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First observation of IR chemiluminescence of Nd^{III} and Yb^{III} perchlorates in the reaction with dispiro(adamantane-1,2-dioxetane) in a melt

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Previously,[1] it has been established that electronic excitation and chemiluminescence of lanthanide (Ln^{III}) perchlorates upon catalysis of decomposition of dispiro(adamantane-1,2-dioxetane) ($(-Ad-O)_2$) in acetonitrile solutions were observed in the visible region of the spectra only in the case of Eu^{III} and Tb^{III}. These phenomena are determined both by the efficiency of the intramolecular energy transfer from the triplet adamantanone molecule ($Ad{=}O_T{}^*$) to excited levels of Ln^{3+} and by the quantum yield of luminescence of Ln^{3+}, which strongly depends on the composition of the coordination sphere of the ion.[1] This raises the question of whether electronic excitation of other lanthanides in the dioxetane—Ln^{III} system is possible. According to the theory of the inductive-resonance energy transfer, the strongest interactions that cause radiationless transitions are realized in solutions with the participation of molecular groups immediately adjacent to the Ln^{3+} ion.[2] In this connection, the Nd^{3+} and Yb^{3+} ions in H-containing media exhibit virtually no luminescence upon excitation due to the transfer of the energy of electronic excitation to the vibrational modes of the O—H and C—H oscillators. Therefore, the rate constant of nonradiative deactivation of Nd^{3+} and Yb^{3+} ions is much larger than the radiative rate constant: $k_{nr} >> k_r$. We expected that elimination of water molecules, which are generally present in acetonitrile solutions, by concentrating an aqueous—acetonitrile azeotrope would enable us to observe chemiluminescence of Nd^{3+} and Yb^{3+} in the reaction with $(-Ad-O)_2$. Actually, we observed chemiluminescence in the near IR region of the spectrum upon thermolysis (90 °C) of a melt containing $Ln(ClO_4)_3$ (0.15 mmol) and $(-Ad-O)_2$ (0.03 mmol), which was prepared by evaporating MeCN (3 mL). The luminescence spectra, which were obtained on a wide-aperture spectrometer equipped with a cooled FEU-83 instru-

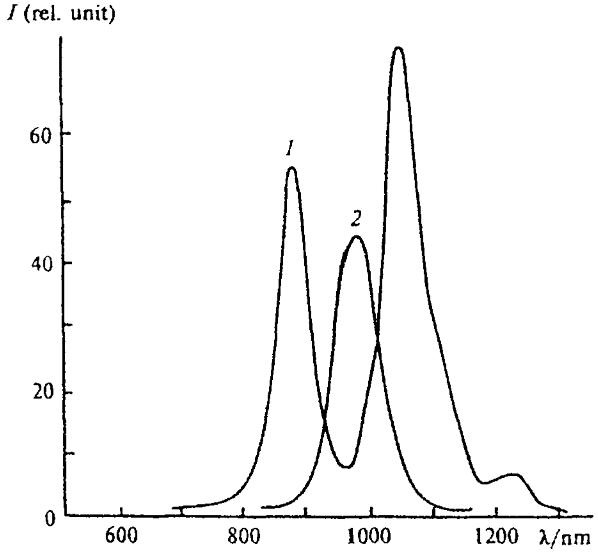

Fig. 1. Chemiluminescence spectra of Nd^{III} (*1*) and Yb^{III} (*2*) upon thermolysis of a melt containing their perchlorates (0.15 mmol) and $(-Ad-O)_2$ (0.03 mmol); 90 °C; the spectral resolution was 15 nm.

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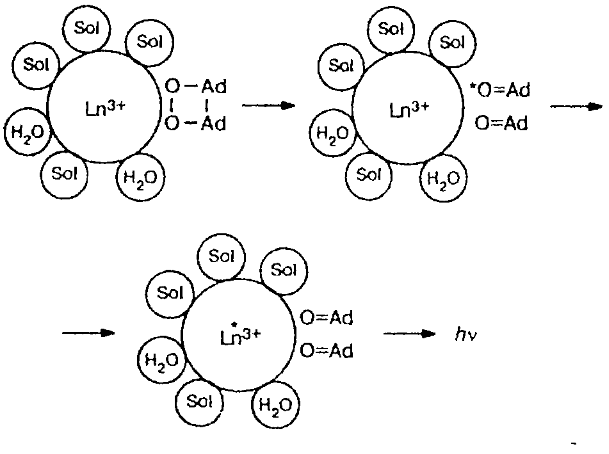
ment, have maxima at 980±10 nm (for the Yb^{III}—(—Ad—O)$_2$ system) and at 880±10 and 1060±10 nm (for the Nd^{III}—(—Ad—O)$_2$ system), which belong to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$, and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions, respectively, in Ln^{3+} ions (Fig. 1). Apparently, the major processes, which cause excitation of Ln^{3+} ions, are the decomposition of (—Ad—O)$_2$ in the coordination sphere of the lanthanide ion and the intracomplex energy transfer from Ad=O_T* to the excited levels of Ln^{3+}.



Sol are solvent molecules.

Excitation of Ln^{3+} according to the mechanism of intermolecular energy transfer Ad=O_T* + Ln^{3+} → Ad=O + Ln^{*3+} ($k_{ct} \approx 10^9$ L mol^{-1} s^{-1})[1] is also possible because the process of internal conversion Ad=O_T* → Ad=O (τ(Ad=O_T*) = $4 \cdot 10^{-9}$ s), which competes with energy transfer,[3] is not the major channel of deactivation of Ad=O_T* under conditions of thermolysis of the (—Ad—O)$_2$—Ln^{III} system.

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Selective oxidation of dialkyl sulfides into dialkyl sulfoxides by chlorine dioxide

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Selective oxidation of organic sulfides **1** to sulfoxides **2** and sulfones **3** is an important task for organic chemistry.[1] Several oxidants (peroxides, oxygen, ozone, and others)[1–3] make it possible to obtain sulfoxides under mild conditions. However, the majority of oxidants used in the present time has no sufficient selectivity, and sulfoxides that formed undergo easily subsequent oxidation to form sulfones.

For the purpose of development of a convenient and simple method for the synthesis of sulfoxides, we oxidized sulfides, dipropyl sulfide (**1a**), and dioctyl sulfide (**1b**) by a new reagent — chlorine dioxide (ClO_2). As has been shown previously,[4] ClO_2 is a selective oxidant of allylic alcohols to α,β-unsaturated carbonyl compounds.

The oxidation of sulfides **1a,b** at a substrate : reagent ratio of 1 : 0.5, without a solvent, using an aqueous solution of ClO_2 (concentration 4—5 g L^{-1}) occurs with almost complete conversion of **1a,b** and results in 95—97% yields of sulfoxides **2a** and dioctyl sulfoxide **2b**. Sulfoxide **2b** was obtained in 90% yield by passing ClO_2

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