Hydrolysis of isobutylaluminum aryloxides studied by ^{1}H NMR and quantum chemical methods

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The results of ^{1}H NMR and quantum chemical studies of hydrolysis of isobutylaluminum aryloxides are presented. According to the data of ^{1}H NMR spectroscopy, the hydrolysis of monomeric diisobutylaluminum aryloxides $(2,6-Bu^t_2—C_6H_3O)AlBu^i_2$ and $(2,6-Bu^t_2,4-Me—C_6H_2O)AlBu^i_2$ occurs selectively at the Al—OAr bond to form the corresponding sterically bulky phenol and polyisobutylaluminoxane. At the molar ratios $Al : H_2O = 2$, the formed sterically bulky phenol reacts slowly with diisobutylaluminum monoaryloxide to form isobutylaluminum diaryloxide. Dimeric aryloxide $[(2-Bu^t—C_6H_4O)AlBu^i_2]_2$ is not hydrolyzed under similar conditions. The quantum chemical calculations confirmed the experimental results: the hydrolysis at the Al—OAr bond has a lower energy barrier than that at the Al—C bond because of the formation of $H_{H_2O}...O_{O—Ar}$ hydrogen bonds.

Key words: hydrolysis, isobutylaluminum aryloxide, organoaluminum compounds, ^{1}H NMR spectroscopy, quantum chemical study.

Hydrolysis of alkylaluminum compounds is the simplest and popular method for the preparation of aluminoxanes, *viz.*, compounds containing —Al—O—Al— fragments. This method is used for obtaining methylaluminoxane (MAO), modified versions of MAO (MMAO), and mixed aluminoxanes that find wide use as efficient activators of catalysts for ion-coordination polymerization and oligomerization of olefins.[1—5]

Aluminoxanes modified by phenols with sterically bulky or electron-withdrawing substituents are promising from the viewpoint of activators of metallocenes and postmetallocenes catalysts for olefin polymerization.[6—14] These activators were found to exhibit a higher activation ability toward the organometallic component of the catalytic system than the non-modified analogs and have a high chemical stability. Several methods for the preparation of these compounds were described. The modification of aluminoxanes by the corresponding substituted phenols is the simplest and popular method.[6—14]

The mechanisms of hydrolysis of alkylaluminum aryloxides remain yet disputable. As asserted in the works devoted to the synthesis of aryloxyalkylaluminoxanes and their application as activators of metallocene catalysts in the copolymerization of ethylene with hex-1-ene,[6,7] the hydrolysis of alkylaluminum aryloxides affords aryloxyalkylaluminoxanes with the evolution of the corresponding alkanes. This route of hydrolysis implies that the reaction proceeds at the Al—C bond. At the same time, it is shown[15] that the hydrolysis of aluminum amides and

alkoxides proceeds *via* the protonation of the heteroatom rather than the carbon atom at the Al—alkyl bond. The authors believe that this hydrolysis route occurs due to a substantial decrease in the basicity of the Al—alkyl group in the presence of the heteroatomic donor ligand at the aluminum atom. The predominant occurrence of the hydrolysis at the Al—OAr bond was also observed in the reaction of water with methylaluminum diaryloxide $AlMe(2,6-Bu^t_2—C_6H_3O)_2$ under the conditions of a tenfold excess of aryloxide toward water in a medium of THF.[16,17] The major hydrolysis product is $2,6-Bu^t_2—C_6H_3OH$ (**1a**). The reaction proceeds *via* the formation of the structurally characterized adduct $(2,6-Bu^t_2—C_6H_3O)_2-AlMe \cdot H_2O \cdot 2THF,$[16] which gradually decomposes at the temperature above 0 °C to form 1.6 equiv. compound **1a**, 0.2 equiv. $MeAl(2,6-Bu^t_2—C_6H_3O)$, and only 0.1 equiv. methane.

	1	R^1	R^2
	a	Bu^t	H
	b	Bu^t	Me
	c	H	H

1a—c
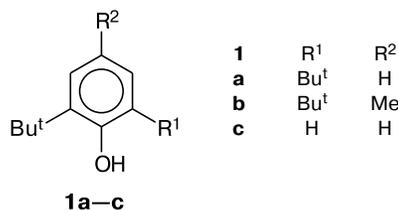
We have previously shown[18,19] that isobutylaluminoxanes obtained by the hydrolysis of triisobutylaluminum (TIBA) are efficient activators of metallocene complexes in reactions of homo- and copolymerization of olefins. It

is also shown[20] that monomeric forms of isobutylaluminum aryloxides are efficient activators in these processes. The primary aim of this work was the preparation of aryloxyisobutylaluminoxane activators (ArO)Al(Bu^i)-(μ-O)-(Bu^i)Al(OAr), which, as we assumed, could be synthesized by the hydrolysis of monomeric forms of diisobutylaluminum aryloxides by analogy to the published works,[6,7] and their application in polymerization processes. However, it was shown by the study of the hydrolysis of two monomeric diisobutylaluminum aryloxides, *viz.*, (2,6-Bu$^t_2$—C$_6$H$_3$O)AlBu$^i_2$ (**2a**) and (2,6-Bu$^t_2$,4-Me—C$_6$H$_2$O)-AlBu$^i_2$ (**2b**), under mild conditions on copper(II) sulfate pentahydrate (CuSO$_4 \cdot$5H$_2$O) or ice particles at the molar ratio Al : H$_2$O = 2 using the ^{1}H NMR method that the hydrolysis occurred selectively at the Al—OAr bond to form the corresponding sterically bulky phenol, which slowly reacted with an excess of diisobutylaluminum monoaryloxide to form isobutylaluminum diaryloxide. It is impossible to obtain aryloxyisobutylaluminoxanes by this method. The quantum chemical simulation of the hydrolysis showed that the reaction route was determined by the kinetics of the process and was related to the formation of a hydrogen bond with the O—Ar fragment resulting in a substantial decrease in the activation energy of O—Ar ligand protonolysis.

Experimental

Toluene (special purity grade) was used. The solvent was dried by distillation over LiAlH$_4$ and stored over molecular sieves (4 Å) in an argon atmosphere. Toluene-d$_8$ (Aldrich Chem. Co.) dried by multiple distillation over activated molecular sieves (4 Å) was used for ^{1}H NMR spectroscopy. Compounds (2,6-Bu$^t_2$,4-R—C$_6$H$_2$O)AlBu$^i_2$ (R = H (**2a**), Me (**2b**)) and [(2-Bu^t—C$_6$H$_4$O)-AlBu$^i_2$]$_2$ (**2c**) were synthesized using a described procedure.[20] Argon was dried by passing through a column with activated molecular sieves (5 Å). All manipulations with organoaluminum compounds were carried out in an atmosphere of purified and dried argon.

Hydrolysis of diisobutylaluminum aryloxides. Hydrolysis of toluene solutions of disiobutylaluminum aryloxides was carried out by two methods: using CuSO$_4 \cdot$5H$_2$O (*A*) and ice (*B*).

A. **Hydrolysis using CuSO$_4 \cdot$5H$_2$O.** A cooled to −78 °C solution of diisobutylaluminum aryloxide in toluene (Al : H$_2$O = 2) was poured to a weighed sample of copper(II) sulfate pentahydrate. The temperature of the obtained suspension was increased to room temperature with stirring. The solution was stirred for 10 h. The solution of the synthesized aluminoxane was filtered off from crystalline hydrate CuSO$_4 \cdot$H$_2$O.

B. **Hydrolysis using ice.** Degassed water was cooled to −78 °C. A cooled to −78 °C solution of diisobutylaluminum aryloxide in toluene (Al : H$_2$O = 2) was slowly added to the formed ice. The obtained suspension was gradually heated to room temperature with continuous stirring until ice was completely dissolved. The overall hydrolysis time was 1 h.

Analysis of diisobutylaluminum aryloxides and hydrolysis products by the NMR method. Toluene solutions of synthesized diisobutylaluminum aryloxides and hydrolysis products in an

atmosphere of dry argon were placed in tubes 5 mm in diameter. NMR spectra were recorded on a Bruker AVANCE III FT-IR spectrometer (500 MHz). The signal of residual methyl protons of toluene-d$_8$ (δ = 2.09) was used for the determination of chemical shifts.

Quantum chemical study. Quantum chemical calculations were performed by the density functional theory (DFT) using the ωB97XD hybrid functional. The 6-311+G(d,p) basis set was used for the H, C, and O atoms. To save computation time, the one-electron basis set on the Al atoms was specified using the ECP10MWB pseudo-potential[21] and the valent electrons of Al were described using the corresponding ECP10MWB basis set.[21] The standard algorithm accomplished in the Gaussian 09 program was used to search for transition states. The found transition state was checked for the imaginary frequency. The polarized continuum model (PCM) approximation[22] was used to take into account the effect of the solvent (toluene).

Results and Discussion

The hydrolysis products of diisobutylaluminum aryloxides were studied for structurally similar sterically bulky diisobutylaluminum aryloxides **2a** and **2b** bearing *tert*-butyl radicals in both *ortho*-positions. Isobutylaluminum aryloxides containing two *tert*-butyl groups in the *ortho*-positions of the aryl fragment of the compounds exist in the monomeric form due to steric hindrances.[23–25] For comparison we studied the hydrolysis of diisobutylaluminum aryloxide with one *tert*-butyl substituent in the *ortho*-position of the O—Ph fragment (**2c**), which exists as a dimer, as will be shown below.
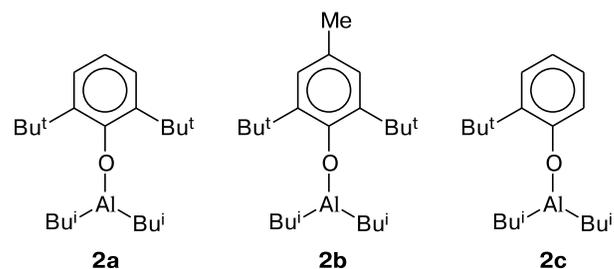
The primary aim of the study was to establish the possibility of forming aryloxide aluminoxane products during hydrolysis of these compounds by analogy to the works.[6,7] The hydrolysis was carried out using copper(II) sulfate pentahydrate (CuSO$_4 \cdot$5H$_2$O) or ice particles dispersed in toluene at the molar ratio Al : H$_2$O = 2 according to the procedures used by us for the synthesis of tetraisobutylaluminoxane (TIBAO) and longer-chain isobutylaluminoxanes (IBAO).[18] The choice of the molar ratio was determined by the aim at obtaining aryloxide aluminoxane products (ArO)Al(Bu^i)-(μ-O)-(Bu^i)Al(OAr), which, as we assumed, should not manifest a tendency to dimerization, unlike TIBAO,[26] and could be used for the activation of metallocene complexes in olefin polymerization. The hydrolysis products were analyzed under the conditions of ^{1}H NMR experiments.

The fragments of the aliphatic range of the ^{1}H NMR spectra of the starting compound **2b** (*a*) and the hydrolysis products of aryloxide obtained using copper(II) sulfate pentahydrate in 10 h (*b*) and in 6 days of the subsequent storage of a toluene solution at room temperature (*c*) are presented in Fig. 1.
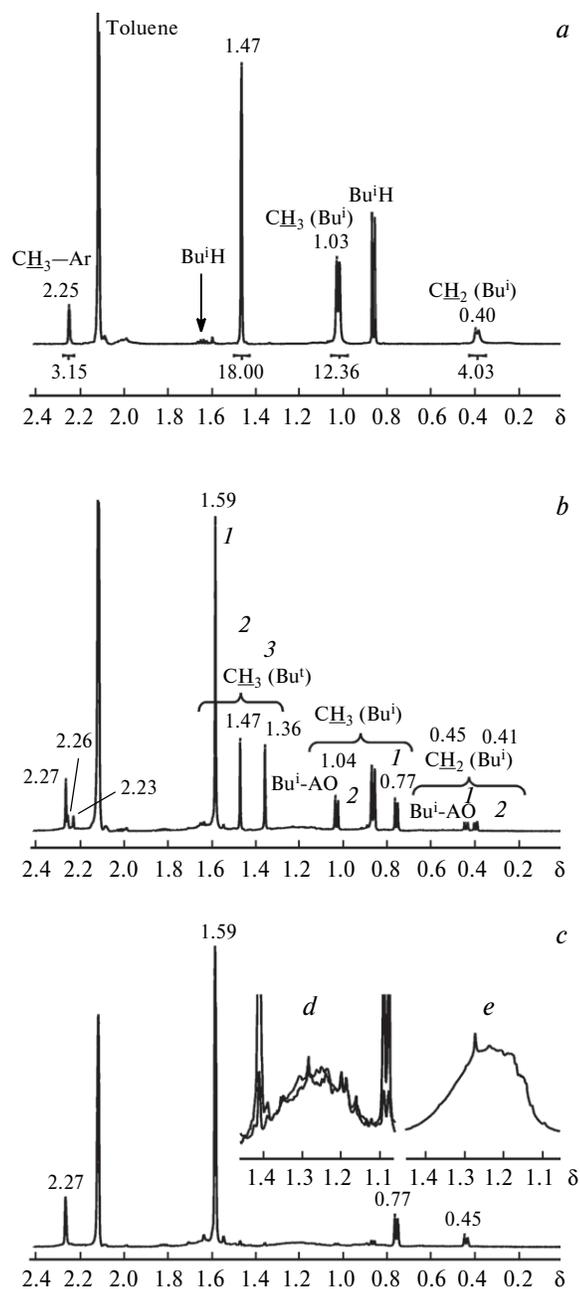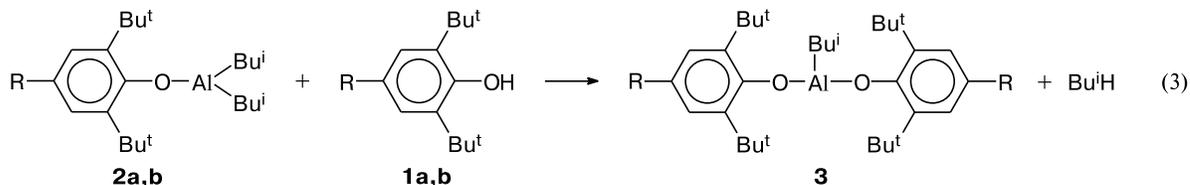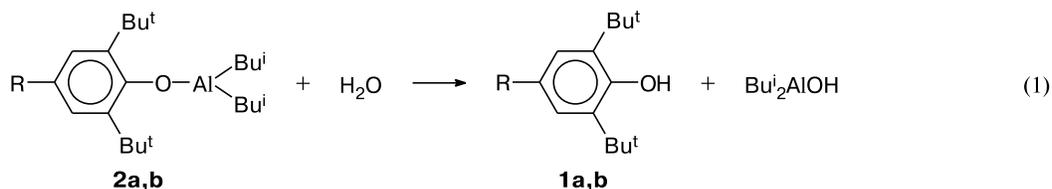

Fig. 1. Fragments of the aliphatic part of the ^{1}H NMR spectra of **2b** (*a*) and its hydrolysis products obtained using copper(II) sulfate pentahydrate in 10 h (*b*) and 6 days (*c*) after hydrolysis: (*1*) dimer, (*2*) monomer, and (*3*) phenol; *d*, isobutylaluminoxane fragments of spectra *b* and *c*; *e*, fragment of ^{1}H NMR spectrum of polyisobutylaluminoxane obtained by the hydrolysis of TIBA with copper(II) sulfate pentahydrate at the molar ratio Al : H$_2$O = 1.[18]

The spectrum of the starting diisobutylaluminum aryloxide is presented in this range by signals of protons of the methyl group C$\underline{H}_3$—Ar (2.25 ppm), *tert*-butyl groups (1.47 ppm), and isobutyl groups (1.03 and 0.40 ppm). After 10 h of hydrolysis, the spectrum of the reaction products contains the signals of the starting compound and also signals of protons of the *tert*-butyl groups of the corresponding sterically bulky phenol **1b** (1.35 ppm) and *tert*-butyl (1.57 ppm) and isobutyl groups (0.75 and 0.43 ppm) of isobutylaluminum diaryloxide, Note that the signals of the *tert*-butyl groups of the starting aryloxide and formed phenol have the same intensity. The spectrum also exhibits broad unresolved low-intensity signals of the isobutyl groups of the aluminoxane structures (0.75—0.5 and 1.4—0.9 ppm, see Fig. 1, *d*). The prolong storage of the sample leads to the transformation of the spectrum in the form of a symbate disappearance of the signals of compound **1b** and residual diisobutylaluminum monoaryloxide reacting to form isobutylaluminum diaryloxide (*c*). The spectrum of the polyisobutylaluminoxane structures are not transformed in the presence of compound **1b**, indicating that the reaction of **1b** with diisobutylaluminum monoaryloxide proceeds selectively and compound **1b** does not react with isobutylaluminoxanes (see Fig. 1, *d*). The shapes and positions of the signals of isobutylaluminoxane are similar to those of the signals of polyisobutylaluminoxane obtained by the hydrolysis of TIBA with copper(II) sulfate pentahydrate at the molar ratio Al : H$_2$O = 1 [18] (see Fig. 1, *e*). A similar pattern of hydrolysis was also observed for compound **2a**. The obtained results indicate the selective hydrolysis of diisobutylaluminum aryloxide at the Al—O bond rather than at the Al—C bond. The complete pattern of the processes occurring at the partial hydrolysis of diisobutylaluminum aryloxides (molar ratio Al : H$_2$O = 2) is shown in Scheme 1.

As in the case of triisobutylaluminum,[18] the hydrolysis by copper(II) sulfate pentahydrate is slower and more selective than the hydrolysis on ice particles, because the dehydration of the pentahydrate is the rate-determining step in this case.[26] For the hydrolysis on ice particles, it is more difficult to avoid local overheatings that can be a reason for side reactions to occur. The fragment of the aliphatic range of the ^{1}H NMR spectrum of the hydrolysis products of compound **2a** on ice particles is shown in Fig. 2. It is seen that the major hydrolysis product at the molar ratio Al : H$_2$O = 2, as well as for the hydrolysis on copper(II) sulfate pentahydrate, is 2,6-di-*tert*-butylphenol (**1a**), which further reacts with an excess of diisobutylaluminum monoaryloxide to form isobutylaluminum diaryloxide (see Scheme 1). A substantial distinction is a significantly lower intensity of the signal of the *tert*-butyl groups of compound **1a** compared to that of diisobutylaluminum monoaryloxide and an almost complete absence of signals of isobutylaluminoxanes in the ranges 0.5—0.75 and 0.9—1.4 ppm. A comparison of the integral

Scheme 1

$$R—C_6H_2(Bu^t)_2—O—Al(Bu^i)_2 + H_2O \longrightarrow R—C_6H_2(Bu^t)_2—OH + Bu^i_2AlOH \qquad (1)$$

2a,b   **1a,b**

$$nBu^i_2AlOH \longrightarrow (Bu^i_2AlOH)_n \longrightarrow \text{Isobutylaluminoxanes} + Bu^iH \qquad (2)$$

$$R—C_6H_2(Bu^t)_2—O—Al(Bu^i)_2 + R—C_6H_2(Bu^t)_2—OH \longrightarrow R—Ar—O—Al(Bu^i)—O—Ar—R + Bu^iH \qquad (3)$$

2a,b   **1a,b**   **3**

R = H, Me

intensities of the *tert*-butyl groups of compound **1a**, diisobutylaluminum monoaryloxide, and isobutylaluminum diaryloxide suggests a ~16% deficiency of the amount of water involved in phenol formation. A possible explanation is the partial consumption of water under the conditions of local overheatings in the deeper hydrolysis of aluminoxanes $(Bu^iAlO)_n$ to form isobutylaluminoxane structures $(Bu^i_{1-x}AlO_{1+x})_n$ insoluble in the reaction mixture.

As mentioned above, compounds **2a** and **2b** are rare representatives of monomeric forms of alkylaluminum aryloxides protected from dimerization by the bulky *tert*-butyl substituents in the *ortho*-positions of the O—Ar fragment. It was of interest to establish an analogy or specifics in the occurrence of hydrolysis of less sterically hindered isobutylaluminum aryloxides. Diisobutylaluminum aryloxide with one *tert*-butyl substituent in the *ortho*-position

of the O—Ar fragment, $[(2\text{-}Bu^t—C_6H_4O)AlBu^i_2]_2$ (**2c**), was chosen as an example. Compound **2c** was synthesized by the reaction of compound **1c** with TIBA at the molar ratio Al : phenol = 1 using an earlier described procedure.[20] The spectrum of the starting compound **1c** in the aliphatic range is presented by a narrow signal of *tert*-butyl groups at 1.43 ppm. The spectrum of product **1c** of the reaction with TIBA in this range recorded at room temperature (Fig. 3, *a*) is presented by the signal of the *tert*-butyl groups (1.50 ppm) and two sets of broad signals of approximately equal intensities of the CH_3 (0.98 and 0.79 ppm) and CH_2 fragments (0.69 and 0.55 ppm) of the isobutyl groups. This pattern indicates the dimeric structure of compound **2c** in which dynamic processes involving isobutyl groups occur. As the temperature of spectrum recording decreases to 0 °C (see Fig. 3, *b*), the dynamic processes in aryloxide **2c** is retarded and the signals of isobutyl groups are presented by narrow doublets of methyl groups and doublets of doublets of methylene protons. An additional isomer of compound **2c** is observed at this temperature, which is indicated by the appearance of a new signal of *tert*-butyl groups at 1.53 ppm and a set of signals in a range of 0.9—1.0 ppm. The further temperature decrease to −20 °C (*c*) showed two doublets of methyl protons at 0.97 and 0.95 ppm and two doublets of methylene protons at 0.90 and 0.70 ppm. The multiplet of methyl protons at 2.00 ppm corresponding to this isomer becomes resolved in the spectrum. The further temperature decrease to −40 °C (*d*) somewhat "slurs" over the pattern because of the overlapping of the signals of the methyl protons of the minor isomer (0.98 ppm) and overlapping of one group of doublets of doublets of the major isomer with one of the signals of its methyl groups (0.85 ppm). The spectrum of compound **2c** recorded at room temperature after cooling
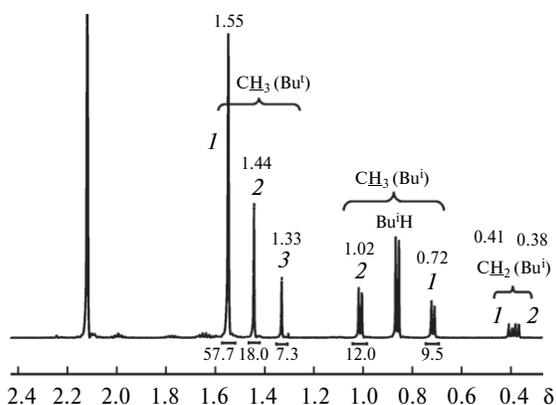

Fig. 2. Fragment of the aliphatic range of the ^{1}H NMR spectrum of hydrolysis product **2a** in ice 6 days after the synthesis: *1*, dimer; *2*, monomer, and *3*, phenol.
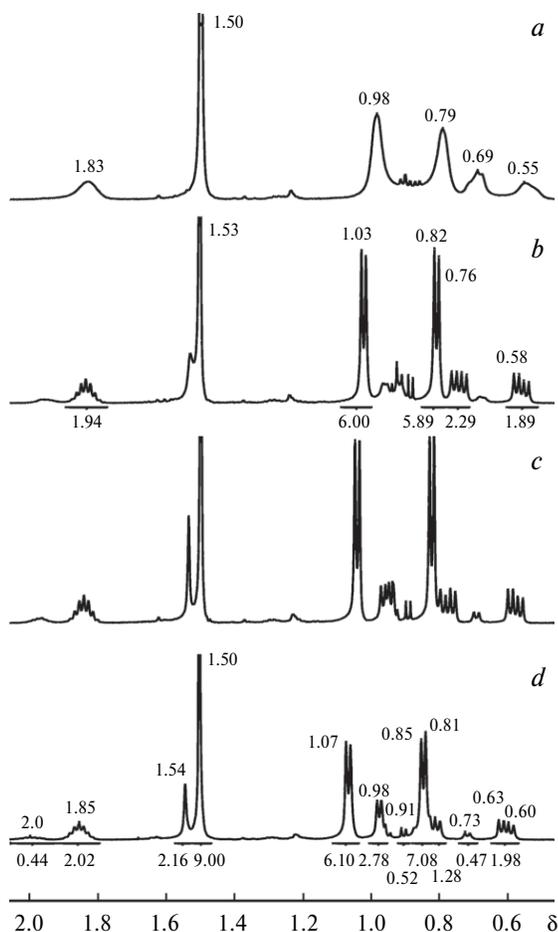
Fig. 3. Fragments of the ^{1}H NMR spectrum of aryloxide **2c** recorded at different temperatures: ~20 °C (*a*), 0 °C (*b*), −20 °C (*c*), and −40 °C (*d*).

completely corresponds to the spectrum to the stepped cooling of the sample. Thus, two isomers presented by two different *tert*-butyl groups and two sets of isobutyl groups were revealed for aryloxide **2c**. The ratio of isomers in a toluene solution is 1 : 5. Probably, the major dimeric form (as the most thermodynamically stable) is the *trans*-form (*tert*-butyl groups in the *ortho*-position are located at different sides of the Al$_2$O$_2$ plane), and the minor dimeric isomer represents the *cis*-form. An indirect confirmation are the published data[27] showing that the structurally similar complex [(2,4-Bu$^t_2$—C$_6$H$_3$O)Al(Bu^i)$_2$]$_2$ exists in the *trans*-form, according to the X-ray diffraction data, whereas the ^{1}H NMR spectrum of the solution at room temperature contains two groups of broadened signals of the methyl and methylene protons of the isobutyl groups.

An attempt of hydrolysis of compound **2c** with copper(II) sulfate pentahydrate (CuSO$_4$·5H$_2$O) and ice was made to study the character of interaction of associated diisobutylaluminum aryloxides. It turned out that no hydrolysis of **2c** occurred at room temperature. An interesting fact is the inability of these compounds to hydrolysis at the Al—C bond. On heating **2c** at 50—60 °C for 1 h, the compound is partially hydrolyzed to form 2-Bu^t—C$_6$H$_3$OH (**1c**).

Quantum chemical study. The experimental results presented on the hydrolysis of sterically hindered monomeric isobutylaluminum aryloxides and the data for the hydrolysis of other alkylaluminum aryloxides[15—17] show that the hydrolysis of these compounds proceeds at the Al—O bond rather than at the Al—C bond, which is the unexpected result since the energy of the Al—O bond is significantly higher (~120 kcal mol$^{−1}$) than that of the Al—C bond (~64 kcal mol$^{−1}$).[28]

There is no theoretical substantiation of hydrolysis for this class of compounds in the literature. Therefore, we simulated the key structures and estimated the energy parameters of the process by the density function theory (DFT) for the hydrolysis of aryloxide **2a**.

At the first stage of the study, we calculated the structure of intermediate AlBu$^i_2$OAr·H$_2$O (**IM**), which represents the tendency of aluminum to the tetracoordinated state (Fig. 4). The Al—O(H$_2$O) bond length in the complex is 2.06 Å and exceeds the length of the Al—O(Ar) bond equal to 1.78 Å. Note that the corresponding distances in the aqua complex of methylaluminum diaryloxide [2,6-Bu$^t_2$—C$_6$H$_3$O]$_2$AlMe·H$_2$O·2THF determined by the X-ray diffraction analysis data (−40 °C) are somewhat shorter and equal to 1.86 and 1.72 Å, respectively.[16] At the same time, the distance in the monoaryloxide complexes of alkylaluminums with Lewis bases (LB) are similar: [2,6-Bu$^t_2$—C$_6$H$_3$O]AlR$_2$·LB: Al—P = 2.50, Al—O = 1.74 Å (R = Me, LB = PMe$_3$)[25]; Al—N = 2.08 Å, Al—O = 1.75 Å (R = Me, LB = (2,6-Me$_2$—Py)[29]; Al—N = 2.04 Å, Al—O = 1.75 Å (R = Et, LB = NH$_2$^{t}Bu)[29]; Al—N = 2.01, Al—O = 1.74 Å (R = Me, LB = NH$_3$)[30]; and Al—O(THF) = 1.91, Al—O = 1.75 Å (R = Et, LB = THF).[31] The hydrogen bond OH···OAr (2.59 Å) in intermediate **IM** should be mentioned. The H(H$_2$O)—C distance is 3.02 Å. On the whole, complex formation leads to a decrease in the energy of the system by 10.55 kcal mol$^{−1}$ compared to infinitely remote reactants.

The transition states were considered for two reaction routes: at the Al—O bond (**TS1**) and at the Al—C bond (**TS2**) (see Fig. 4). Transition state **TS1** is formed due to the interaction of water hydrogen with the oxygen atom of the aryloxy group. The angles of the O—Al—O and H—O$_{H_2O}$—Al bonds in the transition state are smaller by 21° and 32°, respectively, compared to those in **IM**. The Al—O$_{H_2O}$ bond length decreases from 2.06 Å to 1.90 Å, whereas the Al—O$_{Ar}$ bond length increases from 1.78 to 1.98 Å. The reaction coordinate corresponds to the hydrogen atom transfer from one oxygen atom to another, In the transition state, the lengths of two O—H bonds are equal in fact being 1.18 and 1.24 Å (*cf.* the O—H bond in the water molecule equal to 0.96 Å). The potential barrier relative to intermediate **IM** is 14.35 kcal mol$^{−1}$. In this
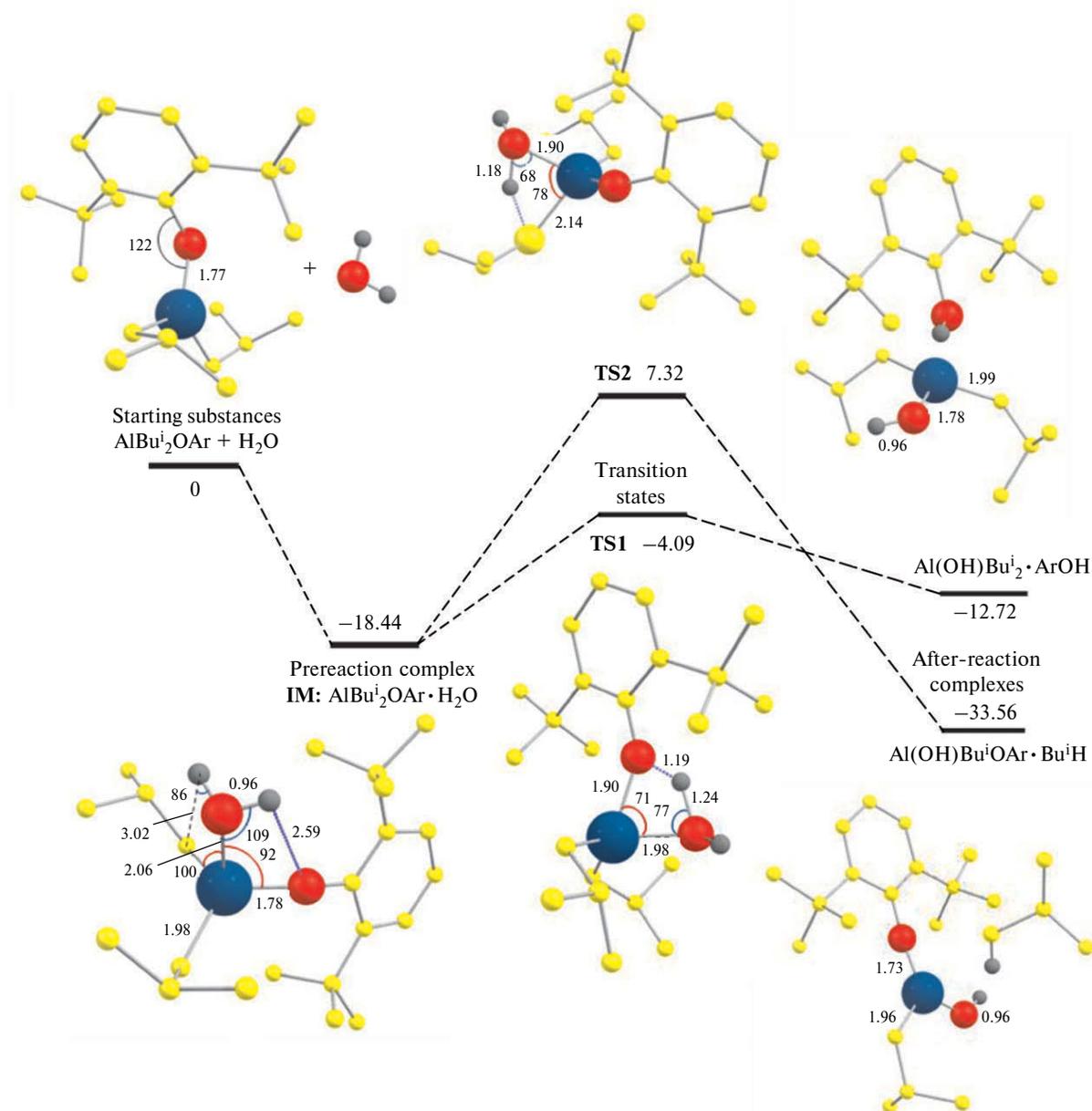
Fig. 4. Potential energy profile showing the hydrolysis of $AlBu^i_2OAr$ at the $Al—O_{Ar}$ (transition state **TS1**) and $Al—C$ (transition state **TS2**) bonds. The relative energies (kcal mol^{-1}) were calculated by the ωB97XD/6-311+G(d,p) method.

Note. Figures 4 and 5 are available in full color in the on-line version on the web-page (http://www.link.springer.com).

case, the hydrolysis products are alkylaluminum hydroxide $AlBu^i_2OH$ and aryloxide **2**. The heat effect of this reaction is -12.72 kcal mol^{-1}. However, a significant energy gain of the reaction is achieved when taking into account further transformations of $AlBu^i_2(OH)$, namely, association and formation of isobutylaluminoxanes. A significant heat release was observed in experiments on hydrolysis. The heat effect of dimerization characteristic of alkylaluminum hydroxides[32] was -44.27 kcal mol^{-1} in our case.

Transition state **TS2** is formed due to the interaction of the hydrogen atoms of water with the carbon atom of one of methylene groups. As in transition state **TS1**, the

O—Al—C and H—O$_{H2O}$—Al angles in **TS2** are decreased by 22° and 28°, respectively, compared to those in intermediate **IM**. The Al—O$_{H2O}$ and Al—C bond lengths are 1.90 and 2.14 Å, whereas in **IM** they are equal to 2.06 and 1.98 Å, respectively. The reaction coordinate corresponds to the hydrogen atom transfer from the oxygen atom of water to the carbon atom of the methylene group. In this transition state, the hydrogen atom is remote from oxygen at 1.18 Å and approached to the carbon atom by 1.48 Å. The potential barrier relative to **IM** is 25.76 kcal mol^{-1}. For the hydrolysis *via* this route, the heat effect is -33.56 kcal mol^{-1}.
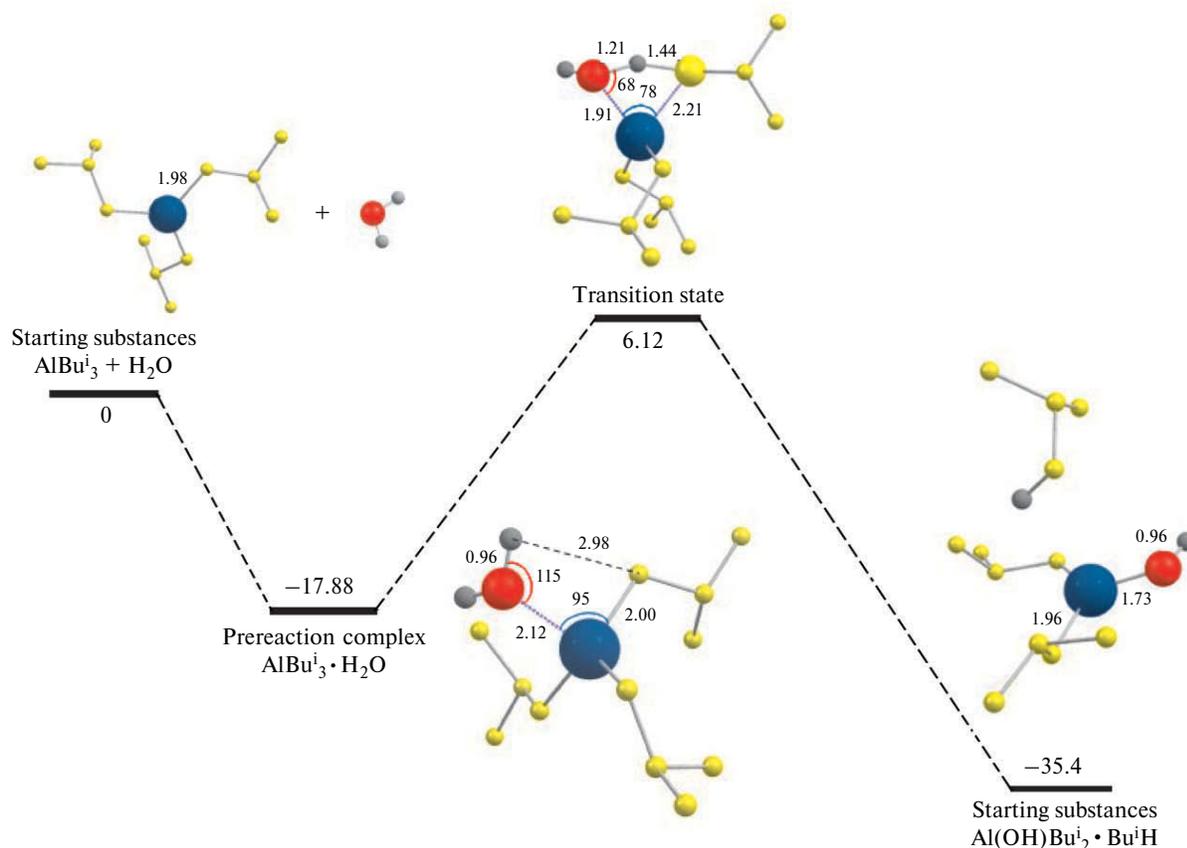
Fig. 5. Potential energy profile showing the hydrolysis of AlBu$^i_3$. The relative energies (kcal mol^{-1}) were calculated by the ωB97XD/6-311+G(d,p) method.

A comparison of two possible routes of hydrolysis shows that transition state **TS1** is characterized by a lower energy barrier (by 11.41 kcal mol^{-1}), which corresponds to a huge difference in the reaction rate through transition states **TS1** and **TS2**. The hydrolysis of the studied compounds proceeding at the Al—O(Ar) bond is considerably facilitated by the formation of a hydrogen bond between the proton of the water molecule and the oxygen atom of the aryloxide group.

The hydrolysis of TIBA was calculated (Fig. 5) to compare with the obtained results for the hydrolysis of compound **2**. In this case, the energy barrier of hydrolysis at the Al—C bond was 24.0 kcal mol^{-1}, which is close to the experimental data (20±2.5 kcal mol^{-1}).[26] This fact confirms that the quantum chemical calculations performed are correct.

To conclude, according to the ^{1}H NMR spectra of the reaction products and quantum chemical calculations it was shown that the hydrolysis of sterically hindered isobutylaluminum diaryloxides bearing *tert*-butyl groups in positions 2 and 6 of the O—Ar fragment proceeded predominantly at Al—O$_{Ar}$ bond rather than the Al—C bond. The structures of the transition states of two types corresponding to the hydrolysis at the Al—C and Al—O$_{Ar}$

bonds, respectively, were considered and optimized. It was shown that the energy barrier for hydrolysis at the Al—C bond was significantly higher than that at the Al—O bond (25.76 and 14.35 kcal mol^{-1}, respectively), which explains the kinetic control of the hydrolysis in experiment. A lower barrier for the reaction at the Al—O(Ar) bond is caused by the formation of the hydrogen bond between the water proton and oxygen atom of the aryloxy fragment.

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