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Characterization of Isobutylaluminoxanes by Electrospray Ionization Mass Spectrometry

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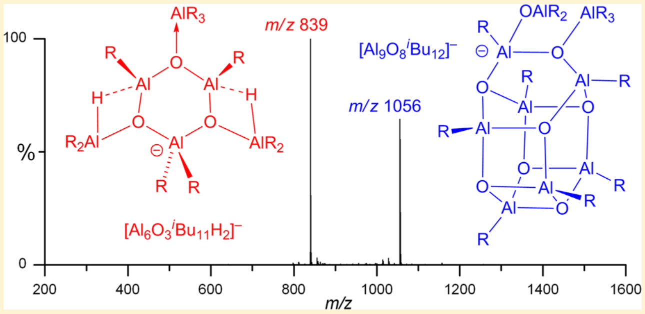
S *Supporting Information*

ABSTRACT: Mass spectrometric analysis of aluminoxanes is difficult due to their high reactivity, thermal instability, involatility, and propensity to form complex mixtures of oligomers. However, the controlled hydrolysis of fluorobenzene solutions of triisobutylaluminum provides surprisingly simple electrospray ionization mass spectra (ESI-MS), consisting of just two main charged species. The most abundant of these can be characterized as $[Al_3O_3{}^iBu_4(Al^iBu_2H)_2(Al^iBu_3)]^-$, using a combination of m/z value, isotope pattern, MS/MS studies, and isotopic labeling.



INTRODUCTION

Alkylaluminoxanes are an important family of organoaluminum compounds formed by the partial hydrolysis of aluminum alkyls[1] or e.g. reactions of carbonyl compounds, including CO_2, with aluminum alkyls.[1b] They find use as Lewis acidic catalysts of ring-opening polymerization and as additives or initiators of anionic and free radical polymerization,[2] but by far their most important use is as cocatalysts for coordination polymerization using transition-metal catalysts. Poly(methylaluminoxane) (PMAO) is widely used for this purpose[3] along with hydrocarbon-soluble versions known as modified methylaluminoxanes (MMAO), which are formed by step growth, copolymerization of trimethylaluminum (TMA) and higher aluminum alkyls such as triisobutylaluminum (TiBAl), or modification of PMAO by TiBAl.[4] Discrete aluminoxanes such as tetraisobutyldialuminoxane, $({}^iBu_2Al)_2O$, also find use as cocatalysts,[5] and in some cases the aluminum alkyls themselves are reported to be effective cocatalysts in olefin polymerization using metallocene or other single-site polymerization catalysts.[6]

The fundamental chemistry involved in activation of metallocene complexes with aluminoxanes is reasonably well understood to involve alkylation (eq 1) followed by ionization (eq 2),[7] where it is known that the most active catalysts of this type feature very weakly coordinating counteranions (WCA).

$$\begin{array}{c}Cp_2ZrCl_2\\ +\\ (MeAlO)_n{\bullet}AlMe_3\end{array} \longrightarrow \begin{array}{c}Cp_2ZrCl(Me)\\ +\\ (MeAlO)_n{\bullet}AlMe_2Cl\end{array} \qquad (1)$$

$$\begin{array}{c}Cp_2ZrCl(Me)\\ +\\ (MeAlO)_n{\bullet}AlMe_2X\\ X = Cl \text{ or } Me\end{array} \rightleftharpoons \begin{array}{c}[Cp_2ZrMe]^+\\ [(MeAlO)_n{\bullet}AlMe_2X_2]^-\end{array} \qquad (2)$$

Structural work on monoalkylaluminoxanes was first reported by Barron and co-workers, who showed that sterically hindered *tert*-butylaluminoxanes possess cagelike structures with tetrahedral aluminum and pyramidal oxygen.[8] Some of these compounds were found to activate metallocene complexes toward olefin polymerization,[8b] indicating a latent Lewis acidity based upon cleavage of strained Al–O rings, so as to generate ion pairs as indicated in eq 2. The study of this process, as well as the structure of aluminoxanes of this type, has been investigated both experimentally by a variety of techniques[9] as well as theoretically.[10]

In view of this established chemistry, the observation that simple alkylaluminum compounds can be used to activate metallocene complexes, presumably in a similar manner, is somewhat counterintuitive. The Lewis acidity of these compounds is significantly lower in comparison with discrete activators such as $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$, which are known to irreversibly ionize dialkylmetallocene complexes.[7] That is, the equilibrium in eq 2 is expected to lie well to the left, favoring the neutral precursors in the case of simple AlR_3 and, to a lesser extent, the more Lewis acidic R_2AlCl byproduct formed when using metal chloride complexes.

However, one expects that the partial, adventitious hydrolysis of AlR_3 (or R_2AlCl) does generate more Lewis acidic compounds such as $(R_2Al)_2O$ and $(RAlO)_n$ and therefore the study of this process as well as of the hydrolyzed products themselves is of some interest. Unfortunately, because of facile redistribution reactions and the limited number of spectroscopic methods for characterizing these air- and moisture-sensitive compounds, our understanding of the chemical nature of this class of compounds remains somewhat incomplete.[1a]

In particular, prior studies which have focused on the hydrolysis of TiBAl demonstrate that a 2:1 ratio of Al to H_2O leads to the production of $({}^iBu_2Al)_2O$, while oligomeric aluminoxanes $({}^iBuAlO)_n$ are formed at a 1:1 ratio or at higher

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temperatures.[11] The former compounds, when unhindered, adopt a cyclic, trimeric structure in solution,[12] while the latter are thought to possess cage structures analogous to those found for *tert*-butylaluminoxanes. In one recent study, a mixed isobutylaluminum hydride—aluminoxane cluster was isolated in low yield and fully characterized by X-ray crystallography following crystallization on long-term storage of $(^{i}Bu_2Al)_2O$.[13]

Predictably, few mass spectrometric studies have been performed on monoalkylaluminoxanes. In addition to the obvious handling issues, polymeric aluminoxanes are involatile[14] and are compatible with few matrices.[15] Electrospray ionization (ESI) and related desolvation techniques have different problems; a solution technique, ESI-MS, requires samples to be soluble and stable in polar solvents (or adulterated nonpolar solvents)[16] and to either carry a permanent charge (+ or −) or readily acquire one through a variety of processes.[17] Additionally, the instrument itself also needs to be completely free of oxygen and moisture to prevent decomposition of air-sensitive samples. These problems conspire together to prevent experiments resulting in sensible results. In fact, we are aware of only one prior ESI-MS study of PMAO in THF, a donor solvent, where the positive ion spectrum was said to be dominated by oxidized MAO species (i.e., $[MeOAlO]_n$) and these problems were alluded to.[18] We have developed key methodological advances that have allowed us to investigate aluminoxane solutions: (1) anaerobic electrospray ionization mass spectrometry (ESI-MS), achieved through the direct coupling of a glovebox to the instrument,[19] and (2) pressurization of the source to prevent ingress of air. ESI sources are operated at approximately atmospheric pressure. However, we measured the source pressure and found it to be slightly below atmospheric (typically by about 1 mbar); therefore, we modified the source compartment so that it could be pressurized so as to prevent sample decomposition and attendant plugging issues. The halobenzenes PhX (X = Cl, Br) and 1,2-difluorobenzene have all been used as solvents in olefin polymerization.[20] Of the halobenzenes, fluorobenzene (FPh) is the most polar and most volatile, making it the best candidate to serve as a good ESI solvent. When it is distilled from P_2O_5, we have found it to be a reliable ESI solvent for reactive species that are otherwise compatible only with nonpolar solvents. It should be emphasized that in ESI-MS, only species which are charged or can readily accept a charge are sensitively detected, and these need not correspond to the major species present in solution. Indeed, given the inherent sensitivity of ESI-MS, charged analytes are readily detectable at sub-micromolar concentrations under favorable conditions in polar media.

■ RESULTS AND DISCUSSION

The first hydrolyzed trialkylaluminum examined was TiBAl. Used as a catalyst activator in its own right,[6c] as well as in conjunction with MAO in the form of MMAO, it is easier to handle than TMA or PMAO. In dry FPh, the ESI-MS spectrum of TiBAl (ca. 0.075 M) has low intensity but a good signal-to-noise ratio and contains two major peaks at *m*/*z* 840 and 874, while minor species are detected at *m*/*z* 798, 812, 832, 846, 974, and 1008 (see the Supporting Information). The ions at *m*/*z* 832, 846, 874, 974, and 1008, on the basis of their isotope patterns, possess one or two Cl atoms (*m*/*z* 1008). The relative intensities of these chlorine-containing ions in comparison to those of the other ions present were variable, depending on experimental conditions.

On the other hand, addition of water to TiBAl in FPh, initially at −78 °C followed by warming to room temperature, provides a strong and unexpectedly simple spectrum, consisting of two main peaks, at *m*/*z* 840 and 1056, with all other peaks present at abundances of a few percent of the base peak at most (Figure 1).

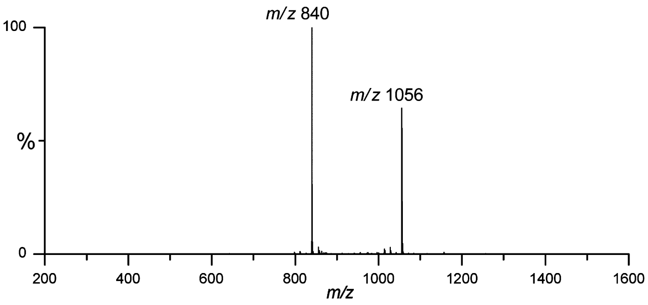


Figure 1. Negative ion mode ESI-MS of triisobutylaluminum in fluorobenzene after reaction with H_2O (ca. 0.5 equiv).

The reproducibility of this experiment was good, in that these were the only two major peaks that appeared under these conditions, though the relative abundance of the two peaks varied depending on the amount of water initially added. In particular, the peak as *m*/*z* 840 dominates at low water content (<0.5 equiv with respect to Al), whereas that at *m*/*z* 1056 is more resistant to hydrolysis and predominates when the Al:H_2O ratio approaches unity, while the TIC (total ion current) decreases with increasing $[H_2O]$ at constant [TiBAl] (see the Supporting Information).

Compositional data for the ion at *m*/*z* 840 are available from a combination of its *m*/*z* value and isotope pattern and from a search for chemically sensible combinations.[21] Searching for combinations of Al_{1-10}, O_{1-10}, and Bu_{1-14} alone provides only $[Bu_{10}Al_7O_5]$ within 0.5 Da, which is not a chemically sensible structure with a 1− charge. Given the precedent for forming DiBAlH in TiBAl solutions via reversible β-H elimination,[13,22] allowing 1−4 H in the formulas increases the number of possible hits, but most can be ruled out. The best chemically sensible match is $[Al_6O_3Bu_{11}H_2]^-$ with a monoisotopic mass of 839.66 Da, and the isotope pattern match for this species is also good. Isotopic labeling also assisted in the determination of the makeup of the ion. Addition of D_2O to the solution resulted in no change to the spectrum, suggesting that the ion does not contain −OH(D) groups. However, addition of $H_2{}^{18}O$ resulted in incorporation of up to three ^{18}O, confirming the O composition (Figure 2).

Limited but useful structural data can be obtained via MS/MS studies, wherein an ion is selected and subjected to collision-induced dissociation with argon atoms in the gas phase. Organometallic species typically fragment via loss of stable neutral molecules. The *m*/*z* 840 species fragments via loss of 198 Da ($AlBu_3$), 142 Da ($AlBu_2H$), and 56 Da (C_4H_8) (Figure 3). The lowest mass product ion is at *m*/*z* 133, corresponding to $[Al_3O_3H_4]^-$. This result suggests the presence of coordinated $AlBu_3$ and $AlBu_2H$ or groups that can readily react to form these neutral fragments and that β-elimination is a reasonably facile process at higher energy (loss of 56 Da).

All product ions can be accounted for by the structure(s) shown in Figure 4 of $[Al_3O_3{}^{i}Bu_4(Al^{i}Bu_2H)_2(Al^{i}Bu_3)]^-$ (see the Supporting Information for MS/MS assignments), which bear some similarity to the crystallographically determined structure

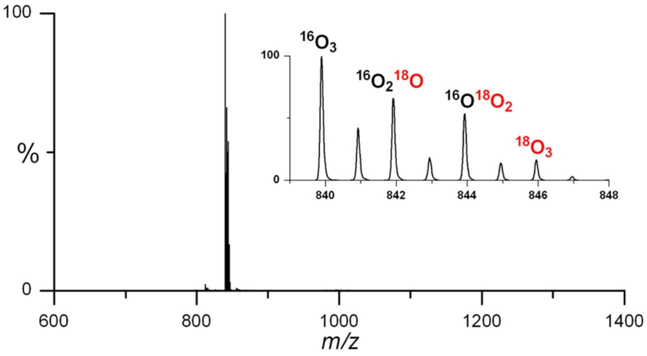


Figure 2. Negative ion mode ESI-MS of triisobutylaluminum in fluorobenzene after reaction with $H_2{}^{18}O$.

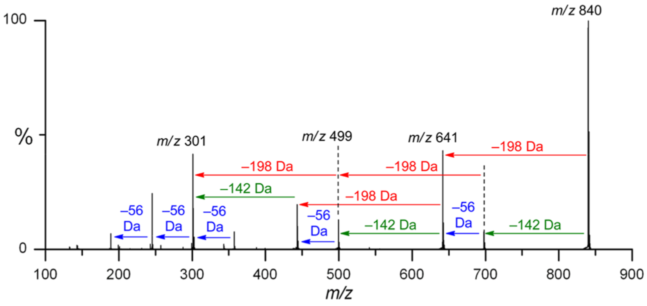


Figure 3. MS/MS analysis of the ion at m/z 840. All product ions can be assigned via loss of $AlBu_3$ (198 Da), $AlBu_2H$ (142 Da), and C_4H_8 (56 Da; see the Supporting Information for the fragmentation sequence).

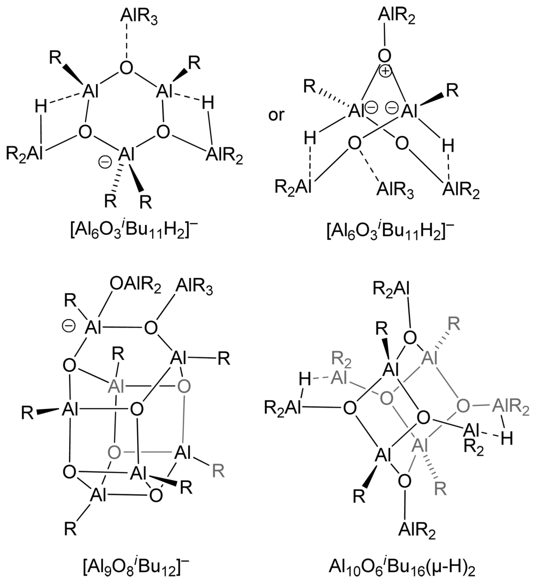


Figure 4. Possible structures for the $[Al_6O_3{}^iBu_{11}H_2]^-$ ion observed at m/z 840 (top) and possible cage structures[8] for the m/z 1056 ion (bottom left) and the crystallographically determined structure of the neutral aluminoxane $Al_{10}O_6{}^iBu_{16}(\mu\text{-}H)_2$ (bottom right; see ref 13) (R = ^{i}Bu in all cases).

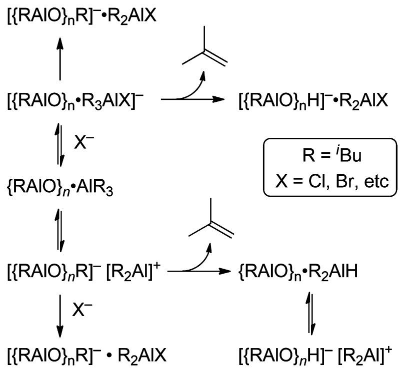
of the isobutylaluminoxane $Al_{10}O_6{}^iBu_{16}(\mu\text{-}H)_2$.[13] The R:Al:O ratio, the cyclic structure, and the presence of H and diisobutylaluminum groups are consistent in both cases. Evidently, the neutral precursor(s) to the m/z 840 ion corresponds to an aluminoxane with an R:Al:O ratio of 4:2:1 or qualitatively speaking a compound related to $({}^iBu_2Al)_2O$. We do note that the major, neutral compound formed under these conditions in solution (i.e., where $Al{:}H_2O \geq 2$) is the latter aluminoxane and that the six-membered, cyclic structure proposed for the m/z 840 anion is analogous to those proposed for unhindered compounds of this type. We also note this motif is commonly found in X-ray structures of e.g. anionic tetraphenylboroxine salts[23] and related organoaluminum compounds.[24]

MS/MS studies were also performed on the ion at m/z 1056 corresponding to $[Al_9O_8{}^iBu_{12}]^-$, and the results indicate easy loss of 2 equiv of TiBAl but no DiBAlH. The number of possible structures for a $[Al_7O_8{}^iBu_6(Al^iBu_3)_2]^-$ ion is large; the neutral precursor to this ion has a formula that corresponds to an isobutylaluminoxane with R:Al:O = 1.22: 1: 0.89. As mentioned in the Introduction, isobutylaluminoxanes are the major products formed at $Al{:}H_2O$ ratios of ∼1:1 and are thought to have structures analogous to those characterized by Barron and co-workers. Shown in Figure 4 is a possibility where an anionic $[(R_2AlO)_2AlR_2]^-$ moiety has been added to an $R_6Al_6O_6$ cage.

Given that the ion at m/z 840 dominates at low water concentrations, it is surprising to find that the other major ion present at trace levels of water appears to form via chlorination of the former—i.e., m/z 874 corresponds to $[Al_6O_3Bu_{11}HCl]^-$. Similarly, minor ions detected at m/z 798 $[Al_6O_4{}^iBu_{10}H]^-$ and 812 (possibly $[Al_5O_2(O^iBu)^iBu_{10}H]^-$) also have monochlorinated analogues at m/z 832 and 846, while other halogenated ions at m/z 974 and 1008 could correspond to $[Al_6O_4{}^iBu_{10}H]^-$ + $^iBu_2AlCl$ and $[Al_6O_4{}^iBu_{10}Cl]^-$ + $^iBu_2AlCl$, respectively. The source of these chlorinated anions appears to be trace levels of chloride anion present in FPh solvent and/or the mass spectrometer; for example, in some experiments where a sample of anhydrous $^nBu_4NX$ (X = Br, I) was used as a calibrant prior to measurement, ions at m/z 840 + Br − H = 918 and 920 in a 1:1 ratio, or m/z 840 + I − H = 966 were readily detected during initial flushing of the tubing and capillary with a solution of TiBAl in FPh.

Formation of an ion with m/z 840 can be rationalized by the presence of small quantities of DiBAlH (and isobutene) in equilibrium with TiBAl,[13,22] combined with the better bridging ability of hydrogen vs alkyl groups. The detection of chlorinated anions, particularly dichlorinated anions, of similar structure suggests that $^iBu_2AlCl$ must be formed in situ in the presence of chloride anion and is incorporated into these structures. One mechanism to account for the formation of $^iBu_2AlCl$ is for a Lewis acidic species (e.g., $AlR_2{}^+$ [25]) to react directly with trace halide ion (Scheme 1). An alternate

Scheme 1



mechanism is that halide ion reversibly binds to AlR_3 (free or sequestered by aluminoxane) and the resulting "ate" complex undergoes alkide or β-hydride abstraction.

This study illustrates the utility of ESI-MS to characterize aluminoxane species, namely the ability to provide compositional information as well as some structural data through MS/MS, by the identification of key groups. A somewhat unexpected result is that these compounds are sufficiently Lewis acidic that they readily scavenge anions such as halides, when present at trace levels, highlighting the very high sensitivity and utility of ESI-MS as an analytical method for their detection and identification.

■ EXPERIMENTAL SECTION

Fluorobenzene was purified by refluxing over P_2O_5 followed by distillation under N_2. Triisobutylaluminum was purchased from Aldrich as a toluene solution. Standard solutions of wet fluorobenzene were made up outside of the glovebox in Schlenkware and added to fluorobenzene solutions of triisobutylaluminum in the glovebox. All materials were handled in a glovebox connected to a Micromass QTof *micro* instrument with a Z-spray electrospray ionization source. The capillary voltage was set at 2900 V, and the source and desolvation gas temperatures were at 70−90 and 140−150 °C, respectively. The desolvation gas flow rate was typically 100−200 L h^{-1}. Samples were infused from a gastight syringe using a syringe pump located in the glovebox, typically at flow rates in excess of 20 μL min^{-1}. The source was pressurized to slightly above atmospheric pressure (+5 mbar) to avoid ingress of air. Mass-to-charge (m/z) values are reported to the nearest whole number.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving additional ESI-MS and ESI-MS/MS and spectral assignment. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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