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Letters to the Editor

Chemiluminescence activated by the Tb^{3+} ion in $(Bu^i{}_2Al)_2O$ aluminoxane oxidation with dioxygen in toluene

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The Ln^{3+} ion is known[1] to activate chemiluminescence (CL) (enhances glow) in hydrocarbon oxidation. Such an effect has not been observed in the autoxidation of organometallic compounds.[2] In this work, we found CL in the autooxidation of the aluminoxane $(Bu^i{}_2Al)_2O$ (**1**) synthesized according to a known procedure[3] and its activation in the presence of the complex $TbCl_3 \cdot 3(Bu^nO)_3PO$ (**2**) prepared as described previously[4] (Fig. 1).

The introduction of aluminoxane **1** (2 mL, $8.1 \cdot 10^{-2}$ mol L^{-1}) into toluene (8 mL), through which O_2 is bubbled, induces CL_1 ($I_{max} = 9.6 \cdot 10^7$ photon s^{-1} mL^{-1}), whose emitter is isobutyric aldehyde Me_2CHCHO^* ($\lambda_{max} = 420 \pm 20$ nm). If toluene contains com-

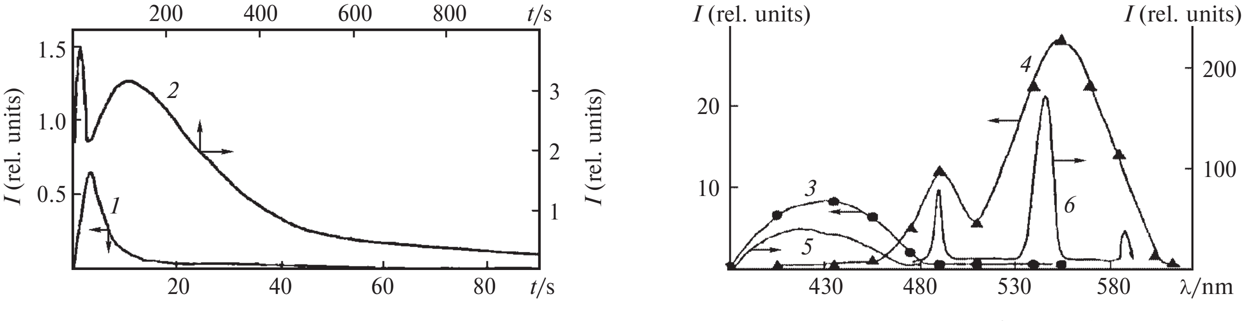

Fig. 1. Kinetics (*1*, *2*) and CL spectra (*3*, *4*) for the oxidation of solutions of aluminoxane **1** ($1.6 \cdot 10^{-2}$ mol L^{-1}) with dioxygen in toluene (298 K) in the absence (*1*, *3*) and presence of $TbCl_3 \cdot 3(Bu^nO)_3PO$ ($2.7 \cdot 10^{-3}$ mol L^{-1}) (*2*, *4*), phosphorescence spectrum of a solution of Me_2CHCHO ($2.7 \cdot 10^{-3}$ mol L^{-1}) in toluene at 77 K (*5*), and photoluminescence spectrum of $TbCl_3 \cdot 3(Bu^nO)_3PO$ ($2.7 \cdot 10^{-3}$ mol L^{-1}) in the presence of aluminoxane **1** ($1.6 \cdot 10^{-2}$ mol L^{-1}) at 298 K (*6*). Chemiluminescence spectra were measured by a set of boundary light filters, and curves *5* and *6* were obtained in an Ar atmosphere, λ_{exc} = 365 nm, an Aminco-Bowman spectrofluorimeter.

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plex **2** ($3.4 \cdot 10^{-3}$ mol L^{-1}), brighter CL_2 is observed ($I^1_{max} = 5.3 \cdot 10^8$ photon s^{-1} mL^{-1}, $I^2_{max} = 4.5 \cdot 10^8$ photon s^{-1} mL^{-1}). The spectrum of CL_2 remains unchanged with time and contains peaks with $\lambda_{max} = 490$, 545 nm, which are characteristic of luminescence of the Tb^{3+}* ions (see Fig. 1).

We found that CL_2 is due to the formation of a complex between **1** and **2**. Immediately after mixing of solutions of **1** (2 mL, $8.1 \cdot 10^{-2}$ mol L^{-1}) and **2** (8 mL, $3.4 \cdot 10^{-3}$ mol L^{-1}) in an Ar atmosphere, complex **3** is formed, whose ^{13}C NMR spectrum (JEOL FX 90Q spectrometer) contains two signals from the CH_2O groups of tributyl phosphate: at 69.3 ($\Delta\nu_{1/2} = 11$ Hz) and 70.7 ppm ($\Delta\nu_{1/2} = 51$ Hz). The first narrow signal was assigned to the free, non-coordinated terminal BuO group. It corresponds to the signal at 68.2 ppm ($\Delta\nu_{1/2} = 17$ Hz) in the spectrum of complex **2**. We attribute the second signal at 70.7 ppm ($\Delta\nu_{1/2} = 51$ Hz), slightly shifted downfield, to a bridged complex in which the O atom of aluminoxane **1** is coordinated to the central Tb^{3+} ion and the Al atom is coordinated to the O atom of the PO group in tributyl phosphate.

The CL_1 and CL_2 processes have common properties characteristic of the known[2] chemiluminescence observed in the oxidation of the Al—C bonds of aluminumalkyls. The CL_1 and CL_2 spectra occur in a region 380—480 nm characteristic of the emission of aldehydes.[2] The addition of an inhibitor (galvinoxyl) results in a sharp decrease in the brightness of CL_1 and CL_2, which is due[2] to binding of the $AlkO_2^{\bullet}$ radicals. Thus, the emitter of non-activated CL_1, aldehyde Me_2CHCHO*, is formed, as in the case of aluminumalkyl autoxidation, by the disproportionation of the $AlkO_2^{\bullet}$ radicals. The activation of luminescence is induced by energy transfer from the Me_2CHCHO* molecule in the triplet state to the Tb^{3+} ion in complex **3**, which transforms to the Tb^{3+}* excited state. We assume that the first kinetic maximum of CL_2 is resulted from the oxidation of free aluminoxane **1**, and the second maximum is a result of a slower oxidation of aluminoxane **1** bound in a complex with compound **2**.

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