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In Situ Study of the Interaction between *tert*-Butyl Chloride and Aluminum Activated with Liquid In–Ga Eutectic

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Abstract—The interaction between *tert*-butyl chloride and activated aluminum was studied by attenuated total reflectance Fourier transform infrared spectroscopy near room temperature (18–25°C). A long induction period of ~240–260 min was observed. The ionic aluminum chloride complexes $[Al_nCl_{3n+1}]^-$ ($n = 1, 2$) and the molecular species $AlCl_3$ were identified at the activated aluminum/*tert*-butyl chloride interface during the reaction. The formation of the $AlCl_4^-$ ion in the liquid medium and the presence of the same ion and a molecular $AlCl_3$–*tert*-butyl chloride complex in the resinous products of the reaction were confirmed by ^{27}Al NMR spectroscopy. The reaction products were analyzed qualitatively by GC/MS. The reactivities of activated aluminum and anhydrous aluminum chloride toward *tert*-butyl chloride under the same conditions were compared. A distinctive feature of the interaction activated aluminum and *tert*-butyl chloride is the dominant formation of the $AlCl_4^-$ ion. By contrast, the interaction between aluminum chloride and *tert*-butyl chloride yields the polynuclear ion $Al_2Cl_7^-$ and, likely, $Al_3Cl_{10}^-$.

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Aluminum metal is presently viewed as a promising material for unconventional energy engineering [1–3] and catalysis [4–10]. By oxidation of aluminum [4] or its activated copper-, nickel-, cobalt-, or zinc-containing alloys with water [5] followed by calcination of the resulting precipitate, it is possible to obtain supports for various processes, including CO oxidation. Gaponik and Mardykin [6] reported the synthesis of higher tri-*n*-alkylaluminums (olefin polymerization cocatalysts) via the reaction between an aluminum and magnesium metal powder and an alkyl halide at 60–70°C. Sadykov and Teregulov [7] studied, by the chemical nuclear polarization method, the interaction between an overstoichiometric amount of iodine vapor–activated aluminum powder and *tert*-butyl chloride at 60–70°C in dioxane and inferred that this reaction occurs via a free-radical mechanism. Sadykov et al. [8] were the first to carry out the conversion of cyclohexane into decalins at room temperature under the action of aluminum halides obtained in situ by reacting an iodine-activated aluminum metal powder with methyl halides CCl_4, $CHCl_3$, $CHBr_3$, CH_2Cl_2, and CH_2Br_2). A carbonium mechanism was suggested for the reactions involved in this synthesis.

We demonstrated earlier that massive aluminum activated with liquid In–Ga eutectic can react with chloroalkanes, including *tert*-butyl chloride, near room temperature to yield a wide variety of products [9, 10]. It was hypothesized that catalytic complexes like aluminum chloride Lewis acids can form on the activated aluminum surface under the action of the reaction medium. Even under mild conditions, these active species can involve hydrocarbons from various homological series into acid-catalyzed reactions, such as isomerization, alkylation, and oligomerization.

Here, we report an in situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) and NMR study of the reaction between activated aluminum and *tert*-butyl chloride for the purpose of identifying the resulting aluminum chloride complexes.

EXPERIMENTAL

Aluminum Samples and Activation of Aluminum with Liquid In–Ga Eutectic

Samples of aluminum metal (Ad-1 brand, USSR State Standard GOST 4784-74, 99.3 wt % Al, main impurities: Si, Fe, Ti, Cu, Mn) were 4 × 4 mm polished plates with a thickness of 3 mm. The activator was In–Ga eutectic (76 wt % Ca, $T_m = 15.9$°C). Aluminum was activated at room temperature by placing a drop (20 μl) of the liquid alloy on the surface of the initial aluminum plate [11]. The contact time was 24–36 h. Because the aluminum surface is covered by oxide layers that are not wetted by the eutectic alloy, the sample was initially scratched with a metallic needle. Anhydrous aluminum chloride (Aldrich) was used as the model compound.

ATR-FT-IR Spectroscopy

The interaction between *tert*-butyl chloride and activated aluminum around room temperature (18–25°C) was studied by ATR-FT-IR spectroscopy on a Nicolet 5700 spectrophotometer (Thermo Electron Corp.). The ATR-FT-IR cell employed a ZnSe crystal in a metallic holder, to which a 30-ml cylindrical glass vessel for the solid and liquid reactants was glued with epoxy. The IR beam was incident on the solid activated aluminum/liquid *tert*-butyl chloride interface from below at an angle of 45°. The effective penetration depth of the IR beam was 0.4–3.3 μm in the 500–4000 cm^{-1} spectral range.

IR spectroscopic measurements were carried out as follows. Liquid *tert*-butyl chloride was poured into the cell, and its background spectrum was recorded. Next, activated aluminum was placed into the cell and IR spectra were recorded at regular intervals of ~10–15 min at a preset cell temperature. The background spectrum of *tert*-butyl chloride or that of the zinc selenide crystal was subtracted from the resulting spectra. The number of scans was 30, and the spectral resolution was 4 cm^{-1}. The interaction between anhydrous aluminum chloride and liquid *tert*-butyl chloride was also studied using this procedure under the same conditions.

NMR Spectroscopy

The structure of the components of liquid media was additionally studied by ^{27}Al and ^{13}C NMR spectroscopy at working frequencies of 52 and 50 MHz, respectively, in a magnetic field of 4.7 T on an AC-200 (Bruker) NMR spectrometer. The external standards were $Si(CH_3)_4$ and 1 M $Al(NO_3)_3 \cdot 9H_2O$ for ^{13}C and ^{27}Al NMR spectroscopy, respectively.

GC/MS

The resulting products were identified by GC/MS using an Agilent 6890/5973N system (Agilent Technologies). Analyses were performed in the temperature-programmed mode, linearly raising the oven temperature from 40 to 250°C at a rate of 10 K/min, with a capillary nonpolar column 0.25 mm in diameter and 30 m in length (HP-5ms, Agilent Technologies). Electron-impact ionization was used. The ionizing electron energy was 70 eV. The mass analyzer was a 195-mm gold-coated quartz quadrupole mass filter. The mass measurement range was 1.6–800 amu. Use of the scanning mode made it possible to identify individual components of complex mixtures. Control of the GC/MS system, analyses, and data processing were carried out using the special-purpose computer program MSD ChemStation and the NIST MS SEARCH 05 mass spectral library, which contains the spectra of 250000 species. The relative amounts of components in the gas and liquid phases were estimated separately.

RESULTS AND DISCUSSION

In the time interval of 2–240 min, no interaction between activated aluminum and liquid *tert*-butyl chloride was observed visually in the IR cell; that is, there was no observable dissolution of the solid phase, gas evolution, or changes in the color of the liquid medium. Throughout this time interval, the ATR-FT-IR spectrum of the reaction medium in the 500–650 cm^{-1} range showed an absorption band at 567 cm^{-1} due to the C–Cl bond, which did not vary with time. No changes relative to the spectrum of the initial liquid *tert*-butyl chloride were also observed in the regions of C–C stretching vibrations in the carbon backbone (780–830 cm^{-1}) and C–H stretching vibrations (2750–3100 cm^{-1}).

The observed induction period of ~240–260 min cannot be explained solely in terms of diffusion as in the reaction between activated aluminum and water, in which the resulting film of boehmite (reaction product) hinders the access of water to aluminum [13, 14]. In our case, the main cause of the induction period is likely the rapid formation of an AlCl(s) surface layer via the dissociative adsorption of the chloroalkane [15, 16], which turns slowly into $AlCl_3(s)$ (because of the negative entropic factor) before the main reaction [17]:

$$3AlCl(s) \rightarrow AlCl_3(s) + 2Al.$$

As the reaction mixture is held in the IR cell, the chemical reaction between activated aluminum and *tert*-butyl chloride begins in 260 min. New absorption bands at 495, 526, and 611 cm^{-1} appear in the ATR-FT-IR spectrum, and the strong band at 567 cm^{-1}, observed in the initial spectrum, disappears (Fig. 1a). Intensive gas evolution is observed in the IR cell, accompanied by the formation of a resinous, dark red substance around the activated aluminum plate. The reaction ends in complete aluminum dissolution in the reaction medium and in the formation of a viscous layer of resinous products.

Taking into account data available from the literature [18–20], we assigned the absorption bands at 495 and 526 cm^{-1} to the $AlCl_4^-$ and $Al_2Cl_7^-$ ions. The IR transmission spectrum of the 1-methyl-3-ethylimidazolium chloride–anhydrous aluminum chloride (1 : 1) ionic liquid was reported to have a broad band at 489 cm^{-1} [18], which was assigned by the authors to vibrations of the tetrahedral anion $AlCl_4^-$. The IR transmission spectra of the 1-butylpyridinium chloride–anhydrous aluminum chloride ionic liquid (1 : 1 and 1 : 2) exhibit broad bands at 490 and 545 cm^{-1} [19], which were assigned to the $AlCl_4^-$ and $Al_2Cl_7^-$

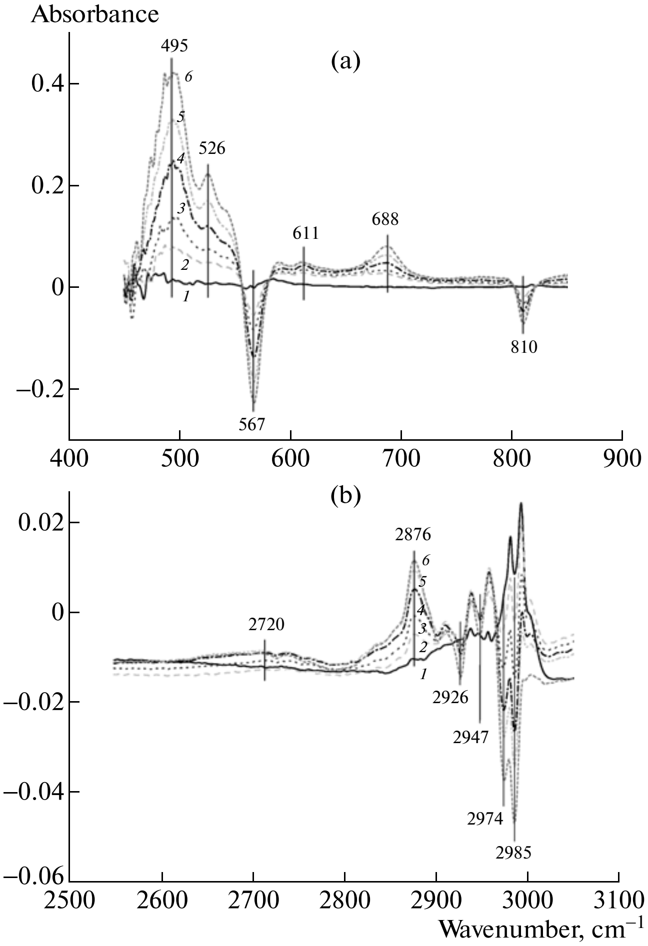

Fig. 1. Time variation of the ATR-FT-IR spectrum in the interaction between activated aluminum and *tert*-butyl chloride ($T = 25°C$) in the region of (a) C–Cl and (b) C–H stretching vibrations: (*1*) 261, (*2*) 308, (*3*) 320, (*4*) 327, (*5*) 331, and (*6*) 342 min.

anions, respectively. Bands at 475 and 517 cm^{-1} were observed in the IR emission spectra of MCl–AlCl$_3$ alloys (M = alkali metal), and, based on normal mode theory, these bands were assigned to the AlCl_4^- and $\mathrm{Al}_2\mathrm{Cl}_7^-$ ions [20].

The weak absorption band at 611 cm^{-1}, which appears in the spectrum simultaneously with the bands at 495 and 526 cm^{-1}, can be due to the molecular species AlCl$_3$, according to other authors [21, 22]. It was observed by low-temperature IR spectroscopy in optical cryostats ($T = 150$ K) [21]. In another study [22], high absorbance in this region was observed for anhydrous aluminum chloride vapor ($T = 700$ K).

Note the systematic weakening of the C–Cl stretching band of *tert*-butyl chloride at 567 cm^{-1} in time, which indicates that the chloroalkane undergoes conversion during the reaction.

The spectrum additionally shows new absorption bands at 1490, 1363, 1105, and 967 cm^{-1}, which are characteristic of branched alkyl substituents and polyisobutylene [23, 24], products of the reaction.

Figure 1b displays ATR-FT-IR spectra in the 2600–3050 cm^{-1} range, which accommodates the H–Cl stretching vibrations of hydrogen chloride [25, 26]. The absorption band at 2876 cm^{-1} arises from the H–Cl stretching vibrations of hydrogen chloride in low-polarity media [25], and the band at 2720 cm^{-1} characterizes the same vibrations of HCl in polar media and ionic liquids [26]. It is possible that the resulting hydrogen chloride favors the dissolution of activated aluminum to yield aluminum chloride.

Thus, its was demonstrated by in situ ATR-FT-IR spectroscopy that the reaction between activated aluminum and *tert*-butyl chloride proceeds via the formation of $[\mathrm{Al}_n\mathrm{Cl}_{3n+1}]^-$ ($n = 1, 2$) ionic complexes, which are possibly stabilized by intermediate carbocations (such as *tert*-$\mathrm{C}_4\mathrm{H}_9^+$) or H$^+$ (HCl). Apparently, the source of these complexes is the observed molecular species AlCl$_3$. It is likely these complexes that are catalytic species in the reaction.

NMR data confirm the results of ATR-FT-IR spectroscopy and indicate the appearance of the AlCl_4^- anion in the liquid medium during the reaction as an intense ^{27}Al signal with a chemical shift of (103.5 ± 0.5) ppm (Fig. 2a) [27]. Figure 2b presents the ^{27}Al NMR spectrum of the resinous products diluted with *tert*-butyl chloride. This spectrum indicates the presence of two aluminum chloride species, namely, AlCl_4^- (103.5 ppm) and, apparently, the [AlCl$_3$–*tert*-C$_4$H$_9$Cl] complex (98.0 ppm). The latter assignment is supported by the fact that, for a solution of anhydrous aluminum chloride in the thionyl chloride–sulfur dioxide mixed solvent, the resonance at $\delta = 97.6$ ppm was attributed to the [AlCl$_3$–SO$_2$] complex [28].

Massive anhydrous aluminum chloride also decomposes *tert*-butyl chloride at room temperature [29]. For comparison, we studied this reaction by ATR-FT-IR spectroscopy. *n*-Hexane was used here as the solvent, otherwise the reaction would occur violently and uncontrollably (Fig. 3).

Initially (~5 min), the ATR-FT-IR spectrum shows a broad band at 527 cm^{-1} with shoulders at 505 and 548 cm^{-1}. Later, a band at 586 cm^{-1} appears, whose intensity grows with time, like the intensity of the 527 cm^{-1} band. It was mentioned above that the 527 cm^{-1} band is assignable to the $\mathrm{Al}_2\mathrm{Cl}_7^-$ anion. The band at 586 cm^{-1} is likely due to the $\mathrm{Al}_3\mathrm{Cl}_{10}^-$ anion. The nearby band at 587 cm^{-1} was also observed in the low-temperature (77–250 K) IR spectra of the products of condensation between anhydrous aluminum chloride and *tert*-butyl chloride in the *n*-octane matrix [30].

Thus, the reaction between aluminum chloride and *tert*-butyl chloride takes place mainly via the formation of the dinuclear ionic complex $\mathrm{Al}_2\mathrm{Cl}_7^-$ and, likely,

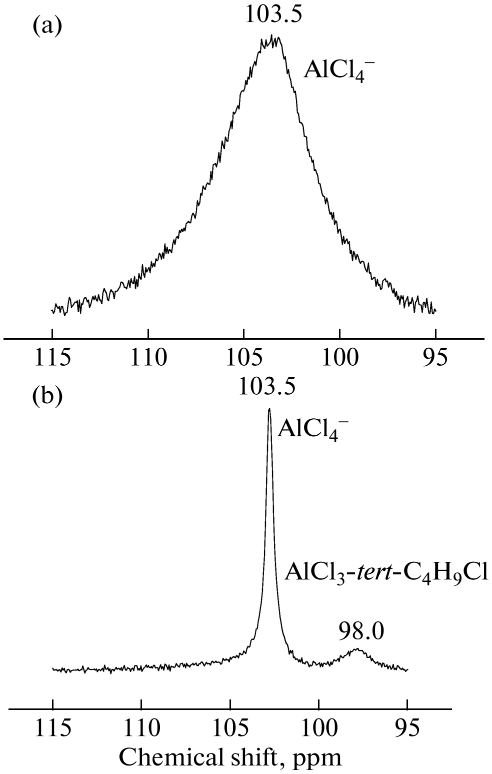

Fig. 2. ^{27}Al NMR of the reaction medium (T = 25°C): (a) interaction between activated aluminum and *tert*-butyl chloride; (b) dilution of the resinous products with and *tert*-butyl chloride.

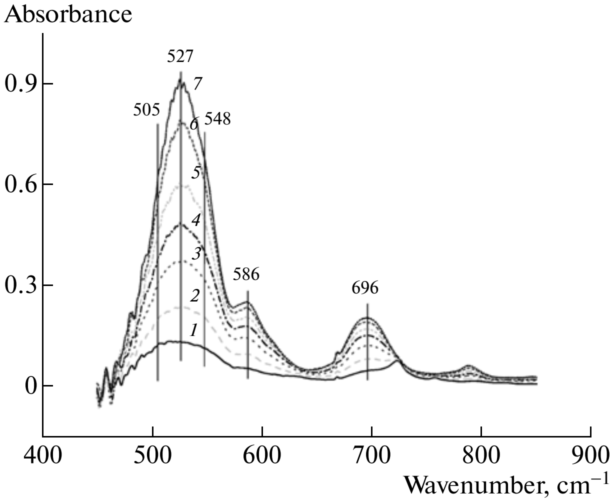

Fig. 3. Time variation of the ATR-FT-IR spectrum in the interaction between anhydrous aluminum chloride and *tert*-butyl chloride (T = 25°C) in the region of C–Cl stretching vibrations: (*1*) 5, (*2*) 9, (*3*) 12, (*4*) 15, (*5*) 22, (*6*) 32, and (*7*) 39 min.

the trinuclear complex $Al_3Cl_{10}^-$. This differentiates the reaction between aluminum chloride and *tert*-butyl chloride from the reaction between activated aluminum and *tert*-butyl chloride: the main product of the latter is $AlCl_4^-$.

According to GC/MS data, the main gas-phase components observed in the reaction between activated aluminum and *tert*-butyl chloride are isobutane (~31 rel. %), hydrogen chloride (~22 rel. %), unreacted *tert*-butyl chloride (~40 rel. %), air (~5 rel. %), and minor amounts of isobutene (<2 rel. %). The major liquid products are 2-chloro-2-methylbutane (~17 rel. %), 2-chloro-2,3-dimethylbutane (~16 rel. %), and 2-chloro-2,5,5-trimethylhexane (~18 rel. %), as well as unreacted *tert*-butyl chloride (~49 rel. %). The presence of these hydrocarbons is confirmed by ^{13}C NMR data.

The presence of chlorinated hydrocarbons with different numbers of carbon atoms can be due to *tert*-butyl chloride conversion proceeding via the formation of radicals [7] or carbene on the surface of activated aluminum [31].

A GC/MS analysis of the resinous products after their hydrolysis indicated the presence of a wide variety of cyclopentadiene and cyclohexa-1,3-diene derivatives. The formation of these compounds is likely due to the conversion of isobutene, a product of the reaction examined, via conjugated oligomerization on the resulting aluminum chloride complexes [10]. Similar alkene conversion processes occur under the action of concentrated sulfuric acid [32] or sulfated zirconia [33].

CONCLUSIONS

Although there is long induction period in the interaction between activated aluminum and *tert*-butyl chloride, this reaction continues until the complete dissolution of the metal, yielding gaseous, liquid, and resinous products. Due to the continuous generation of $[Al_nCl_{3n+1}]^-$ (n = 1, 2) ionic complexes on the aluminum surface, the dominant route of the reaction is the conjugated oligomerization of isobutylene, an intermediate compound.

The ability of activated aluminum to react with chloroalkanes opens up the possibility of carrying out isobutane alkylation with butenes on this catalyst. This can be done, e.g., in the presence of a controllable amount of *tert*-butyl chloride owing to the in situ formation of aluminum chloride complexes of different compositions.

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