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Letters to the Editor

Radical $\text{Ph}_3\text{C}^{\bullet}$ as activator of chemiluminescence in the oxidation of $\text{Bu}^{\text{i}}{}_3\text{Al}$ with oxygen in toluene

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Some organic molecules and metal ions and complexes are known to activate (intensify) chemiluminescence (CL) observed in reactions of organic,[1] inorganic,[2] and organometallic compounds.[3] Earlier,[4] it was shown that the radical $\text{Ph}_3\text{C}^{\bullet}$ (**1**) stabilized by the solid matrix of the peroxide $\text{Ph}_3\text{COOCPh}_3$ activates the CL induced by the thermolysis of this peroxide. The literature data on CL activation by free radicals in solution are lacking, though the energy transfer to radicals during photoexcitation was reported.[5]

In the present work, we discovered with radical **1** as an example that organic radicals in solution can also function as CL activators. For instance, we found that addition of radical **1** affects the spectrum and intensity of the known[3] CL observed in the autooxidation of aluminumalkyls. When O_2 was bubbled through a solution of

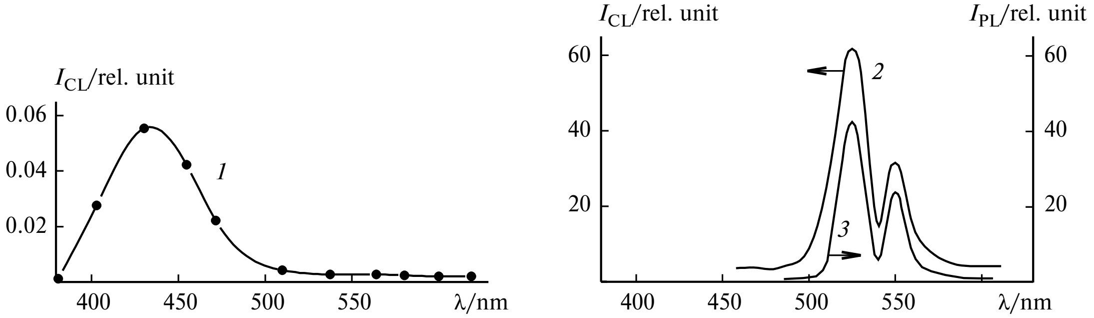

Fig. 1. Chemiluminescence (CL) spectra in the autooxidation of $\text{Bu}^{\text{i}}{}_3\text{Al}$ in toluene at 298 K: $\text{Bu}^{\text{i}}{}_3\text{Al}$ ($3 \cdot 10^{-1}$ mol L^{-1}) (*1*) and $\text{Bu}^{\text{i}}{}_3\text{Al}$ in the presence of $\text{Ph}_3\text{C}^{\bullet}$ ($1.2 \cdot 10^{-3}$ mol L^{-1}) (*2*); the CL_2 spectrum (for explanation see text) was recorded with a set of boundary light filters. The photoluminescence (PL) spectrum of the radical $\text{Ph}_3\text{C}^{\bullet}$ in toluene ($1.2 \cdot 10^{-3}$ mol L^{-1}) in an argon atmosphere at 298 K (*3*) was recorded on an Aminco-Bowman spectrofluorimeter ($\lambda_{\text{ex}} = 334$ nm).

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Bu^i_3Al (**2**) in toluene ($2.5 \cdot 10^{-2}$ mol L^{-1}, $V = 5$ mL) in the presence of radical **1** ($1.2 \cdot 10^{-3}$ mol L^{-1}; prepared as described in Ref. 6), CL_1 is excited and its intensity ($I_{max} = 5.2 \cdot 10^9$ photon s^{-1} cm^{-3}) is higher by more than three orders of magnitude than the intensity of CL_2 ($I_{max} = 4.8 \cdot 10^6$ photon s^{-1} cm^{-3}) observed in the absence of radical **1**. The CL_1 intensity grows more significantly with an increase in the concentration of radical **1**. The emitter of CL_2 is[3] the triplet-excited aldehyde Me_2CHCHO^* ($\lambda_{max} = 420 \pm 20$ nm) formed as the result of the disproportionation of radicals $Bu^iO_2^•$. The spectrum of CL_1 ($\lambda_{max} = 525$ and 550 nm) was recorded with the use of an MDR-23 monochromator and is identical with the photoluminescence spectrum of a solution of **1** (Fig. 1).

Mixing of solutions of compounds **1** and **2** in an argon atmosphere was not accompanied by CL or any changes in the absorption and photoluminescence spectra of compound **1**, thus suggesting the absence of interactions between species **1** and **2**. The autooxidation of compound **2** in the presence of radical **1** is accompanied by more intense CL but the kinetic dependences of the CL intensity and the absorption of O_2 remain unchanged. These data indicate that the CL activation by radical **1** is of physical nature and is due to energy transfer from the triplet-excited aldehyde Me_2CHCHO^* to radical **1**, which passes into a doublet[5] state and deactivates itself through emission of green CL_1 quanta.

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