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On the Mechanism of the Chemiluminescent Condensation of Aniline with Butyraldehyde Catalyzed by $LnCl_3 \cdot 6H_2O$

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Abstract—The mechanism of the chemiluminescent condensation of aniline with butyraldehyde into 3-ethyl-2-propylquinoline catalyzed by $LnCl_3 \cdot 6H_2O$ (Ln = Tb, Ho) is reported. A likely scheme of the catalytic condensation of aniline with butyraldehyde has been developed by simulation of separate steps of the reaction using chemiluminescence and photoluminescence methods and quantum-chemical calculations of the heats of these steps.

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It was found earlier [1] that the condensation of aniline (**1**) with butyraldehyde (**2**) into 3-ethyl-2-propylquinoline (**3**) catalyzed by $LnCl_3 \cdot 6H_2O$ crystalline hydrates is accompanied by chemiluminescence (CL). Chemiluminescence is also observed in the absence of the crystalline hydrates. However, it is important that the yield of compound **3** and the CL brightness in the presence of the catalyst are much higher; i.e., the catalytic formation of **3** and CL are interrelated. The nature of the emitter of this CL depends on the nature of the lanthanide (Ln = Tb, Eu, or Ho). For the crystalline hydrates of Tb and Eu, the CL emitters are the excited ions Tb^{3+*} and Eu^{3+*}, respectively. They are presumably generated due to energy transfer from the triplet excited state of the final product **3** ($^3C_{14}H_{17}N^*$) [1]. In the case of the holmium crystalline hydrate, the CL emitter is $^3C_{14}H_{17}N^*$ because Ho^{3+} does not luminesce in solutions.

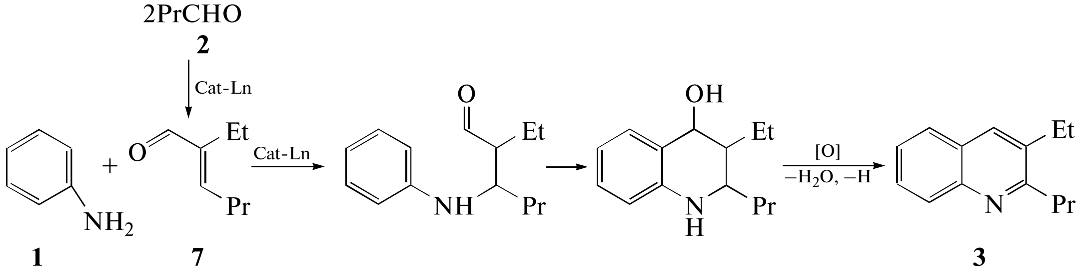
In this work, we simulated separate steps of the condensation of **1** with **2** catalyzed by $HoCl_3 \cdot 6H_2O$ and $TbCl_3 \cdot 6H_2O$ using luminescence techniques and quantum chemical calculations (AM1/RHF method) of the heats of possible steps of CL generation and suggested a probable mechanism for the formation of **3** in the ground and electron-excited states.

EXPERIMENTAL

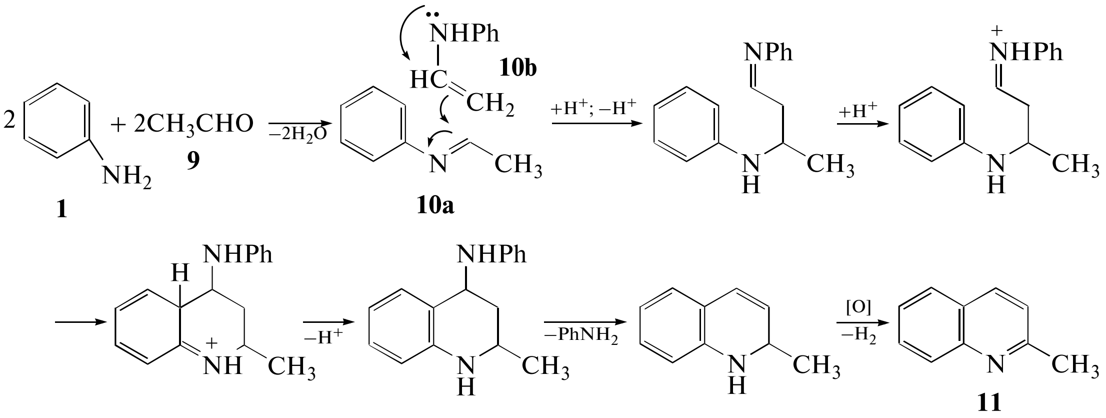
Crystalline hydrates were reagent grade. Other reagents and dimethylformamide (DMF) were high-purity grade. Amines **1** and 2,6-xylidine (**4**) were distilled in vacuo (10 Torr) at 70 and 91°C, respectively. Aldehyde **2** and benzaldehyde (**5**) were distilled from hydroquinone [2] under atmospheric pressure, and DMF was purified as described in [2] with subsequent distillation from BaO. 4-Anilino-3-[(phenylimino)methyl]heptane (**6**) was synthesized according to an earlier reported procedure [3]. A solution of the catalyst for the condensation of **1** with **2** was prepared by dissolving the crystalline hydrate (0.2 mmol) in DMF (3 ml) at room temperature.

The condensation of **1** with **2** was carried out in a 20-ml quartz cell equipped with a reflux condenser and a liquid inlet assembly. The cell, placed in a chemiluminescence chamber, was filled with a solution of the catalyst (3 ml) and compound **1** (10 mmol), and compound **2** (25 mmol) was charge into the liquid inlet device. The chamber was hermetically sealed, and compound **2** was forced into the cell with an Ar flow. The reaction was conducted under bubbling argon, and CL was measured simultaneously. The reactions of compounds **1** with **5** and **4** with **2** were carried out similarly. In the first case, compound **5** was placed in the liquid inlet device. In the second case, compound **4** was introduced into the cell instead of compound **1**. When the cyclization of compound **6** was studied, the cell contained a solution of **6** (5 mmol) in DMF (1.5 ml) and the liquid inlet device contained a solution of the crystalline hydrate (0.2 mmol) in DMF (1.5 ml).

The Ln^{3+} content was determined by titration with EDTA [4], and the water contents of the crystalline hydrate and reaction products were determined by the Fischer method [4]. The products of all condensation reactions were analyzed on a Carlo Erba GC 6000 chromatograph (column 3 m in length and 4 mm in diameter, PEG-6000 stationary liquid phase (15%) on Chromaton N-AW-DMCS) and a CHROM 5 chromatograph (column 3 m in length and 4 mm in diameter, SE-30 stationary liquid phase (5%) on Chromaton N-AW-HMDS). The elemental analysis of the $LnCl_3 \cdot 4DMF$ complex was carried out on a Carlo Erba 106 CHN analyzer. Photoluminescence (PL) spectra were recorded on an Aminko Bowman spec-



Scheme 1.



Scheme 2.

trofluorimeter. The lifetime of the terbium ion (τ Tb^{3+*}) was measured with an LGI-23 pulsed nitrogen laser ($\lambda_{exc} = 337$ nm, measurement error of 10%). The setup and procedure for CL measurements were described earlier [5]. CL spectra were recorded using cut-off light filters [6].

RESULTS AND DISCCUSION

There has been only one mechanistic study on reactions of aromatic amines with aldehydes catalyzed by metal complexes [7], in which a likely mechanism of the condensation of **1** with **2** into **3** catalyzed by the three-component system $LnCl_3$–Ph_3P–DMF (Cat-Ln) is discussed (Scheme 1).

According to Scheme 1, the first step of the reaction is the interaction of two molecules of **2** yielding 2-ethyl-2-hexenal (**7**), which then reacts with **1**. This mechanism is based on the known scheme of the condensation of **1** with acetaldehyde catalyzed by HCl [8] (omitted here), which is alternative to Scheme 2. Scheme 1 was confirmed [7] by the experiment in which product **3** was obtained by the condensation of **1** with **7** catalyzed by Cat-Ln (100°C, 6 h, ethanol, 84% yield). Unlike Selimov et al. [7], we studied the same reaction catalyzed by the crystalline hydrate and found that compound **7** was absent from the reaction products [1, 9]. We identified compound **3** (target product) and *N*-butylaniline (**8**) (<5%, by-product) as the products of condensation between **1** and **2**. We believe that the formation of **7** in the reaction catalyzed by Cat-Ln [7] and its absence in the reaction catalyzed by the crystalline hydrate [1, 9] are due to the fact that the synthesis condition in the former case (Cat-Ln, 100°C, 6 h) [7] are much more severs than were used in catalysis by the crystalline hydrate (20°C, <5 min) [1, 9]. This conclusion is confirmed by our experimental results obtained for solutions of **2** and the crystalline hydrate combined at 20 and 100°C. Product **7** forms only at 100°C (60% yield).

Based on the above results, we believe that the condensation of **1** with **2** catalyzed by the crystalline hydrate differs from Scheme 1 and the first step of this reaction is the formation of a Schiff base. Schiff bases form readily in reactions of aldehydes and primary amines even below room temperature [10].

The possibility of the direct interaction between **1** and **2** without the intermediate formation of the aldehyde dimer was confirmed by earlier works in which the mechanism of the condensation of **1** with acetaldehyde (**9**) catalyzed by HCl is presented [8, 11] (Scheme 2).

According to Scheme 2, the Schiff base *N*-ethylideneaniline forms in the first step. *N*-Ethylidene-

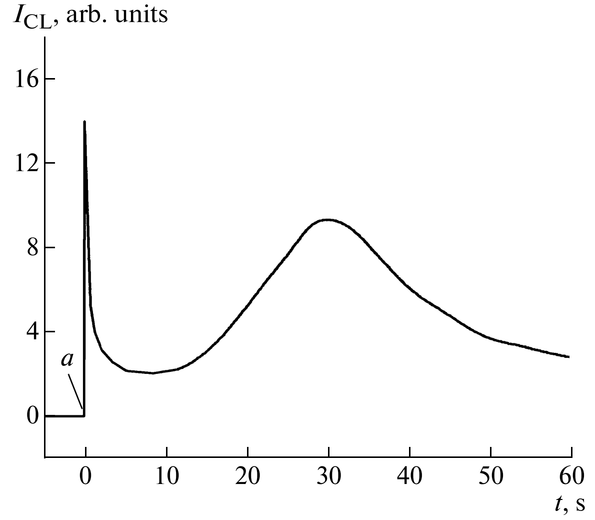


Fig. 1. Chemiluminescence kinetics in the reaction of aniline (10 mmol) with butyraldehyde (25 mmol) catalyzed by $\mathrm{HoCl_3 \cdot 6H_2O}$ (0.2 mmol) in DMF at 20°C. (*a*) The instant butyraldehyde was added.

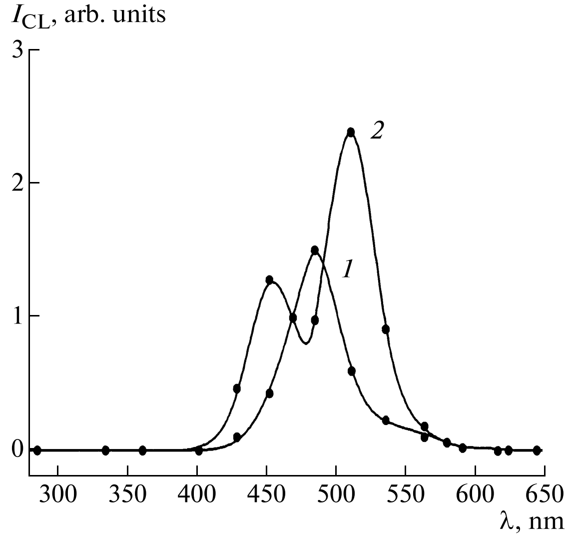


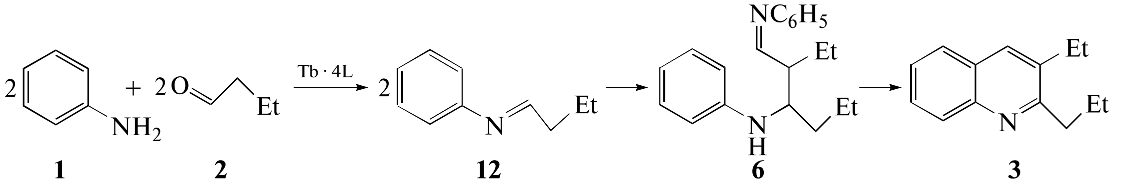
Fig. 2. Chemiluminescence spectra for the reaction of aniline (10 mmol) with butyraldehyde (25 mmol) catalyzed by $\mathrm{HoCl_3 \cdot 6H_2O}$ (0.2 mmol) in DMF at 20°C: (*1*) first and (*2*) second maxima (Fig. 1). The CL spectra were measured using a set of vut-off light filters.

aniline exists in solution in two forms, namely, the nucleophilic molecule of enamine (**10a**) and the electrophilic molecule of aldimine (**10b**). In 2-methylquinoline (**11**) formation, the quinoline ring results from the autocondensation of two Schiff base molecules and subsequent transformations as shown in Scheme 2. For this reason, we used Scheme 2 when selecting model reactions for identifying the light-emitting of the condensation of **1** with **2**.

Since the crystalline hydrate catalyst of the condensation of **1** with **2** is loaded into the reactor as a DMF solution, before simulation of the reactions it was interesting to identify the initial form of the lanthanide reacting with the other reactants. The dissolution of the crystalline hydrate in DMF produces colorless homogeneous solutions. It was found for $\mathrm{TbCl_3 \cdot 6H_2O}$ as an example that a syrupy liquid remains after the removal of DMF from these solutions. According to elemental analysis data and the Fischer determination of the water content, this liquid is the $\mathrm{TbCl_3 \cdot 4DMF}$ complex (**Tb · 4L**). The τ $\mathrm{Tb^{3+*}}$ value for the Tb · 4L complex (1300 μs) is larger than that for $\mathrm{TbCl_3 \cdot 6H_2O}$ (425 ± 40 μs). Based on data of other authors [12], we explain this by the removal of the water molecules, which are quenchers of $\mathrm{Tb^{3+}}$ photoluminescence, from the coordination sphere of the $\mathrm{Tb^{3+}}$ ion upon the dissolution of $\mathrm{TbCl_3 \cdot 6H_2O}$ in DMF. Thus, the lanthanide is involved in catalytic condensation in the form of the Tb · 4L complex.

When solutions of Tb · 4L are mixed with solutions of **1** in a ratio of 1 : 100, the PL of terbium (+3) is completely quenched, whereas at the 1 : 1 ratio the τ $\mathrm{Tb^{3+*}}$ value decreases from 1300 to 800 ± 80 μs. This suggests that a more complicated complex of Tb · 4L with **1** forms upon the addition of a solution of Tb · 4L to **1**.

In the present work, we also obtained new data on CL accompanying the catalytic condensation of **1** with **2**. Two maxima were found in the time dependence of the CL intensity in the reaction of **1** with **2** in DMF catalyzed by $\mathrm{HoCl_3 \cdot 6H_2O}$ (**$\mathrm{CL_1}$**): a narrow one ($I_{\mathrm{max}} = 6.0 \times 10^8$ photon $\mathrm{s^{-1}}$ $\mathrm{ml^{-1}}$) and a broad one ($I_{\mathrm{max}} = 8.0 \times 10^8$ photon $\mathrm{s^{-1}}$ $\mathrm{ml^{-1}}$) (Fig. 1). The $\mathrm{CL_I}$ spectrum in the time interval of the first maximum contains one diffuse peak at 490 nm, while that observed in the time interval of the second maximum shows peaks at 450 and 515 nm (Fig. 2). Therefore, two different CL emitters ($\mathrm{E_I^1}$ and $\mathrm{E_I^2}$) are generated in the reaction of **1** with **2** and they are responsible for the first and second CL peaks, respectively. The maxima in the $\mathrm{CL_I}$ spectrum caused by emission from $\mathrm{E_I^2}$ fall in the region where the known phosphorescence of quinoline is observed [13] (Fig. 2). The two strongest maxima in the $\mathrm{CL_I}$ spectrum (455 ± 25 and 512 ± 25 nm) and phosphorescence spectrum (455 and 500 nm) spectra are close together. This indicates that the $\mathrm{E_I^2}$ emitter is the triplet excited state of **3**. The other stable participants of the reaction, namely, **1**, **2**, and *N*-butylaniline (**8**), as well as the $\mathrm{Ho^{3+}}$ ion, do not luminesce in the spectral range of $\mathrm{CL_I}$ [14–16] and, hence, cannot be $\mathrm{CL_I}$ emitters such as $\mathrm{E_I^1}$ or $\mathrm{E_I^2}$. The $\mathrm{E_I^1}$ emitter is a labile intermediate of the condensation of **1** with **2** with a short lifetime. This is indicated by the initial



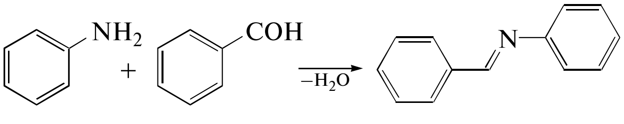
Scheme 3.

portion of the CL_1 curve, which is like a flash of light (Fig. 1). Since E_1^1 and E_1^2 emit in the same spectral range (Fig. 2), it can be assumed that they are similar in nature.

In order to identify E_1^1 and elucidate the mechanism of the formation of **3** in the ground and electronically excited states, the three possible steps of the synthesis of **3** were simulated and CL was sought and recorded (Scheme 3).

The simulation of the hypothetical steps of heterocyclization was complicated by the fast reaction of **1** with **2** catalyzed by Tb · 4L (<5 min at the 100% conversion of **1**) [1, 9]. This is likely due to the high instability of the intermediates. To solve this problem, simulation in two cases was carried out for compounds that are most similar in nature to the starting reactants and hypothetical intermediates and are converted into more stable products.

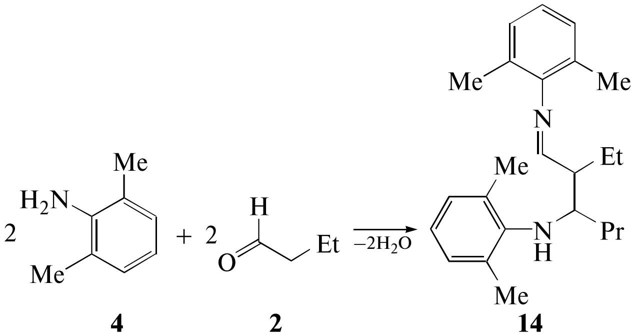
When studying the possibility of CL generation in the first step of the condensation of **1** with **2** (Scheme 3), which yields the Schiff base *N*-butylideneaniline (**12**), a compound readily undergoing further autocondensation [3], aldehyde **5** was taken instead of aldehyde **2**. In this case, stable Schiff base **13** forms as the final reaction product (Scheme 4).



Scheme 4.

It was found that the reaction between **1** and **5** catalyzed by Tb · 4L is not accompanied by CL. Since the Schiff bases **12** (Scheme 3) and **13** (Scheme 4) form via the formation of the same type of C=N bond and, hence, with similar heats of reaction, it can be inferred that the formation of Schiff base **12** via the reaction between **1** and **2** (Scheme 3) does not generate CL either.

Another possible CL-emitting step is the condensation of two molecules of Schiff base **12** into **6** (Scheme 3). To study the possibility of CL generation in this step, amine **4** was condensed with **2** in the presence of the crystalline hydrate catalyst (Scheme 5). Amine **4** was taken instead of **1** because this reaction (Scheme 5) yields stable compound **14**, whereas the reaction of **1** with **2** (Scheme 3) produces compound **6**, which undergoes further cyclization [17]. No CL was observed in the reaction represented by Scheme 5.

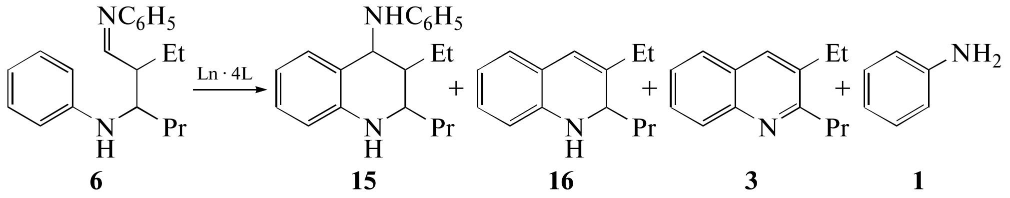


Scheme 5.

Therefore, the second step of the condensation of **1** with **2** (Scheme 3) is not accompanied by CL.

According to Scheme 3, product **3** results from the catalytic transformation of **6**. Intermediate **6** was obtained by an independent method [3], which made it possible to verify the possibility of its cyclization catalyzed by $TbCl_3 \cdot 6H_2O$ in DMF (Scheme 6). Compound **1**, **3**, 4-anilino-3-ethyl-2-propyl-1,2,3,4-tetrahydroquinoline (**15**), and 3-ethyl-2-propyl-1,2-dihydroquinoline (**16**) were identified as the cyclization products in 2 : 1 : 1 : 1 ratios (Scheme 6).

The cyclization of **6** is accompanied by CL (I_{max} = 5.4 × 10^8 photon s^{-1} ml^{-1}) (**CL_2**), whose kinetics (Fig. 3) is described by a curve with a broad maximum. The CL_2 spectrum (Fig. 3) coincides with the known spectrum of CL [1] recorde for the reaction of **1** with **2** catalyzed by $TbCl_3 \cdot 6H_2O$ and contains the luminescence maxima of Tb^{3+*} (490 and 540 nm). Therefore, the CL and CL_2 emitter is the Tb^{3+*} ion.



Scheme 6.

Thus, of the three simulated reactions, only the cyclization of **6** is accompanied by CL. This suggests that the CL appearing upon the condensation of **1** with **2** catalyzed by the crystalline hydrate, whose emitter is Tb^{3+*}, is due to the cyclization of **6** (Scheme 3).

According to earlier studies [8, 17, 18], the cyclization of **6** can proceed via two routes (Schemes 7, 8).

To see which of these reactions (Schemes 7, 8) is thermodynamically more favorable as a CL exciter, the heats of the reactions ($\boldsymbol{\Delta_r H^0}$) were calculated by the AM1/RHF method [19] (Hyperchem 5.0 program [20]) as the difference between the enthalpies of formation ($\boldsymbol{\Delta_f H^0}$) of the final products and the starting compounds for steps 1–4. The following $\Delta_r H^0$ values were obtained:

$$\Delta_r H_1^0 = \Delta_f H^0(\mathbf{17}) - \Delta_f H^0(\mathbf{6})$$

$$= 63.3 - 34.2 = 29.1 \text{ kcal/mol},$$

$$\Delta_r H_2^0 = \Delta_f H^0(\mathbf{16}) + \Delta_f H^0(\mathbf{1}) - \Delta_f H^0(\mathbf{17})$$

$$= 8.1 + 20.8 - 63.3 = -34.4 \text{ kcal/mol},$$

$$\Delta_r H_3^0 = \Delta_f H^0(\mathbf{15}) - \Delta_f H^0(\mathbf{6})$$

$$= 13.9 - 34.2 = -20.3 \text{ kcal/mol},$$

$$\Delta_r H_4^0 = \Delta_f H^0(\mathbf{16}) + \Delta_f H^0(\mathbf{1}) - \Delta_f H^0(\mathbf{15})$$

$$= 8.1 + 20.8 - 13.9 = 15.0 \text{ kcal/mol}.$$

Thus, the cyclization of **17** into **16** with the simultaneous elimination of **1** is the most exothermic reaction. This process is likely responsible for the appearance of CL upon the condensation of **1** with **2**. The energy E_{exc} necessary for the excitation of the E_1^{1*} emitter, as estimated from the position of the maximum ($\lambda_{max} \approx 490$ nm, 2.53 eV) in the CL_1 spectrum (Fig. 2, spectrum *1*), is ~60 kcal/mol. Since $E_{exc} = -\Delta_r H^0 + E_{act}$ (where E_{act} is the activation energy of the reaction) [21], the formation of excited compound **16** via Scheme 6 will be possible if E_{act} is not lower than 25.6 kcal/mol. Because there are no E_{act} data for this reaction in the literature, E_{act} was calculated from the known Polanyi equation $E_{act} = 0.32D - 26.9$ (where D is the bond dissociation energy) to be 28.6 kcal/mol. Therefore, $E_{exc} = 34.4 + 28.6 = 63.0$ kcal/mol, which is quite sufficient for the excitation of intermediate **16** via Scheme 7 (step 2). Another product of this reaction is aniline, which cannot be the CL_1 emitter, because, according to spectroscopic data [14, 15], the generation of its singlet and triplet states requires E_S = 95 kcal/mol and E_T = 76 kcal/mol, respectively, which is higher than E_{exc}.

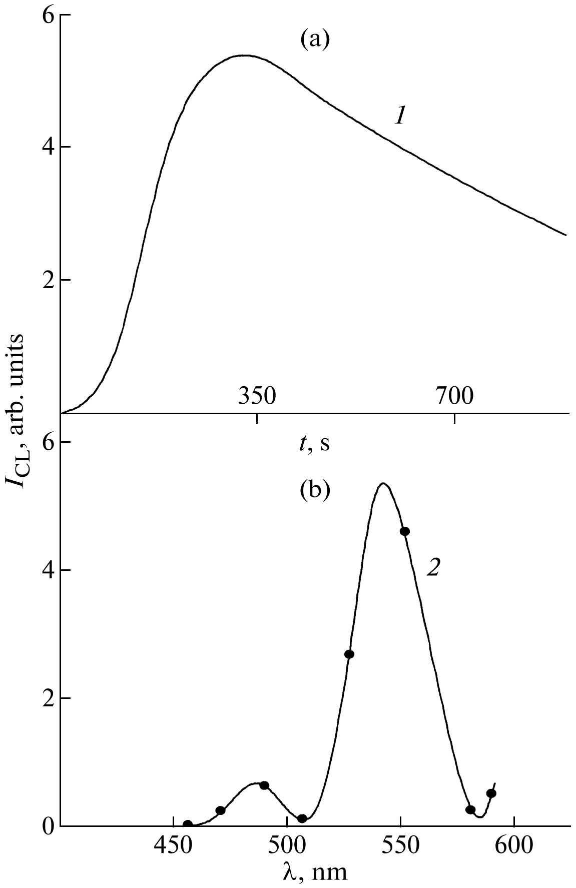
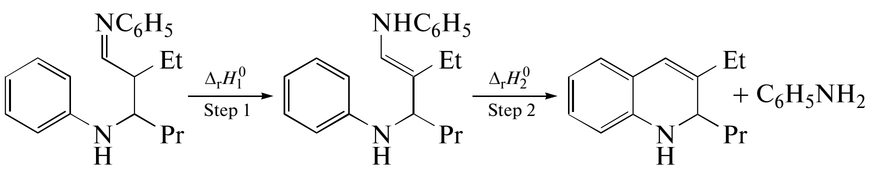
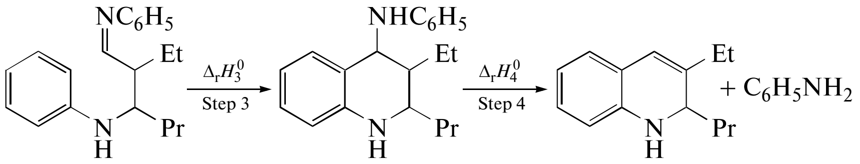


Fig. 3. Chemiluminescence (a) kinetics and (b) spectra for the cyclization of compound **6** catalyzed by $TbCl_3 \cdot 6H_2O$ in DMF. The CL spectra were measured using a set of cutoff light filters.



6 **17** **16** **1**

Scheme 7.



6 **15** **16** **1**

Scheme 8.

Based on the obtained results, we suggest the following simplified scheme of CL_1 excitation in the condensation of **1** with **2** catalyzed by the crystalline hydrate:

$$C_6H_5NH_2 + C_4H_8O \xrightarrow{Ln \cdot 4L} {}^3E_1^{1*}, \qquad (I)$$

$${}^3E_1^{1*} \rightarrow E_1^1 + h\nu_1, \qquad (II)$$

$${}^3E_1^{1*} + E_1^2 \rightarrow E_1^1 + {}^3E_1^{2*} \rightarrow E_1^2 + h\nu_2, \qquad (III)$$

$${}^3E_1^{1*} + Tb^{3+} \rightarrow E_1^1 + Tb^{3+*} \rightarrow Tb^{3+} + h\nu_3, \qquad (IV)$$

where $Ln \cdot 4L = LnCl_3 \cdot 4DMF$ (Ln = Tb, Ho),

E_1^1 is 3-ethyl-2-propyl-1,2-dihydroquinoline,

and E_1^2 is 3-ethyl-2-propylquinoline.

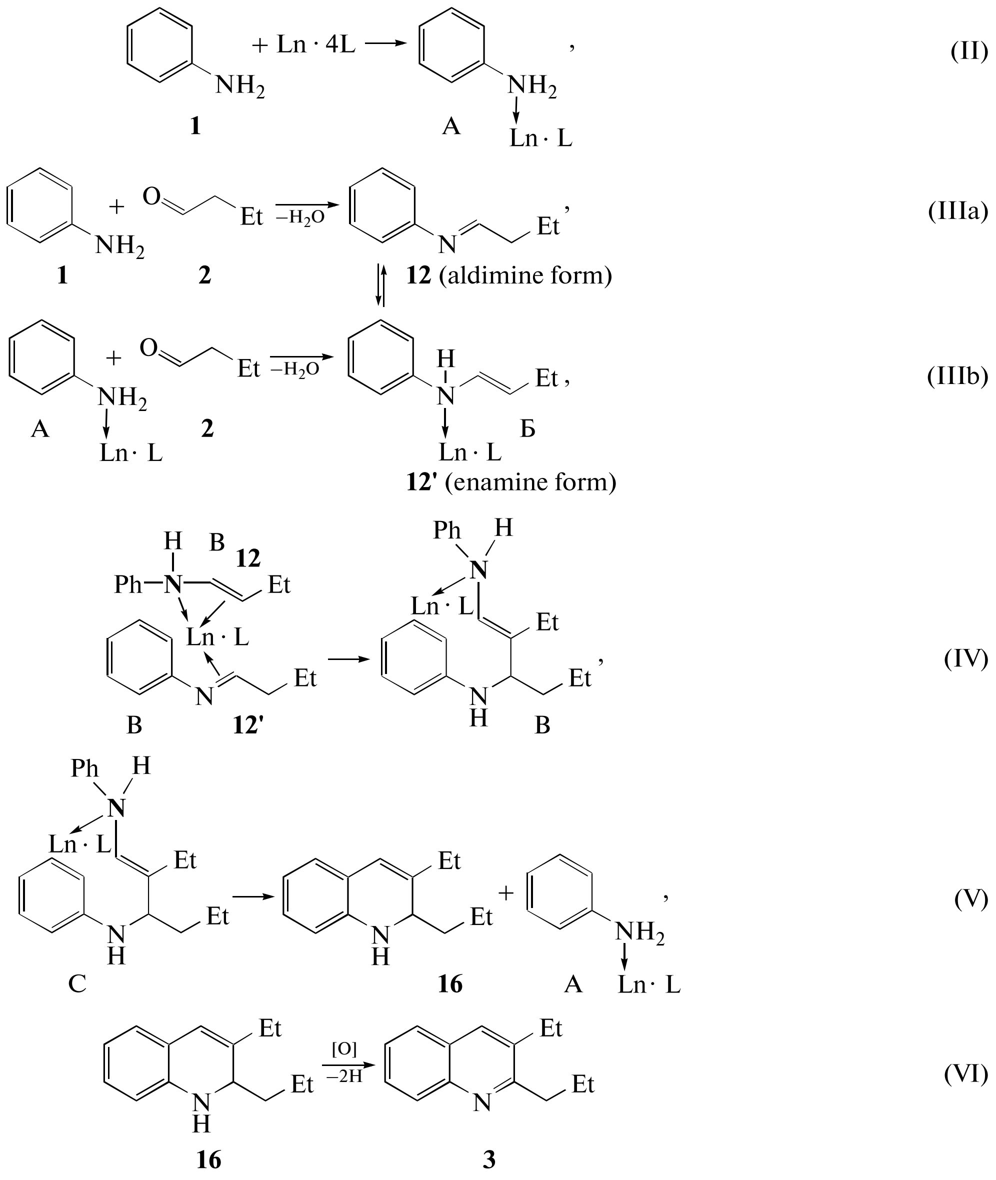
Scheme 9.

In this scheme, the first step is the formation of the triplet excited molecule ${}^3E_1^{1*}$ (I), which is then deactivated, in a way depending on the nature of the crystalline hydrate catalyst. When the crystalline hydrate is $HoCl_3 \cdot 6H_2O$, phosphorescence (II) is observed and energy is transferred to E_1^2 to bring it into the triplet excited state, which is also deactivated with phosphorescence emission (III). For the Tb crystalline hydrate, energy transfer to the Tb^{3+} ion brings it into the emitting excited state (reaction (IV)). Energy transfer from ${}^3E_1^{1*}$ to E_1^2 (product **3**) is confirmed by the high intensity of the first CL peak in the condensation of **1** with **2** (catalyzed by $HoCl_3 \cdot 6H_2O$) in the presence of **3** synthesized separately and introduced into the system before the reaction. In this case, the CL spectrum observed in the region of the first maximum is due to emission from ${}^3E_1^{2*}$. Thus, we found that the Ln^{3+} ion accepts energy from intermediate **16** rather than product **3** (as was assumed earlier [1]).

The above results of the simulation of possible chemiluminescent steps of the condensation of **1** with **2** catalyzed by the crystalline hydrate suggest the following probable mechanism for the formation of **3** (Scheme 10).

The dissolution of the crystalline hydrate catalyst in DMF (I) produces the $LnCl_3 \cdot 4DMF$ complex (τ Tb^{3+*} = 1300 ± 130 μs), which forms complex **A** (τ Tb^{3+*} = 800 ± 80 μs) with a small proportion of molecules **1** via reaction (II). The major portion of **1** is in free and reacts with **2** via reaction (IIIa) to form a Schiff base in the aldimine form (**12**). Complex **A** reacts with **2** via reaction (IIIb) to form the Schiff base in the enamine form (**12'**) as a component of complex **B**. The two forms of Schiff bases **12** and **12'** in complex **B** react via reaction (IV) yielding compound **17** (Scheme 7), which is bound with Ln into complex **C**. Next, complex **C** simultaneously undergoes cyclization and elimination via reaction (V) to evolve a rather large amount of energy (~64 kcal/mol), As a result, compound **17** is formed in the ground and excited states (CL emitter E_1^2) and complex **A** is formed, which starts a new catalytic cycle. The oxidative con-

$$\mathrm{LnCl_3 \cdot 6H_2O} + x\mathrm{DMF} \rightarrow \mathrm{LnCl_3 \cdot 4DMF} + \mathrm{6(H_2O) \cdot (DMF)_m} + (x - 6m)\mathrm{DMF} \qquad \text{(I)}$$



where Ln · L = Ln · xDMF (Ln = Tb, Ho; $x \leq 4$).

Scheme 10.

version of **17** into the target product **3** via reaction (VI) is possible due to the presence of the following oxidizers in the reaction system: dissolved oxygen, compound **12**, and excess compound **2**.

CONCLUSIONS

The simulation of separate steps of the reaction using the chemiluminescence and photoluminescence methods and thermodynamic calculations allowed us to suggest a probable scheme for the formation of 3-ethyl-2-propylquinoline in the condensation of aniline with butyraldehyde catalyzed by $\mathrm{LnCl_3 \cdot 6H_2O}$.

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