Temperature deactivation of excited Tb^{3+} in the presence of 1,2-dioxetane in acetonitrile

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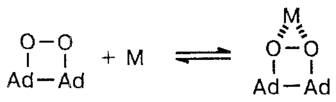
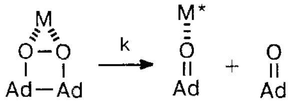
Quenching the fluorescence (FL) of terbium perchlorate by 2,2′-adamantane-2,2′-dioxide (**1**) was shown to have a chemical character and was caused by the formation of the [**1**...Tb^{3+}] complex. The dependence of the lifetime (τ) of FL of Tb^{*3+} in acetonitrile on the temperature and concentration of **1** has been studied. The temperature dependence of τ is caused by a rearrangement of the inner sphere of the aquasolvate complexes of Tb^{3+}, which leads to the replacement of H_2O with MeCN and **1**. The energy of replacing the H_2O molecule in the inner sphere of complexes with a solvent molecule has been calculated.

Key words: chemiluminescence, fluorescence, $Tb(ClO_4)_3 \cdot 6H_2O$, 2,2′-adamantane-2,2′-dioxide, lifetime, quenching.

Chelate complexes of lanthanides can effectively activate the chemiluminescence (CL) of dioxetanes and catalyze their decomposition.[1] Earlier it was found that the catalyzed decomposition of dioxetanes, which results in the formation of excited products, is caused by the formation of metal—peroxide complexes (reactions 1, 2).[1–4]

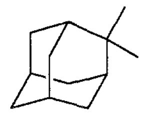


(1)



(2)

M — a lanthanide ion, Ad —



Thus, during the catalytic process the dynamics of complex formation determines the feasibility and the modes of the transfer of electron excitation energy from the dioxetane molecules, which act as energy conservators, to the lanthanide ions.

Methods for determining the compositions of lanthanide ion complexes based on the analysis of the lifetime of CL of these ions, have been elaborated.[5,6] In the present work the complexation of Tb^{3+} ions with adamanthylideneadamanthane-1,2-dioxetane in liquid and frozen solutions of acetonitrile has been studied by kinetic spectroscopy.

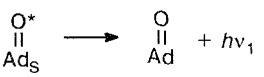
Experimental

2,2′-Adamantane-2,2′-dioxide (**1**) was synthesized by the procedure described earlier.[7] Acetonitrile was purified by azeotropic distillation with H_2O. $Tb(ClO_4)_3 \cdot nH_2O$ was prepared from a Tb^{3+} carbonate of analytical grade and dried *in vacuo* at 360 K. Intensities were measured and the CL spectra were recorded on an instrument similar to one described previously.[2] The lifetime (τ) of the excited Tb^{3+} was determined using a device that was reported in the literature.[8] Solvents were cooled to required temperatures by nitrogen vapor. The fluorescence (FL) spectra were recorded on a Hitachi MPF-4 spectrofluorimeter.

Results and Discussion

It is known[7] that the thermolysis of dioxetane **1** results in the formation of adamantanone (**2**) in the singlet and triplet excited states.

(3)



(4)

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$$\text{Ad}{=}\text{O}^* + \text{Tb}^{3+} \longrightarrow \text{Tb}^{*3+} + \text{Ad}{=}\text{O} \qquad (5)$$

$$\text{Tb}^{*3+} \longrightarrow \text{Tb}^{3+} + h\nu_2 \qquad (6)$$

The luminescence is caused by deactivation of the excited compound **2** (λ_{max} = 420 nm). We found that the addition of Tb^{3+} to a solution of **1** in MeCN not only changes the intensity and spectral composition of CL (see Fig. 1), but also catalyzes the thermodestruction of dioxetane. The activation energy (E_a), which was determined from the quasi-stationary intensity of CL during the decomposition of **1** (10^{-2} mol L^{-1}) in the presence of Tb^{3+} (10^{-2} mol L^{-1}), decreases from 35.4±2.3 to 28.6±2.0 kcal mol^{-1}. Therefore, the intensification of CL of **1** is caused not only by the transfer of energy (reaction 5), but also by the acceleration of the decomposition of **1**, which results in the formation of the electron excited products:

$$\mathbf{1} + \text{Tb}^{3+} \rightleftharpoons [\mathbf{1}...\text{Tb}^{3+}] \xrightarrow{k_2} \mathbf{2} + [\mathbf{2}...\text{Tb}^{*3+}]\,. \qquad (7)$$

The catalysis occurs due to the formation of the [**1**...Tb^{3+}] complex, as we have shown in the case of Eu^{3+} chelates (see Refs. 3, 4). Dioxetane can coordinate itself to Tb^{3+} through the oxygen atoms (reaction 1). The formation of this complex leads to the redistribution of the electron density in the dioxetane molecule, which facilitates the cleavage of the strained O—O bond and thus accelerates the thermodestruction of **1**. Apparently, the formation of the dioxetane complex with Tb^{*3+} must change the luminescent properties of the latter. In fact, dioxetane **1** does quench the FL of Tb^{3+}. Quenching is described by the Stern—Volmer law (see Fig. 1) with the bimolecular quenching rate constant $k_b = 1 \cdot 10^5$ L mol^{-1} s^{-1}. The low k_b value (5 orders of magnitude lower than for the diffusionally controlled reaction) indicates that the quenching of Tb^{*3+} by dioxetane is ineffective, apparently, due to the steric hindrances. The data on the temperature quenching of Tb^{*3+} in the presence of **1** make it possible to evaluate the activation energy of ligand substitution in the first coordination sphere of Tb^{*3+}. However, the temperature dependence of τ for Tb^{*3+} in MeCN is unusual: increasing the temperature gives rise to a decrease, rather than an increase in τ (see Fig. 2).

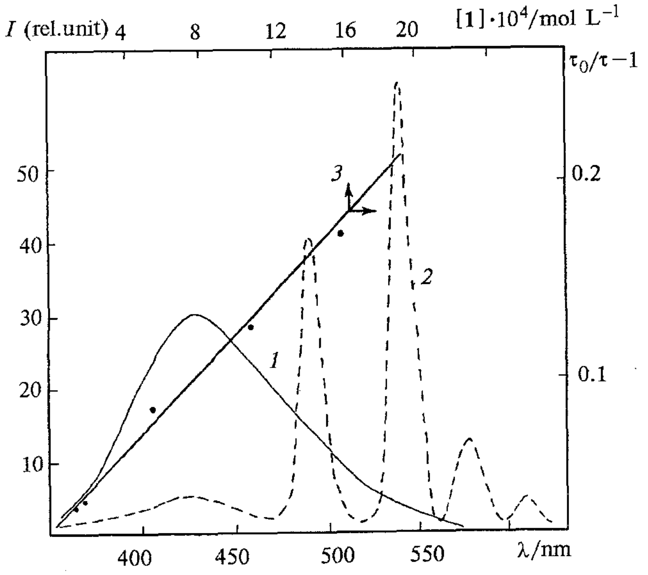

Fig. 1. CL spectra of the thermolysis of **1** (10^{-2} mol L^{-1}, MeCN, 360 K); [Tb^{3+}] = 0 (*1*); [Tb^{3+}] = 10^{-2} mol L^{-1} (*2*); the Stern—Volmer dependence of Tb^{3+} PL quenching (10^{-2} mol L^{-1}) by dioxetane **1** (MeCN, 300 K) (*3*).

Such an abnormal dependence of τ was observed in the case of the hexahydrates of the Tb^{*3+} and Eu^{*3+} nitrates in solvents with donor numbers smaller than the donor number of water.[9] We explained the increase in τ with increasing temperature by the rearrangement of the inner sphere of the mixed aquasolvate complexes, *i.e.*, by the replacement of the H_2O molecules with solvent molecules (*P*) according to Eq. (8).

$$[\text{Tb}^{3+}...n\text{H}_2\text{O}]\cdot P \overset{t}{\rightleftharpoons} [\text{Tb}^{3+}...(n-1)\text{H}_2\text{O}]\cdot P\ \text{H}_2\text{O} \qquad (8)$$

It is known that lanthanide ions in aquacomplexes

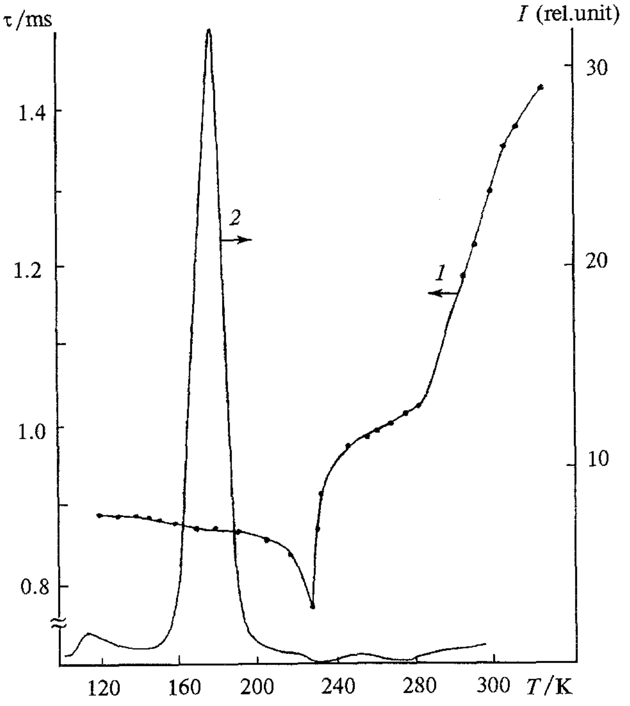

Fig. 2. Temperature dependences of the lifetime τ of Tb^{*3+} (10^{-2} mol L^{-1}) (*1*), and the intensity of the radiothermoluminescence of Tb^{*3+} (10^{-2} mol L^{-1}) (*2*) in acetonitrile.

have the greatest rate constants of radiationless deactivation (k_d).[9] The replacement of the H_2O molecules with solvent molecules in the inner sphere of the complex would, therefore, result in a decrease in k_d and (since $1/\tau = k_i + k_d$) an increase in τ. According to the considerations mentioned above, the composition of the complexes can change from completely hydrated complexes to anhydrous complexes as the temperature increases. For Tb^{3+} and Eu^{3+} nitrates, the ratios between the complexes that are present in the solution are not abruptly changed by the temperature, and the value of τ increases monotonically.[9] On the other hand, as we concluded from the results obtained, the establishment of the equilibrium involving participation of the Tb^{3+} perchlorate and MeCN is governed not only by the changing temperature, but also by the aggregate state of the solution (see Fig. 2). In the solid frozen solution the value of τ for Tb^{*3+} monotonically decreases with increasing temperature, goes through a minimum at the melting point of MeCN (227 K), and increases in the liquid solution. In the liquid MeCN phase, the value of τ for Tb^{3+} also changes non-monotonically, and the dependence of τ on T has two parts with different gradients of τ. The temperature quenching of Tb^{*3+} in the solid solution is caused by the increased mobility of the molecules in the coordination environment of the Tb^{*3+} ion. The occurrence of rotational mobility in the solid solution is confirmed by the radiothermoluminescence peak at 180 K (see Fig. 2), which correlates with an insignificant decrease in τ of Tb^{*3+}. The abrupt decrease in τ when MeCN melts is due to the increased vibrational mobility of the solvent molecules. The minimum in the temperature dependence of τ of Tb^{*3+} at the melting point of MeCN is caused by the rate of freezing of the solution. When the samples are cooled quickly, the replacement of the MeCN molecules with H_2O is not complete. As a result, Tb^{3+} complexes with acetonitrile in the first coordination sphere are conserved in the frozen solutions. When a sample is heated, at the melting point of acetonitrile the rearrangement of the inner sphere of Tb^{3+} occurs accompanied by the replacement of the MeCN molecules with H_2O, which gives rise to the abrupt decrease in the τ of Tb^{*3+}. In the liquid phase, heating leads to a shift in the equilibrium in the direction of the formation of complexes with acetonitrile that are incorporated into the first coordination sphere of the Tb^{3+} ion (reaction 8), and, therefore, to an increase in τ. Apparently, in the case of slow freezing, there is no minimum in the temperature dependence of τ of Tb^{*3+}.

The following equation for calculating the energy required for the replacement of one water molecule in the first coordination sphere of the lanthanide ion with a solvent molecule was suggested earlier[9] for lanthanide—water—solvent systems:

$$\frac{k_d(\min) - k_d(T)}{k_d(T) - k_d(\max)} = C \cdot e^{-\Delta E/RT} \qquad (9)$$

In this equation, $\kappa_d(\min)$ is the rate constant of radiationless deactivation at the minimum temperature in the temperature interval studied, $k_d(\max)$ is the limiting value at high temperatures, $k_d(T)$ is the deactivation rate constant at an actual temperature, and C is the ratio between the statistical weights of two states, in one of which all water is tied up in complexes, and in the other of which it is free. It should be noted that this equation is applicable only in the temperature interval where τ changes monotonically. Eq. (9) may be written as follows:

$$\frac{1/\tau(\min) - 1/\tau(T)}{1/\tau(T) - 1/\tau(\max)} = C \cdot e^{-\Delta E/RT} , \qquad (10)$$

where $\tau(T)$ is the life time of Tb^{*3+} at an actual temperature, $\tau(\min)$ is the minimal value at m.p. of MeCN (227 K), and $\tau(\max)$ is the maximal value at the high temperature (350 K).

The plot of the linear anamorphosis of Eq. (10) (see Fig. 3) shows that the points fall satisfactorily on a straight line with the correlation coefficient $R = 0.996$ in the 280—350 K temperature range. The value of ΔE, 8.1±1.2 kcal mol^{-1}, was determined from the slope of the straight line. This is the energy necessary for the replacement of one H_2O molecule in $Tb(ClO_4)_3 \cdot nH_2O$ with a MeCN molecule. The value of ΔE for the replacement of one molecule of water in $Tb(ClO_4)_3 \cdot 6H_2O$

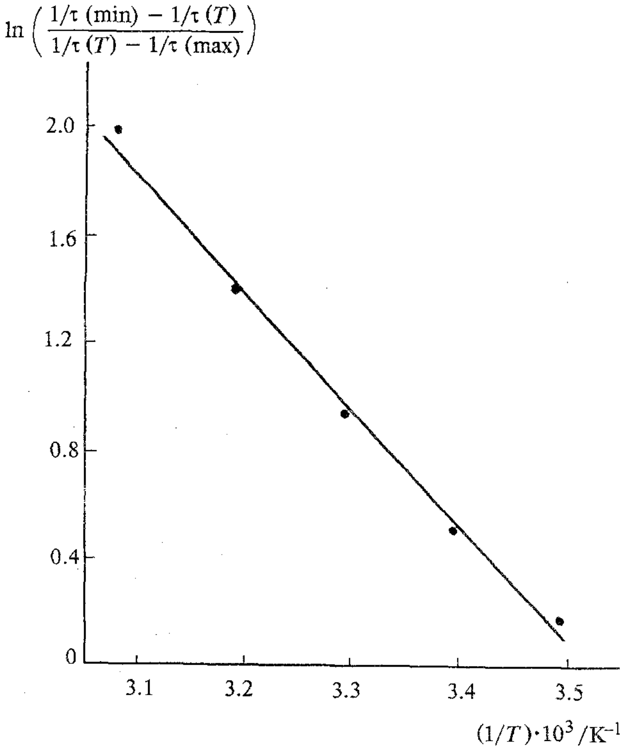

Fig. 3. Linear anamorphosis of the temperature dependence of τ of Tb^{*3+} (10^{-2} mol L^{-1}) in MeCN (ΔT = 280÷350 K).

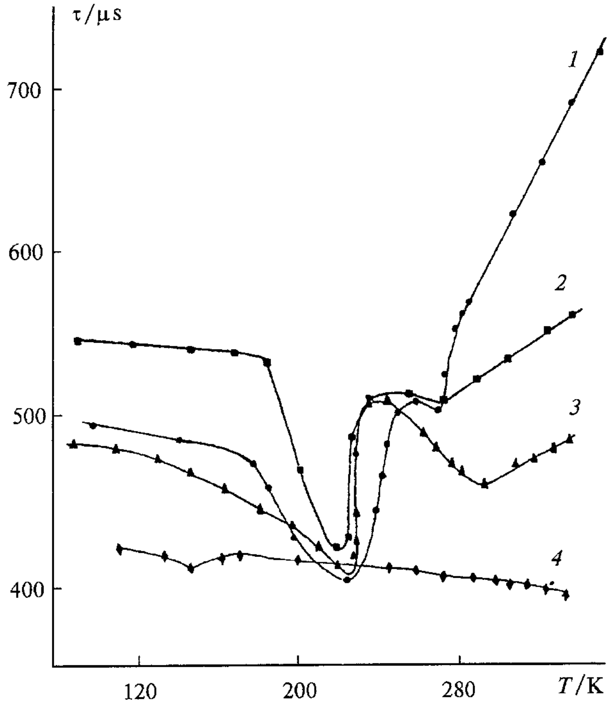

Fig. 4. Temperature dependence of τ of Tb^{*3+} (10^{-2} mol L^{-1}) in MeCN in the presence of dioxetane **1** ([C]/mol L^{-1}): *1*, 10^{-3}; *2*, $2.5 \cdot 10^{-3}$; *3*, $5 \cdot 10^{-3}$; *4*, temperature dependence of τ of Tb^{*3+} (10^{-2} mol L^{-1}) in H_2O.

with a molecule of acetone was reported earlier[9] to be 8.6 kcal mol^{-1}.

In the presence of dioxetane **1**, along with the mixed aqueous-solvate complexes, complexes of Tb^{3+} with dioxetane are formed in solution, and Eq. (8) is changed to:

$$[Tb^{3+}...nH_2O] \cdot \mathbf{1} \cdot P \xrightleftharpoons{t} [Tb^{3+}...(n-2)H_2O] \cdot \mathbf{1} \cdot P\ 2H_2O. \quad (11)$$

When FL of Tb^{*3+} is quenched by dioxetane, an increase in the temperature results in an analogous change in τ (Fig. 4). On the other hand, there are a number of differences. At the melting point of MeCN the τ of Tb^{*3+} equals the τ value of the terbium ion in aqueous solutions (see Fig. 4). This fact shows that only aquacomplexes of Tb^{3+} are present in the solution when MeCN melts. In the liquid phase of MeCN, the presence of **1** causes the inflection on the curve of the dependence of τ on *T* to be converted into a clear maximum that becomes more intense as the concentration of **1** increases. It should be noted that the position of the maximum is independent of the concentration of dioxetane (273 K) (see Fig. 4). The maximum on the τ *vs.* *T* curve at 273 K is apparently caused by the influence of the phase transition of H_2O on the character of the equilibrium that is established in the lanthanide—water—dioxetane—acetonirile system.

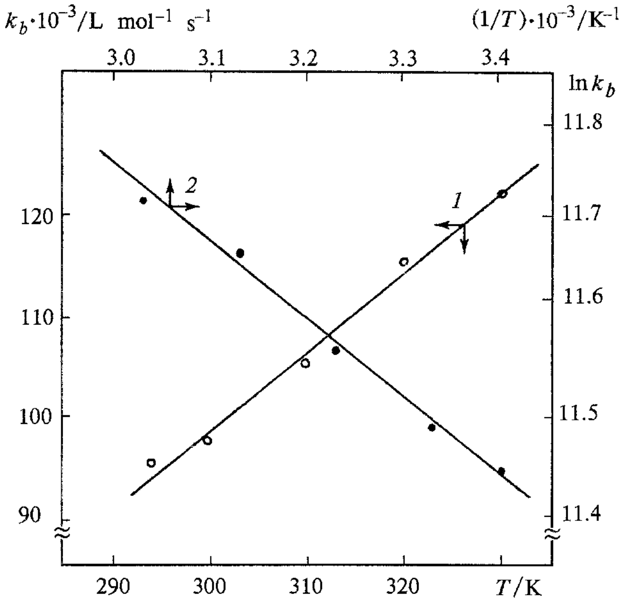

Fig. 5. Temperature dependence of the bimolecular rate constant of Tb^{*3+} PL quenching (10^{-2} mol L^{-1}) by dioxetane **1** (MeCN, ΔT = 290—330 K) (*1*); dependence of ln k_b on T/K^{-1} (*2*).

The activation parameters of the ligand exchange in the inner coordination sphere of the Tb^{3+} ions with participation of dioxetane molecules, the solvent, and water may be determined from the Arrehnius dependence for the rate constant of radiationless deactivation:

$$k_d = A_0 \cdot e^{-E_a/RT} \quad (12)$$

or, because $\tau = 1/(k_i + k_d)$,

$$1/\tau - 1/\tau_0 = A_0 \cdot e^{-E_a/RT}, \quad (13)$$

where τ is the lifetime of Tb^{*3+} at 280—320 K and $\tau_0 = 1/k_i$ is the irradiation lifetime of Tb^{*3+}. The radiation lifetime of terbium perchlorate is 4.75 ms.[10] The E_a values were determined from the slope of the linear anamorphosis of Eq. (13). These are the effective values of the activation energy of the competitive processes that occur in the first coordination sphere of Tb^{*3+} with participation of H_2O, MeCN, and **1**, and are equal to (kcal mol^{-1}) 1.61 (in the absence of **1**), 1.01, 0.35, and 0.32 (the measurement error is 10 %) at the concentrations of **1** (mol L^{-1}) of $1 \cdot 10^{-3}$, $2.5 \cdot 10^{-3}$, and $5.0 \cdot 10^{-3}$, respectively. Such low values of E_a in the presence of dioxetane indicates instability of the $[Tb^{3+}...\mathbf{1}]^*$ complex, and a shift of the equilibrium in the direction that favors the formation of a complex between Tb^{*3+} and MeCN.

The slope of the dependence of τ *vs.* *T* in the 290—330 K temperature range depends on the concentration of **1** and decreases when it is increased (see

Fig. 4). The Stern—Volmer dependence of the quenching of Tb^{*3+} PL by dioxetane **1** is fulfilled at each fixed temperature in the 290—330 K temperature range. Since increasing the temperature results in increased diffusion coefficients, a higher value of k_b may be expected as the temperature increases. In fact, the value of k_b linearly increases in the 290—330 K temperature interval (see Fig. 5). The activation energy of the quenching of Tb^{*3+} PL by dioxetane was found to be 1.5±0.2 kcal mol^{-1} from the ln k_b *vs.* $1/T$ dependence (Fig. 5).

Thus, the investigation of the temperature dependences of the lifetimes of excited lanthanide ions makes it possible to obtain quantitative information on the dynamics of the rapid exchange of ligands in their coordination sphere.

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