Lanthanide(III) ion as a luminescent and catalytically active reaction center of aniline condensation with butyraldehyde

R. G. Bulgakov,* S. P. Kuleschov, and A. R. Makhmutov

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

A new type of chemiluminescence catalytic conversion in which the lanthanide(III) ion is a luminescent and highly efficient catalytically active center was found. Chemiluminescence (CL) is generated in the condensation reaction of aniline with butyraldehyde in DMF to form 3-ethyl-2-propylquinoline. The reaction is catalyzed by $LnCl_3 \cdot 6H_2O$ (Ln = Eu, Tb, and Ho). When $EuCl_3 \cdot 6H_2O$ and $TbCl_3 \cdot 6H_2O$ salts are used as catalysts, the CL emitters are the Eu^{3+*} and Tb^{3+*} excited ions. In the case of $HoCl_3 \cdot 6H_2O$, the emitter is 3-ethyl-2-propylquinoline in the triplet-excited state.

Key words: chemiluminescence, lanthanide catalysis, crystalline hydrates of lanthanide trichlorides, condensation reaction, synthesis of 3-ethyl-2-propylquinoline.

Numerous types of chemiluminescence conversions of organic compounds are presently known,[1—3] although the lanthanide(III) ion is the emitter of chemiluminescence (CL) and catalyst only for the decomposition of *o*-cyclic peroxides (dioxetanes). This type of CL has been observed[4] for the first time during the decomposition of 9-(2-adamantalidene)-*N*-methylacridane-1,2-dioxetane (300 K) in the presence of the $Eu(fod)_3$ complex (tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionato)europium(III)). This CL cannot be explained only by simple energy transfer to the Eu^{3+} ion from the primary emitter, *viz*., excited *N*-methylacridone, *i.e*., similarly to CL activation upon the liquid-phase oxidation of hydrocarbons with the tris(2-thenoyltrifluoroacetonato)phenanthrolineeuropium(III)) complex.[1] It has been found[4] that the enhancement of CL is mainly caused by the catalytic effect of the $Eu(fod)_3$ complex on dioxetane (DO) decomposition. Later[5—7] CL has been observed for the catalytic decomposition of adamantylideneadamantane-1,2-dioxetane and tetramethyl-1,2-dioxetane under the action of lanthanide acetylacetonates $Eu(acac)_3$ and $Tb(acac)_3$. The observed effects of CL enhancement during the decomposition of dioxetanes are characterized[5—7] as luminescence catalysis. However, the authors[4] admit that the $Eu(fod)_3$ additives only insignificantly catalyze dioxetane decomposition and an increase in the rate constants of adamatylideneadamantane-1,2-dioxetane and tetramethyl-1,2-dioxetane decomposition by the $Eu(acac)_3$, $Tb(acac)_3$, and $Tb(ClO_4)_3$ complexes, according to published data,[5—7] is achieved only at $[Ln^{3+}] \le [DO]$.

Based on the aforesaid, we can assert that no examples are described where the Ln^{3+} ions, being CL emitters, would manifest the properties of efficient catalysts for the chemical reaction in which this CL is generated. Search for and investigation of such reactions is urgent for both studying mechanisms of the chemical generation of excited states of the Ln^{3+*} ions and understanding the mechanism of action of catalysts based on the lanthanide complexes.

In the present work, we studied a possibility of generation of emitting electron-excited states of the lanthanide ions in the known[8,9] reaction of aniline (**1**) condensation with butyraldehyde (**2**) catalyzed by the $LnCl_3 \cdot 6H_2O$ complexes. We have earlier[8,9] found the catalytic effect of $LnCl_3 \cdot 6H_2O$ on this reaction.

Experimental

Complex $LnCl_3 \cdot 6H_2O$ (reagent grade) was used. Aniline (**1**, reagent grade) was purified by distillation *in vacuo* (70 °C, 10 Torr). Butyraldehyde (**2**, pure grade) and DMF (pure grade) were distilled above hydroquinone and BaO, respectively.[10] Condensation of compounds **1** and **2** was carried out in a glass CL cell (V = 20 mL) placed in a light-proof chamber of the CL setup. Dimethylformamide (7 mL) was added to the cell containing a weighed sample of $LnCl_3 \cdot 6H_2O$ (0.54 mmol), and stirring was switched on. After $LnCl_3 \cdot 6H_2O$ was completely dissolved, compound **1** (20 mmol) was loaded, and then compound **2** (44 mmol) was pressed out from the doser with an argon flow. Chemiluminescence was detected through the optically transparent bottom of the cell. After the reaction, the solution was analyzed for a content of the target product, *viz*., 3-ethyl-2-propylquinoline, according to earlier published procedures.[8,9]

The photoluminescence (PL) spectrum was recorded on an Aminco—Bowman spectrofluorimeter. The setup and CL measurement procedure have been described earlier.[11] The CL spec-

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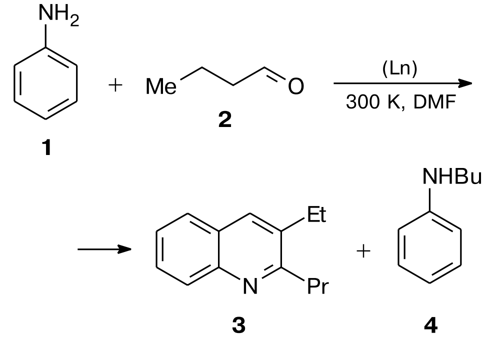
tra were detected using boundary light filters according to a known procedure[12] (for Ln = Eu, Ho) or with an MDR-23 monochromator (Ln = Tb).

Results and Discussion

It was found that on mixing compounds **1** and **2** in DMF in the presence of $LnCl_3 \cdot 6H_2O$ CL generates, which is observed with the unaided eye in the case of Ln = Eu and Tb, whereas the red and green emission (CL_1) is observed in a slightly darkened room. The CL_1 spectra coincide with the PL spectra of solutions of $TbCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ in DMF (Fig. 1). Thus, the CL_1 emitters are the excited ions Tb^{3+*} and Eu^{3+*}. The less pronounced CL_2 (Ln = Ho) is observed in a shorter-wavelength region at λ = 450—550 nm (see Fig. 1). The Ho^{3+*} ion cannot be a CL_2 emitter, because it has no PL in solutions,[13] *i.e.*, the CL_2 emitter is one of other participants of the condensation reaction, which proceeds[8,9] *via* Scheme 1.

Scheme 1



The major reaction product is 3-ethyl-2-propylquinoline (**3**), and *N*-butylaniline (**4**) is formed in minor amounts. The reaction occurs within 1—5 min,[8,9] which agrees with the steep fall (85—90% for ~1—3 min) shown by the kinetic CL curve (omitted). When the reaction occurs without the $LnCl_3 \cdot 6H_2O$ catalysts, the yield of quinoline is insignificant (≤5%) according to the GLC data, and the CL intensity is so weak that its spectrum cannot be measured even when using boundary light filters.

The PL spectrum of product **4** appears at 300—370 nm,[14] *i.e.*, compound **4** is not either the CL_2 emitter. Published data on the PL spectrum of product **3** are lacking. We also failed to detect the PL of product **3** (300, 77 K) because, most likely, of its very low intensity. At the same time, the PL spectrum of quinoline[15] is known (77 K), which contains phosphorescence (PS) and fluorescence maxima (see Fig. 1). It is seen that the PS of quinoline appears in the same spectral region as CL_2 and positions of two most intense maxima of the compared spectra are close. One of the difficulties in observation of the luminescence of compound **3** upon photoexcitation and its detection in the CL system is probably that of higher sensitivity of CL measurements due to the absence of the exciting light. The matter is that the low-intensity PL should be detected at the maximally open gap of the detecting monochromator, due to which the exciting light penetrates through the monochromator gap and thus disguises the weak PL. Note that similar situation is often met. For instance, the PS of benzophenone is not observed at room temperature,[16] whereas in the CL systems[17,18] it is easily detected at 300 K. Taking account into account the above facts, we believe that the most probable CL_2 emitter is the triplet-excited state of compound **3**, *i.e.*, $^3C_{14}H_{17}N^*$. Investigation of the mechanism of CL_2 excitation is the subject of our further studies.

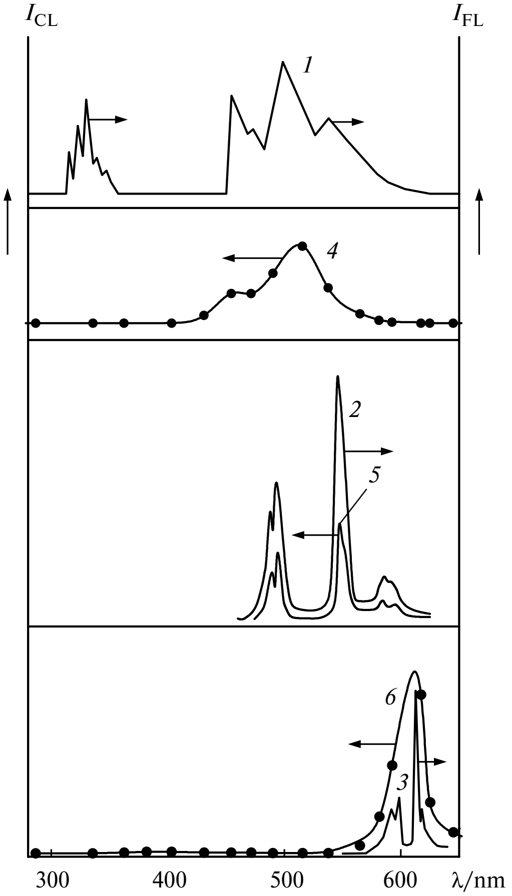
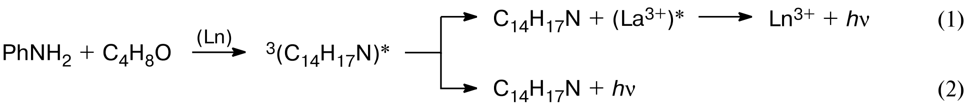


Fig. 1. Phosphorescence (*1—3*) and chemiluminescence (*4—6*) spectra for the reaction of aniline **1** (1.67 mol L^{-1}) and butyraldehyde **2** (3.67 mol L^{-1}) in DMF (300 K) in the presence of Ln^{3+} ($4.5 \cdot 10^{-2}$ mol L^{-1}): *1*, quinoline (77 K)[15]; *2*, $TbCl_3 \cdot 6H_2O$ ($4.5 \cdot 10^{-2}$ mol L^{-1}) in DMF (300 K), λ_{exc} = 313 nm; *3*, $EuCl_3 \cdot 6H_2O$ ($4.5 \cdot 10^{-2}$ mol L^{-1}) in DMF (300 K), λ_{exc} = 365 nm; *4*, CL_2 spectrum (Ln = Ho); *5*, CL_1 spectrum (Ln = Tb); *6*, CL_1 spectrum (Ln = En).

The condensation reaction is exothermic: the temperature of the reaction solution after mixing of the reactants increases from 300 to 343 K. The estimation of the thermal effect of the catalytic condensation by the posi-

Scheme 2



tion of the short-wavelength maximum in the CL_2 spectrum (400 nm) gives $\Delta H° \geq 3.1$ eV (71.5 kcal mol^{-1}).

The CL kinetic curves (Ln = Tb, Eu, and Ho) are recorded as narrow maxima, whose intensity (I_{max}/photon s^{-1} mL^{-1}) decreases in the series: Tb ($2.7 \cdot 10^{11}$) > Eu ($8 \cdot 10^8$) > Ho ($2 \cdot 10^8$). This sequence does not coincide with the row of catalytic activity found[8,9] for the lanthanide ions Tb ≈ Ho (95) > Eu (66) from the change in the yield of product **3** (in %). Analysis of these series shows that at the same level of catalytic activity of the Tb and Ho ions the brightness of CL_1 and CL_2 differs substantially, which is due to different luminescence intensities of the CL_1 (Tb^{3+*}) and CL_2 ($^3C_{14}H_{17}N^*$) emitters.

Based on the obtained results, we can propose a simplified scheme of CL_1 and CL_2 excitation (Scheme 2, Eqs (1) and (2), respectively).

Regardless of the Ln nature, the triplet-excited state $^3C_{14}H_{17}N^*$ is formed. Then $^3C_{14}H_{17}N^*$ is deactivated *via* two routes depending on the luminescence properties of Ln^{3+*}: *via* route (2) with PS emission (in the case of Ln = Ho) or *via* route (1) with energy transfer to the Ln^{3+} ions (Ln = Tb, Eu) to form Tb^{3+*} or Eu^{3+*} (CL_1 emitters). The absence of PS of product **3** in the CL_1 spectra confirms the fact of energy transfer from $^3C_{14}H_{17}N^*$ to the Tb^{3+} and Eu^{3+} ions. This is especially clear for Eu^{3+*}, whose luminescence spectrum contains no maxima in the PS region of product **3**.

Substantial differences between the known CL systems of decomposition of dioxetanes[1—5] and the CL reaction studied in this work should be mentioned in conclusion. The CL observed is generated in another type of the chemiluminescence catalytic reaction, namely, condensation, which exemplifies a highly efficient catalytic performance with the complete conversion of the substrates in the presence of catalytic amounts of the lanthanide compounds.

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