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# Reactions of Lanthanide Acetylacetonates with Triethylaluminum

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**Abstract**—The reactions of lanthanide acetylacetonates $Ln(acac)_3 \cdot H_2O$ (Ln = Nd, Tb, Ho, Lu) with $Et_3Al$ in toluene were studied by spectral methods (photoluminescence; taumetry; NMR, IR, and UV–vis spectroscopy) using GLC, volumetry, and chemical analysis.

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## INTRODUCTION

Systems based on transition metal acetylacetonates (TMAA) and organoaluminum compounds (OAC) are widely used in the catalysis of chemical reactions of different types [1, 2]. The reaction products and the mechanisms of formation of catalytic complexes in these systems are well studied for Ti, Ni, Co, Fe, Cr, and Pd compounds [3–8]. At the same time, data on reactions of lanthanide acetylacetonates $Ln(acac)_3 \cdot xH_2O$ (LAA) with OAC are lacking, although investigation of LAA–OAC systems is essential both for gaining a deeper insight into the Ziegler–Natta catalysts and for studying the reactivity of lanthanide complexes.

In this work, we studied, for the first time, the reactions of $Ln(acac)_3 \cdot H_2O$ (Ln = Nd, Tb, Ho, Lu) with triethylaluminum (TEA) using a wide range of physicochemical methods, including luminescence. The efficiency of the latter in studying the synthesis and effects of Ziegler–Natta lanthanide catalysts was shown in earlier works [9–11]. Nd, Tb, Ho, and Lu lanthanides were chosen from the lanthanide series for the following reasons. The absorption spectra of the Nd and Ho complexes contain bands due to supersensitive transitions, whose parameters are highly sensitive to changes in the coordination environment of the lanthanide [12]. The Lu complex has the highest solubility in aromatic solvents, and its $^1H$ NMR spectra are very informative [13]. The Tb complex is characterized by bright photoluminescence (PL) [12].

## EXPERIMENTAL

Lanthanide acetylacetonates were synthesized and recrystallized according to a known procedure [14]. A commercial gasoline solution of TEA (95%) was distilled in vacuo [15] (according to $^1H$ NMR data, the alkoxyaluminum derivative content was <1%). Butadiene (99.8%) was purified according to a standard procedure [9]. Tetraethylaluminoxane $(Et_2Al)_2O$ was synthesized according to [16]. The solvents (toluene and benzene) were purified [17] by distillation from sodium metal. Argon was passed through a Poglotitel Gazov gas purifier.

The reactions of LAA with TEA were carried out at 20°C under an argon atmosphere in a temperature-controlled glass reactor fitted with a magnetic stirrer and attached to a gas burette for measuring the volume of the gas evolved. The reactor was charged with LAA (0.04 mmol) and toluene (10 ml), the mixture was stirred until the complete dissolution of LAA, and TEA was added (TEA/LAA = 2–10). The reaction was performed until the gas stopped evolving, and the resulting solution was subjected to spectral analysis. IR and UV–vis absorption spectra, $^1H$ NMR and PL spectra, and the $Tb^{3+*}$ ion lifetime ($\tau$) were recorded using sealed quartz cells or tubes under an Ar atmosphere.

Butadiene was dimerized with the LAA–TEA system in a steel autoclave ($V = 17$ cm$^3$). The autoclave cooled to 5°C was sequentially loaded with LAA (0.03 mmol), toluene (3 ml), butadiene (120 mmol), and TEA (TEA/Ln = 6–12). The reaction was carried out under continuous stirring at $T = 80$–120°C for 3 h. Next, the reaction mixture was cooled down and decomposed with a 10% HCl solution. The organic phase was analyzed by GLC.

The coordinated water content of LAA was determined by the Fischer method [18]. Ethane and 4-vinylcyclohexene (VCH) were analyzed on a Carlo Erba GC 6000 chromatograph (3 m × 4 mm column, poly(ethylene glycol) 6000, 15% on Chromatone for ethane; 3 m × 3 mm column, 15% Apiezon L on Chromaton N-AW-DMCS for VCH). Absorption spectra in the IR and UV–vis regions were recorded on Specord 75IR and Specord M40 spectrophotometers. $^1H$ NMR spectra were obtained on a JEOL FX-90Q spectrometer, and PL spectra were recorded on an Aminco Bowman spectrofluorimeter. The $\tau(Tb^{3+*})$ value was measured using a taumetric unit including an LGI-21 pulsed nitrogen

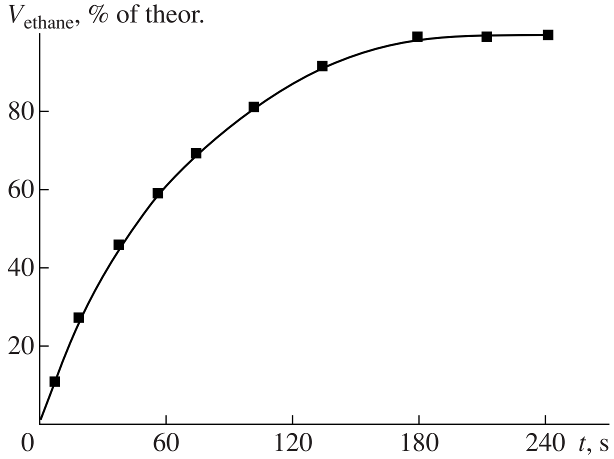


**Fig. 1.** Kinetics of ethane evolution in the reaction of $Ho(acac)_3 \cdot H_2O$ with $Et_3Al$ in toluene at [Ho] = $4 \times 10^{-3}$ mol/l, Al/Ln = 6, and $T = 20°C$.

laser ($\lambda_{\text{exc}} = 337$ nm; the measurement error and lower measurement limit are 10% and 10 μs, respectively).

## RESULTS AND DISCUSSION

**Volumetric data.** The addition of TEA to LAA solutions in toluene (20°C) is accompanied by gas evolution (Fig. 1). According to the results of analyses of the liquid and gas phases, the gas was ethane. The formation rate and amount of evolved EtH are independent of the lanthanide nature. At Al/Ln = 2–10, the amount of EtH corresponds to the stoichiometry of the equation

$$H_2O + 2Et_3Al \longrightarrow (Et_2Al)_2O + 2EtH.$$

The evolution of EtH ceases in ~3–8 min, which is much sooner than in the known heterogeneous reaction of the $LnCl_3 \cdot 6H_2O$ crystalline hydrates with TEA (>2 h) [9, 19].

**IR spectra.** The IR spectra of the LAA–TEA system were studied for the Lu complex as an example, which is the most soluble in benzene ([Lu] = $10^{-2}$ mol/l). The spectrum of $Lu(acac)_3 \cdot H_2O$ contains the following absorption bands ($cm^{-1}$): 1602 ν(C=O); 1518 ν(C=C); 915, 1020 ν(C–C + C=O); 1382, 1187, 1068, 1014, 1260 ν(C–H + C–C); 789, 766, 749, 722, 646 ν(Ln–O); 422, 529, 551 ($\nu_{\text{ring}}$); 3250–3500 ν(OH). They correlate well with the known spectra of LAA [20, 21]. After TEA was added (Al/Ln = 2), the following changes occurred in the spectra. Two less intense bands appear at 1595 and 1589 $cm^{-1}$ instead of the absorption band at 1602 $cm^{-1}$, and the absorption bands at 1020 and 915 $cm^{-1}$ undergo low-frequency shifts to 985 and 890 $cm^{-1}$, respectively. The diffuse band due to the stretching vibrations of the OH groups (3250–3500 $cm^{-1}$) disappears. In addition, new absorption bands appear at 735 and 790–815 $cm^{-1}$(Al–O–Al) and at 480, 545, and 654 $cm^{-1}$ (Al–C). Based on published data [22], they can be assigned to aluminoxane $(Et_2Al)_2O$, which is the reaction product of water of crystallization in LAA with TEA. Spectra for Al/Ln > 2 were not recorded.

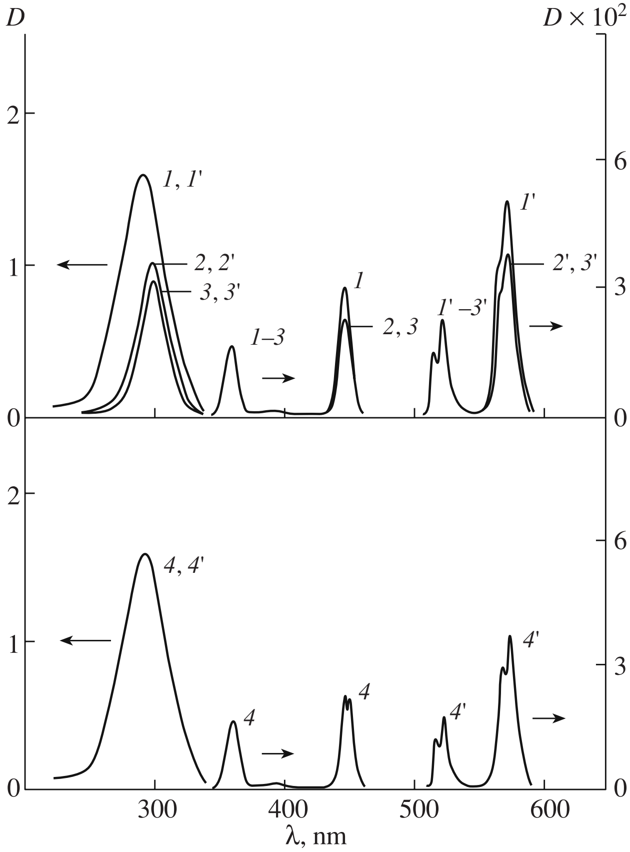


**Fig. 2.** Absorption spectra of solutions: (*1*, *1'*) $Ln(acac)_3 \cdot H_2O$ complexes and (*2*, *2'*–*4*, *4'*) $Ln(acac)_3 \cdot H_2O–Et_3Al$ system at Al/Ln = (*2*, *2'*) 2 and (*3*, *3'*) 6, (*4*, *4'*) after the action of $O_2$ on the reaction products in the $Ln(acac)_3 \cdot H_2O–Et_3Al$ system at Al/Ln = 6. Ln = (*1*–*4*) Ho and (*1'* –*4'*) Nd ([Ln] = $4 \times 10^{-3}$ mol/l, $T = 20°C$, toluene as solvent).

**UV–vis spectra.** The spectra of the LAA complexes in toluene (Fig. 2) have a diffuse maximum at 293 ± 0.5 nm (ε = 40000 l $mol^{-1}$ $cm^{-1}$), whose position is independent of the Ln nature and coincides with an earlier reported spectrum [14]. This maximum is due to the intraligand $\pi \longrightarrow \pi^*$ transition in the carbonyl group [14, 23]. In the case of Ho and Nd, the spectrum contains, in addition to the maximum at 293 nm, narrow lanthanide *f–f* absorption maxima at 361 and 452 nm ($^5I_8 \longrightarrow {}^3G_6$, $^5I_8 \longrightarrow {}^5G_6$) and at 522 and 575 nm ($^4I_{9/2} \longrightarrow {}^{2,4}G_{7/2,\,5/2}$, $^4I_{9/2} \longrightarrow {}^4G_{7/2}$), respectively. The maxima at 452 (Ho) and 575 (Nd) nm are due to supersensitive transitions [12]. The shorter wavelength *f–f* maxima of Ho and Nd are disguised by the absorption of toluene. The addition of TEA to solutions of LAA (Al/Ln = 2) results in the shift of the maximum at 293 nm to 300 nm (ε = 25500 l $mol^{-1}$ $cm^{-1}$) and in a decrease in its intensity. At Al/Ln = 2–6, the position of the maximum at 300 nm remains unchanged and its intensity decreases ($\varepsilon = 22\,500$ l mol$^{-1}$ cm$^{-1}$ for Al/Ln = 6). No other changes occur in the spectrum at Al/Ln > 6. The oscillator forces of the transitions responsible for the supersensitive transition peaks decrease for both Ho and Nd by ~25%, and the peak positions remain unchanged (Fig. 2).

The absorption spectra change substantially (Fig. 2) upon $O_2$ bubbling through the solutions resulting from the reaction of LAA with TEA (Al/Ln = 2). For instance, the peak at 300 nm returns to its initial position (293 nm), as in the spectrum of LAA before the addition of TEA, and the peaks of the supersensitive transitions at 452 (Ho) and 574 (Nd) nm are split into peaks at 449 and 453 and at 570 and 576 nm, respectively.

**PL spectra and $\tau(Tb^{3+*})$.** The PL spectrum of a toluene solution of $Tb(acac)_3 \cdot H_2O$ (not presented) contains peaks at 491 ($^5D_4$–$^7F_6$), 545, 548 ($^5D_4$–$^7F_5$), and 584 ($^5D_4$–$^7F_4$) nm characteristic of $Tb^{3+*}$ [12]. The $\tau(Tb^{3+*})$ value in toluene measured by us for $Tb(acac)_3 \cdot H_2O$ (740 μs) and the same quantity reported for $Tb(acac)_3 \cdot 3H_2O$ (730 μs) [24] coincide within the measurement error. When TEA is added (Al/Tb = 2), the PL intensity of the $Tb(acac)_3 \cdot H_2O$ complex decreases without changes in peak positions in the PL spectrum. The $\tau(Tb^{3+*})$ value decreases to 150 μs (Fig. 3). The subsequent addition of TEA results in an insignificant (~7%) decrease in the PL intensity and $\tau(Tb^{3+*})$ within the Al/Ln range from 2 to 6, and a further increase in the metal ratio (Al/Ln > 6) does not change the PL intensity and $\tau(Tb^{3+*})$.

After $O_2$ bubbling through the solution resulting from the interaction in the $Tb(acac)_3 \cdot H_2O$–TEA system (Al/Ln = 2), the PL intensity and $\tau(Tb^{3+*})$ increase to the levels characteristic of the initial $Tb(acac)_3 \cdot H_2O$ complex.

**$^1$H NMR spectra.** The reactions of LAA with TEA were studied by NMR spectroscopy using the diamagnetic complex $Lu(acac)_3 \cdot H_2O$ as an example. Note that NMR data for LAA are lacking: there has been only a single relevant publication [13], although lanthanide β-diketonates are widely used in NMR spectroscopy as shift reagents [25]. This is because of the low solubility of LAA and the broadening of the $^1$H NMR signals even at room temperature [13]. The $^1$H NMR spectra of the initial reactants in $C_7D_8$ contain the following signals, δ, ppm: $Lu(acac)_3 \cdot H_2O$ 1.80, 1.93 (s, 6H, $CH_3$), 5.30 (s, 3H, CH); TEA 0.28 (q, 2H, $CH_2$, $^3J = 8$ Hz), 1.09 (t, 3H, $CH_3$, $^3J = 8$ Hz). After the addition of TEA (Al/Lu = 2), the broadened signal of the methinic proton of the acac ligand at 5.30 ppm shifts to 5.40 ppm (without changing its half-width) and one signal at 1.80 ppm remains of the two methyl proton signals at 1.80 and 1.93 ppm. In addition, the spectrum exhibits the following signals from aluminoxane, δ, ppm: 0.30 (q, 2H, $CH_2$, $^3J = 8$ Hz) and 1.10 ppm (t, 3H, $CH_3$, $^3J = 8$ Hz), which are virtually the same as the signals of TEA [26].

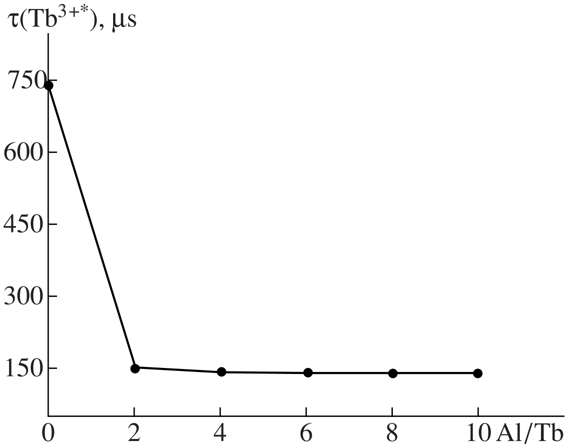


**Fig. 3.** Plot of $\tau(Tb^{3+*})$ versus the $Et_3Al$ content for a toluene solution of $Tb(acac)_3 \cdot H_2O$ at $[Tb] = 4 \times 10^{-3}$ mol/l and $T = 20$°C.

**Butadiene dimerization.** We studied the conversion of butadiene under the action of LAA–TEA systems. As can be seen from the table, the LAA–TEA systems manifest some catalytic activity in butadiene dimerization (butadiene conversion of ≤6%).

## RESULTS AND DISCUSSION

The anhydrous LAA complexes and the complexes containing one to three water molecules were described earlier [23, 27]. According to our analysis (Fischer method), the LAAs contain one $H_2O$ molecule. We believe that, in the initial solutions, LAA ($[Ln] = 4 \times 10^{-3}$ mol/l) exists as the dimer $[Ln(acac)_3 \cdot H_2O]_2$, because such dimers are known to be formed in aromatic solvents even at lower LAA concentrations ($[Ln] \geq 10^{-3}$ mol/l) [13, 28–31]. The results of volumetric analysis and IR spectroscopic data indicate that alu-

Dimerization and trimerization of butadiene in toluene by the LAA–TEA and $Ni(acac)_2$–TEA catalytic systems, respectively

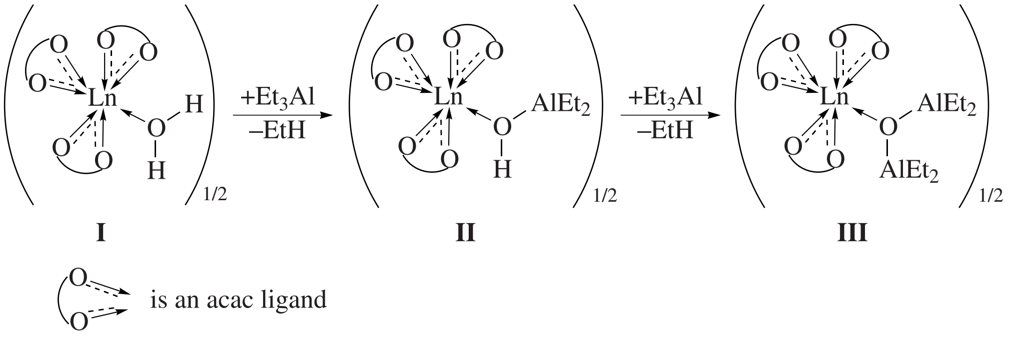
| Ln | $T$, °C | Butadiene conversion, % | Product |
|---|---|---|---|
| Tb | 80 | 5 | VCH |
| Tb | 100 | 6 | VCH |
| Tb | 120 | 6 | VCH |
| Nd | 80 | 4 | VCH |
| Pr | 80 | 6 | VCH |
| Ho | 80 | 6 | VCH |
| Ni* | 35 | 100 | Cyclododecatrienes |

Note: Al/Ln = 3.
The yield of VCH and the total yield of cyclododecatrienes are 100%.
* According to published data [40].

minoxane and ethane are the reaction products in the LAA–TEA system at any Al/Ln ratio. The UV-vis and IR absorption and $^1$H NMR spectra show that $Et_2Al(acac)$, which was previously identified in the reactions of TMAA with TEA [3–8], does not form in the LAA–TEA system. We observed no absorption maxima or NMR signals characteristic of $Et_2Al(acac)$ [3–8] (UV: $\lambda_{max} = 314$ nm; IR: 1585, 1530, 1408, 1380, 1295, 1218, 1187, 485 cm$^{-1}$; $^1$H NMR: acac 4.95 (s, 1H, CH) and 1.61 (s, 6H, $CH_3$), Et 0.53 (q, 2H, $CH_2$, $^1J$ = 8.24 Hz) and 1.54 (t, 3H, $CH_3$, $^1J$ = 8.24 Hz)). The analysis of the PL spectra shows that the oxidation state of the $Ln^{3+}$ ion remains unchanged. Luminescence measurements also suggest that the bonds of all three acac ligands with the lanthanide are retained after the interaction in the LAA–TEA system. This is indicated by the restoration of the initial PL intensity and $\tau(Tb^{3+*})$ value as a result of the action of oxygen on the solutions resulting from the interaction in the $Tb(acac)_3 \cdot H_2O$–TEA system. Taking into account the aforesaid and the known ability of OAC to react actively with the water of crystallization of lanthanide salts [9, 11, 19], the interaction between LAA and TEA can be described by the empirical reaction

$$[Ln(acac)_3 \cdot H_2O]_2 + nEt_3Al \longrightarrow [Ln(acac)_3]_2 + 2(Et_2Al)_2O + 4EtH + (n-4)Et_3Al. \qquad (I)$$

Free water is known to react with TEA ($Al/H_2O = 2$) in toluene in two steps: the first step yields $HOAlEt_2$, which then reacts with the second TEA molecule to give aluminoxane [32, 33]. This suggests that reaction (I) proceeds according to the following scheme:



**Scheme**

Half of the LAA dimer is shown in simplified form as structure **I** in the scheme. The attack of the first TEA molecule on the coordination water of LAA results in the formation of ethane and an intermediate hydroxyl-containing adduct (structure **II**) in which the coordination between the lanthanide and the oxygen atom is retained (before the reaction of the oxygen atom belonging to the water molecule). The reaction of this adduct with the second TEA molecule affords a complex (structure **III**) in which the oxygen atom of aluminoxane is coordinated to the lanthanide. The complete removal of water molecules from the coordination sphere of the lanthanide is confirmed by the amount of EtH evolved in the reaction (2 mol per mole of LAA) and by the disappearance of the IR absorption bands due to $H_2O$.

The alternative reaction mechanism involving the formation of individual products (anhydrous dimer $[Ln(acac)_3]_2$ and aluminoxane) seems improbable for the following reasons. Firstly, the dehydration of LAA upon interaction with TEA results in a shift of the acac ligand peak from 293 to 300 nm, whereas the absorption peak of the anhydrous $Ho(acac)_3$ complex [27] occurs at shorter wavelengths than the $Ho(acac)_3 \cdot H_2O$ peak [23]. The maximum at 300 nm cannot be due to aluminoxane, because the latter does not absorb at 280–500 nm. Secondly, the dehydration of $[Tb(acac)_3 \cdot H_2O]_2$ with the formation of anhydrous $[Tb(acac)_3]_2$ cannot be responsible for the observed marked change of $\tau(Tb^{3+*})$ from 740 to 150 μs, because the $\tau(Tb^{3+*})$ values for $Ln(acac)_3 \cdot 3H_2O$ and $Ln(acac)_3 \cdot H_2O$ in toluene are nearly identical (730 and 740 μs). Therefore, it is improbable that the removal of one more water molecule can be the cause of this dramatic (fivefold) shortening of the lifetime of $Tb^{3+*}$ coordinated with several ligand (acac) molecules, which determine the luminescence properties of the $Tb^{3+}$ ion. The sharp decrease in the PL intensity and $\tau(Tb^{3+*})$ observed upon the addition of TEA to LAA (at Al/Ln = 2) can be due to the dynamic quenching of $Tb^{3+*}$ by aluminoxane. However, if this were the case, these parameters would also decrease substantially at Al/Ln > 2. In fact, no decrease of these parameters is observed experimentally (Fig. 3).

The formation of an LAA complex with aluminoxane seems to be quite likely in the light of the known ability of lanthanides [34] and aluminoxane aluminum [15] to coordinate with oxygen atoms of compounds of various classes. In addition, the formation of similar complexes was discussed in a report devoted to diene polymerization in the presence of the $NdCl_3 \cdot 3TBP$–$(iso\text{-}Bu_2Al)_2O$ system [35]. Two possible bridged structures of the complexes are suggested. The first has a bond between the lanthanide and the aluminoxane oxygen atom. In the second structure, the lanthanide is bonded with the carbon atom of the isobutyl moiety.

At this stage of investigation, the results obtained do not allow us to describe unambiguously the structure of the LAA complex with aluminoxane formed in the LAA–TEA system. In addition to the compound with structure **III**, complexes of other types, including those with Ln–C units, can be the final reaction product in the LAA–TEA system. This conclusion is confirmed by the following arguments. The sharp decrease in the PL intensity and $\tau(Tb^{3+*})$ was observed earlier [9, 11] to result from the formation of Tb–C–Al units (where C is the carbon atom of *iso*-$Bu_3Al$) in the reaction of $TbCl_3 \cdot 3TBP$ (where TBP is $(C_4H_9O)_3PO$) with *iso*-$Bu_3Al$. By contrast, the organic terbium complexes containing Tb–O bonds (acac as the ligand) are characterized by rather high PL intensity and large $\tau(Tb^{3+*})$ values [11, 12, 36]. Furthermore, upon the action of oxygen on the reaction products of the $TbCl_3 \cdot 3TBP$–*iso*-$Bu_3Al$ system, the PL intensity and $\tau(Tb^{3+*})$ increased, as in our case. When oxygen interacts with the reaction products of the LAA–TEA system, aluminoxane is oxidized due to oxygen insertion into the reactive Al–Et bond to form $(EtO)_2AlOAl(OEt)_2$. In the case of a product having Ln–C units, this is accompanied by oxygen attacking the even more reactive bond Ln–Et [25]. We believe that the restoration of the PL intensity and $\tau(Tb^{3+*})$ under the action of oxygen is caused just by the transformation of the Ln–Et bond into an Ln–OEt bond. The alternative interpretation of this effect in terms of Al–Et bond oxidation yielding only $(EtO)_2AlOAl(OEt)_2$ seems improbable because this compound exerts no effect on the PL intensity or $\tau(Tb^{3+*})$. This was established experimentally by adding, to LAA, the alkoxide $(EtO)_2AlOAl(OEt)_2$ synthesized by an independent method [15].

The results of our study indicate several significant distinctions between the reactions of TEA with LAA and TMAA. Firstly, no lanthanide is reduced by TEA in the LAA–TEA system. If this reduction had taken place, it would have easily been detected owing to the substantial absorption and PL spectral differences between the trivalent and divalent lanthanides [12]. By contrast, in the reactions of TMAA with TEA the metals are reduced to the zero-valence state. Secondly, upon the action of TEA on LAA, the acac ligands remain in the coordination sphere of the lanthanide, whereas TMAA loses one or even all acac ligands to form $Et_2Al(acac)$ or $Al(acac)_3$ [3–8]. Thirdly, EtH is the only gaseous product of the reactions of LAA with TEA, and the amount of EtH (2 mol) is independent of the Al/Ln ratio. In the case of TMAA, a wide variety of gaseous products is formed (hydrogen, ethylene, ethane, *cis*- and *trans*-but-2-enes, but-1-ene, and butane), whose yields depend on the Al/Ln ratio and varies between 1.54 and 5.15 mol. In the LAA–TEA system, EtH results from the reaction of the water of crystallization of LAA with TEA. On the contrary, the gaseous products in the TMAA–TEA system are mainly formed due to transformations of unstable intermediates (alkyl and hydride derivatives of metals in the oxidation states 2 and 1) and due to TEA decomposition by zero-valence metals or alkyl radicals [3–8, 37].

Our results provide an explanation for the absence of catalytic activity in the LAA–$R_3Al$ systems (R = Et, *iso*-Bu) in diene polymerization [38]. We believe that the retention of three acac ligands coordinated to the lanthanide is among the main causes of the catalytic inertness of the LAA–$R_3Al$ system. This inference is confirmed by published data [39], according to which the catalysis of diene polymerization by the $LnCl_3 \cdot 3TBP$–$R_3Al$ system begins only after all ligand (TBP) molecules are removed from the coordination sphere of the lanthanide. The presence or absence of acac ligands coordinated to the metal also governs the catalytic activity of “metal complex–$Et_3Al$” systems in butadiene dimerization and trimerization. We studied the dimerization of butadiene in the presence of the LAA–TEA system. The results obtained were compared to data available on butadiene trimerization with the $Ni(acac)_2$–TEA system [40] (table). The butadiene conversion was found to be as low as ≤6% (table), whereas the butadiene conversion in the trimerization reaction reaches 100% [40]. This high yield is due to the fact that, in the $Ni(acac)_2$–TEA system, as distinct from the LAA–TEA system, the acac ligands are abstracted from the metal and Ni(II) is reduced to Ni(0).

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