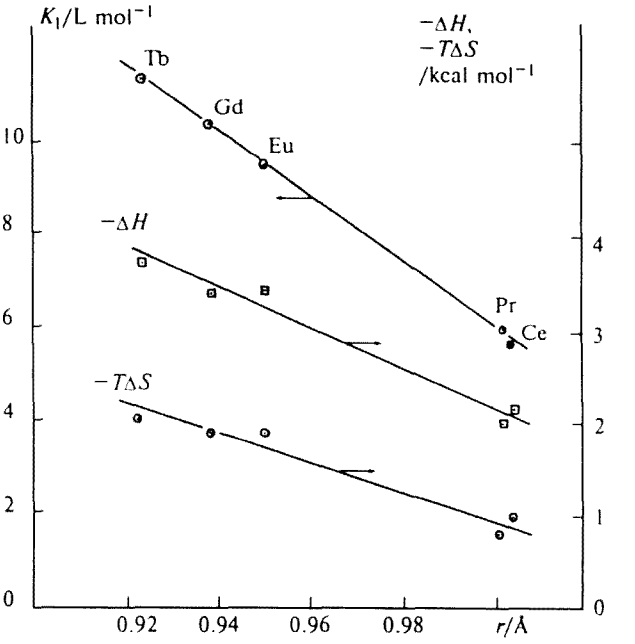


Fig. 4. Dependences of the stability constants of complex $\mathbf{1} \cdot Ln^{III}$ and of thermodynamic parameters of complexation on the radii of the lanthanide ions (T = 348 K).

is likely that the higher value of K_1 in the series of lanthanides in question points to a more stable coordination bond between Ln^{III} and peroxide, which results in a stronger perturbation of the electron orbitals and, eventually, in weakening the O—O bond in dioxetane.

Data of Table 3 show that all complexes form in an exothermic reaction. However, the entropy factor is negative, which does not favor the complexation. A change in the enthalpy of the complexation reaction is due to a difference between the energy required for complete or partial desolvation of Ln^{III} and the energy released in the interaction between the metal and peroxide. Ion ClO_4^- is a weak complexing agent.[10] In acetonitrile solutions, acetonitrile is within the first coordination sphere of the lanthanide ion, and it replaces water molecules therein in the temperature range from 423 to 460 K.[8] It is reasonable to assume that dioxetane also enters in the labile first coordination sphere of Ln^{III}; in this case the solvent molecules, making room for compound **1**, do not leave the sphere of reacting species and do not compensate the entropy decrease:

$$[Ln^{III} \cdot n\text{Solv}] + \mathbf{1} \rightleftharpoons [Ln^{III} \cdot \mathbf{1} \cdot n\text{Solv}], \qquad (15)$$

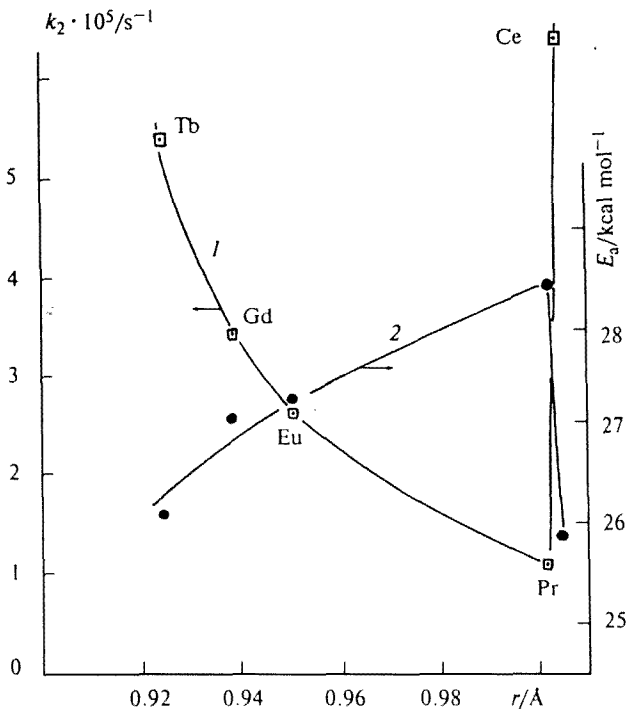


Fig. 5. Dependences of the rate constant (curve *1*) and the activation energy (curve *2*) of decomposition of **1** in complex $\mathbf{1} \cdot Ln^{III}$ on the radii of the lanthanide ions (T = 360 K).

Table 3. Activation parameters of the decomposition of **1** in complexes **1** · Ln^{III} and thermodynamic parameters of complexation at $T = 348$ K

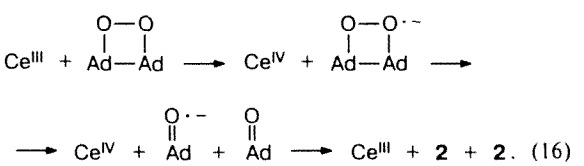
$Ln(ClO_4)_3$	E_a /kcal mol^{-1}	log$A$	$-\Delta H$ /kcal mol^{-1}	$-\Delta S$ /cal mol^{-1} deg^{-1}	$-\Delta G$ /kcal mol^{-1}
$Tb(ClO_4)_3$	26.1	11.6	3.7	5.8	1.6
$Gd(ClO_4)_3$	27.1	12.0	3.4	5.1	1.5
$Eu(ClO_4)_3$	27.3	12.0	3.4	5.1	1.5
$Pr(ClO_4)_3$	28.4	12.3	2.0	2.2	1.2
$Ce(ClO_4)_3$	25.9	11.7	2.1	2.6	1.2

Note. Average errors for E_a are ±0.4 kcal mol^{-1}, for log$A$ are ±0.6, and those for thermodynamic parameters are ±10%.

although the establishment of such an equilibrium is energetically favorable in the temperature range from 423 to 468 K since $\Delta G < 0$.

As is seen from Fig. 4, the stability constant, complexation enthalpy, and entropy increase as the ionic radii of Ln^{III} ions decrease. This tendency reflects an important contribution of the ionic interaction in the formation of these complexes.

Note the low value of the activation energy and relatively high value of k_2 for the reaction of decomposition of dioxetane **1** in the **1** · Ce^{III} complex (Fig. 5). It can be assumed that a decrease in E_a and increase in k_2, with a general tendency in the variation of the latter parameter, is associated with a relatively low value of the oxidation potential ($E_{Ce^{IV}/Ce^{III}} = 1.2$ V)[11] as compared to that of the other lanthanides, which possibly results in the decomposition of **1** following the electron-transfer mechanism:



$$Ce^{III} + \underset{\text{Ad—Ad}}{\overset{\text{O—O}}{|\ \ |}} \longrightarrow Ce^{IV} + \underset{\text{Ad—Ad}}{\overset{\text{O—O}^{\cdot -}}{|\ \ |}} \longrightarrow$$

$$\longrightarrow Ce^{IV} + \underset{\text{Ad}}{\overset{\text{O}^{\cdot -}}{\|}} + \underset{\text{Ad}}{\overset{\text{O}}{\|}} \longrightarrow Ce^{III} + \mathbf{2} + \mathbf{2}. \quad (16)$$

The above mechanism is characteristic of the reaction of dioxetanes and metals with variable valency.[12]

Thus, the catalytic action of lanthanide ions is based on their complexation with dioxetane **1**; the higher stability of the complex formed by the metal ion is, the higher is its catalytic capability.

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