Mass Spectrometric Characterization of Methylaluminoxane

Tyler K. Trefz, Matthew A. Henderson, Miles Y. Wang, Scott Collins,* and J. Scott McIndoe*

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC V8W 3V6, Canada

Supporting Information

ABSTRACT: Electrospray ionization mass spectrometric studies of poly(methylaluminoxane) (MAO) in the presence of Cp2ZrMe2, octamethyltrisiloxane (OMTS), or [Bu4N]Cl in fluorobenzene solution are reported. The results concur with the hypothesis that MAO is partially ionized in sufficiently polar media, where the contact ion pairs are of the general formula [Me2Al]\((\text{MeAlO}_x\text{AlMe}_y\text{Me})\]. A limited number of compositions of this type are detected; the most abundant has \(x = 23\) and \(y = 7\), where the cation \([\text{Me}_2\text{Al}(\text{OMTS})]^+\) (with \(m/z = 239\)) and the anion (with \(m/z = 1853\)) were detected in the presence of OMTS, which stabilizes the \(\text{Me}_2\text{Al}\) cation. The results demonstrate that MAO ionizes \(\text{Cp}_2\text{ZrMe}_2\) by acting as a source of this electrophilic cation, giving rise to an ion pair featuring a large and weakly coordinating aluminoxanate counterion.

MAO is made by the controlled hydrolysis of trimethylaluminum or by reaction of \(\text{AlMe}_3\) with, for example, C==O compounds,\(^4\) resulting in an oligomeric mixture that has defined definitive structural characterization. There are few diagnostic spectroscopic handles, and the MAO oligomers can interconvert in the presence of free \(\text{AlMe}_3\). Proton NMR studies have indicated that the empirical formula of the MAO repeat unit is \([\text{AlO}_{0.75-\alpha}\text{Me}_{1.4-\beta}^\alpha]\),\(^5\) while multinuclear NMR studies confirm the presence of tetrahedral AlMe groups and pyramidal O.\(^6\)

The X-ray structures of discrete tert-butylaluminoxanes (TBAO) reveal cages featuring tetrahedral Al and pyramidal O, and some of these were used to activate metallocene complexes for olefin polymerization.\(^7\) Analogous cage structures for MAO are supported by theoretical studies,\(^8\) while much larger, symmetrical cages have been studied for the parent aluminoxane (HAO),\(^9\) and it has been shown recently that extended structures, such as nanotubes, are favored over cages for MAO compared with TBAO.\(^10\)

The TBAO cages are known to undergo cleavage, due to “latent Lewis acidity” or ring strain,\(^7\) to afford contact ion pairs on reaction with metallocene complexes. In the case of MAO, similar behavior has been invoked,\(^2c,8\) with formation of more dissociated ion pairs, at sufficiently high Al:M ratios. The latter findings are based on extensive solution NMR, UV-vis, and other spectroscopic studies of the metallocenium ions formed in situ from metallocene complexes and MAO.\(^3,11\)

The hydrodynamic radius (\(r_h\)) and MW (molecular weight) of MAO, as well as the ion pairs formed from MAO and \(\text{Cp}_2\text{ZrMe}_2\), have been estimated by a number of techniques.\(^12\) Values of \(r_h\) between 7.5 and 9.7 Å and MW values between 0.5 and 3.0 kg mol\(^{-1}\) have been reported for MAO at ambient temperature. A larger value of \(r_h = 12–12.5\) Å has been reported for ion pairs derived from MAO.\(^12a\) The various, and disparate, estimates of MW vs size can be reconciled if the shape of MAO oligomers and the ion pairs derived from this material are not spherical.\(^10a\) In particular, for rigid-rod molecules with one long axis, \(r_h\) will approximate the length of this axis as the molecule randomly tumbles in solution, while MW scales with \(r_h\) instead of \(r_h^3\).\(^13\) What is required is a measurement of absolute MW for MAO or these ion pairs in solution to shed further light on this issue.

Electrospray ionization mass spectrometry (ESI-MS) is an obvious choice for detection of ions in MAO solutions, at least in polar media, but few MS studies of MAO have been reported.\(^14\) Repo and co-workers have reported detection of MAO using ESI-MS in THF and found that the positive ion spectra consisted of oxidized material.\(^15\) Analysis of metallocenium ions by ESI-MS, initially by Chen\(^16\) and later by Metzger,\(^17\) has shed light on the reactivity of the metal complex, but these studies were not concerned with the identity of the anionic components of MAO. We report here the first systematic, negative and positive ion studies of MAO by ESI-MS in fluorobenzene (PhF).

Received: March 26, 2013
Published: May 17, 2013
When a solution of MAO in toluene (1.54 M, Aldrich Chemical Co.) is diluted with anhydrous PhF to ca. 0.05 M and the solution injected into an ESI mass spectrometer under anaerobic conditions, the total ion current (TIC) is very low (<10 counts), consistent with a solution of nonpolar material containing few ions. On the other hand, addition of small amounts of an electrolyte such as [Bu₄N][Cl, or neutral additives such as 18-crown-6, octamethyltrisiloxane (OMTS), and Cp₂ZrMe₂, leads to a significant increase in negative ion intensity. At low levels of these additives the spectra are surprisingly simple, consisting of one major peak at m/z 1853 (Figure 1), with the other ions routinely detected summarized in Table 1.

It is important to point out that the same ions are detected, regardless of the nature of the additive. In particular, chlorine-containing ions do not predominate in mixtures of MAO + [Bu₄N][Cl, except at higher levels of added salt, and they appear to form via chlorination of the parent ions, as they are separated in mass by +20 Da (i.e., M–CH₃ + Cl; see, e.g., the ion at m/z 1873 in Figure 1a). It appears that some ions are more susceptible to chlorination than others. For example, the intensities of the ions at m/z 2157 and 2177 are nearly equal in Figure 1a vs the very different intensities for 1853 and 1873. There is a unique, chlorinated ion detected at m/z 1541 in the presence of [Bu₄N][Cl (Figure 1a) that may have no precursor ion and that is also very susceptible to further chlorination with ions detected at m/z 1561, 1581, and 1601 with 2, 3, and 4 Cl atoms, respectively. MS/MS experiments reveal that all chlorinated ions easily lose chlorine, as AlMe₂Cl, and at low collision energies (see Supporting Information).

In the presence of OMTS or Cp₂ZrMe₂ the spectra are similar (Figure 1b,c). In the positive ion spectrum, a single, intense peak at m/z 293 is observed in the presence of OMTS, whose nominal mass and isotope pattern are consistent with [Me₄Al(OMTS)]⁺. While the dominant ion observed in the presence of Cp₂ZrMe₂ is [Cp₂Zr(μ-Cl)AlMe₂]⁻, a discovery made when MAO solution came in contact with stopcock grease. The ion [(18-crown-6)AlMe₂]⁻ was observed in the presence of 18-crown-6 at much lower levels of this additive (see Supporting Information).

At higher levels of these additives, and at higher total [Al], doubly charged ions appear in the negative ion mass spectrum at m/z 800–1300 with an increase in complexity (see, e.g., Figure 1b). These doubly charged ions form at the expense of the higher mass, singly charged ions.

Finally, at sufficiently high levels of added [Bu₄N][Cl, phase separation due to ion-pair aggregation is observed (cloudiness at these concentrations). The TIC of the PhF phase decreases significantly, and the spectra are dominated by low molecular weight ions derived from AlMe₂Cl, AlMe₃Cl (formed in situ, vide infra), and ion clusters involving these ions (see Supporting Information).

Our interpretation of these events is as follows: At sufficiently low levels of additives, only the most reactive components of MAO form “free” or solvated ions, which are detected by ESI-MS, with the vast majority of species existing as neutrals or tightly bound ion pairs. As electrolyte or additive concentration increases, formation of solvated ions increases due to the increased dielectric constant of the medium or by ion exchange (vide infra); evidently, some of the anions that form can support an additional negative charge under these conditions. Finally, a liquid clathrate or aggregated ionic phase forms, and only the least Lewis acidic and neutral components, which remain in the PhF phase, are detectable.

These findings mean that the accepted view of MAO as a mixture of neutral Lewis acids that abstract halide or methide ions from neutral metalloocene complexes should be refined. Instead, a more consistent interpretation is that MAO serves as a source of [AlMe₂]⁺, which is the most reactive Lewis acid present in these mixtures. As [Bu₄N][Cl is titrated in, the available [AlMe₂]⁺ reacts with Cl⁻ to form AlMe₂Cl, leading to formation of less strongly bound [Bu₄N][MAO] ion pairs, which are more sensitively detected by ESI-MS. At sufficiently high levels of AlMe₂Cl, MAO and the derived ions are modified via redistribution reactions.

To assign a composition, each ion detected was selected for MS/MS studies, and their fragmentation patterns were analyzed. For example, the ion at m/z 1811 fragments with 10 successive losses of 72 Da as the collision energy is increased to its maximum value of 200 V (Figure 2). At higher collision energies, a second set of ions, also separated by 72 Da, but 16 Da lower in mass compared to the previous series is evident.

Figure 1. (a) ESI-MS spectra of MAO (0.037 M) and [Bu₄N][Cl (Al:Cl = 37:1), (b) MAO (0.055 M) and OMTS (Al:OMTS = 26:1), and (c) MAO (0.067 M) and Cp₂ZrMe₂ (0.23 mM, Al:Zr = 290:1) in PhF. Major singly charged ions detected are listed in Table 1.
Table 1. Summary of Singly Charged Anions Detected in MAO When Treated with Cp₂ZrMe₂, OMTS, or [Bu₄N]Cl

<table>
<thead>
<tr>
<th>obsd m/z</th>
<th>intensity (%)b</th>
<th>emp. formula</th>
<th>calc m/z</th>
<th>formula for anion based on [MeAl(O)₂⁺] +</th>
<th>MS/MS resultsc</th>
<th>formula for anion based on [(MeAl(O)₆)₃⁺] +</th>
<th>Me-Al-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1333.4</td>
<td>7.4</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1333.2</td>
<td>[Al₂O₃(MeAlO)₃(MeAl₃)₉]⁻</td>
<td>x = 19, y = 3</td>
<td>1.32:1.0:86</td>
<td></td>
</tr>
<tr>
<td>1375.4</td>
<td>6.6</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1375.3</td>
<td>[Al₂O₃(MeAlO)₉(MeAl₃)₁₀]⁻</td>
<td>x = 16, y = 6</td>
<td>1.59:1.0:73</td>
<td></td>
</tr>
<tr>
<td>1491.4</td>
<td>3.6</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1491.3</td>
<td>[Al₂O₃(MeAlO)₉(MeAl₃)₁₀]⁻</td>
<td>x = 18, y = 6</td>
<td>1.54:1.0:75</td>
<td></td>
</tr>
<tr>
<td>1695.5</td>
<td>1.3</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1695.2</td>
<td>[Al₂O₃(MeAlO)₉(MeAl₃)₁₀]⁻</td>
<td>x = 24, y = 4</td>
<td>1.32:1.0:85</td>
<td></td>
</tr>
<tr>
<td>1811.4</td>
<td>17.4</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1811.2</td>
<td>[Al₂O₃(MeAlO)₉(MeAl₃)₁₀]⁻</td>
<td>x = 26, y = 4</td>
<td>1.30:1.0:87</td>
<td></td>
</tr>
<tr>
<td>1853.4</td>
<td>100</td>
<td>C₈H₁₅Al₂O₉</td>
<td>1853.4</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 23, y = 7</td>
<td>1.30:1.0:77</td>
<td></td>
</tr>
<tr>
<td>2027.4</td>
<td>1.5</td>
<td>C₈H₁₅Al₂O₉</td>
<td>2027.4</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 26, y = 7</td>
<td>1.45:1.0:79</td>
<td></td>
</tr>
<tr>
<td>2115.5</td>
<td>1.2</td>
<td>C₈H₁₅Al₂O₉</td>
<td>2115.3</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 30, y = 5</td>
<td>1.31:1.0:86</td>
<td></td>
</tr>
<tr>
<td>2157.5</td>
<td>4.3</td>
<td>C₈H₁₅Al₂O₉</td>
<td>2157.4</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 27, y = 8</td>
<td>1.49:1.0:77</td>
<td></td>
</tr>
<tr>
<td>2173.5</td>
<td>1.3</td>
<td>C₈H₁₅Al₂O₉</td>
<td>2173.3</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 31, y = 5</td>
<td>1.31:1.0:86</td>
<td></td>
</tr>
<tr>
<td>2215.6</td>
<td>1.0</td>
<td>C₈H₁₅Al₂O₉</td>
<td>2215.4</td>
<td>[(MeAlO)₂₄(AlMe₃)₁₀]⁻</td>
<td>x = 28, y = 8</td>
<td>1.47:1.0:78</td>
<td></td>
</tr>
</tbody>
</table>

“Additional ions at m/z 1541 ([Al₂O₃(MeAlO)ₙ⟩₉(AlMe₃)₉(AlMe₂Cl)]⁻ according to MS/MS spectra, 1561, 1581, 1601 and at M+ 20 Da for the other ions listed are seen in the presence of [Bu₄N]Cl with a relative intensity dependent on salt concentration. See Figure 1a and text for discussion.

bRelative intensities are based on the spectrum depicted in Figure 1b and are given as percentages of the base peak. *MS/MS spectra indicate how many AlMe₃ or AlMe₃ equivalents are present; see text.

Figure 2. MS/MS spectrum of the anion with m/z 1811. Ten losses of 72 Da from the parent ion are indicated by red arrows with a second series of fragment ions occurring at ~16 Da, between m/z 1075 and 1507, depicted by blue arrows.

Evidently, these ions fragment by loss of AlMe₃, and also by loss of CH₄ at higher energy. We suspect some of the AlMe₃ lost arises via direct dissociation, while at higher energy, more elaborate rearrangements may be involved, as suggested in eq 3 for an aluminoxane fragment. We are unable to distinguish between genuine losses of AlMe₃ and those formed by rearrangement.

On the basis of these results, the anion at m/z 1811 can be formulated as [(Al₂O₃)(MeAlO)₉(AlMe₃)₁₀]⁻, consisting of an anionic aluminoxane core, decorated by 10 AlMe₃ groups. All of the ions characterized by MS/MS were analyzed in this fashion (see Supporting Information), and their resulting compositions are listed in Table 1.

As we accept that not all of the observed losses are genuine, and noting the mass relationship (AlOMe₃) ≡ AlO₃ + AlMe₃, an equivalent formulation for m/z 1811 is [(Al₂O₃)(MeAlO)₉(AlMe₃)₁₀]⁻. A more logical anionic fragment than [Al₂O₃]⁻ is [Me₃AlOAl(Me)O]⁻, the addition of Me⁺ to the simplest, cyclic aluminoxane, or the addition of AlMe₃ to [Al₂O₃]⁻. We can thus formulate this anion as [(MeAlO)₂₄(OAl(Me)OAlMe₂)⟩(AlMe₃)₉⟩⁻ or [(MeAl-O)₂₅(AlMe₃)₉]⁻, recognizing that two MeAlO units make up the anionic fragment. The last formulation corresponds to the classical view of MAO, with anions being formed via formal methide abstraction. These compositions are also listed in Table 1.

Although these compositions are somewhat arbitrary because we are not able to quantitate the amount of bound AlMe₃, it is satisfying to note that the composition of each ion is similar to the average composition of MAO determined by ¹H NMR spectroscopy (see Table 1). We note the compositions show considerable variation with respect to AlMe₃ vs MeAlO units (13–27 mol % AlMe₃) and the ions are not strictly ordered by their degree of polymerization given common mass differences of 42 vs 58 Da. We do note that those ions with the same number of MeAlO units, differing only in the amount of AlMe₃, at m/z 1811 and 2027, show the same fragment ions in their MS/MS spectra, confirming a structural homology.

Our results show that the anions (and ion pairs) present in PhF in the presence of [Bu₄N]Cl, OMTS, or Cp₂ZrMe₂ are much lower in MW than the estimate based on diffusion measurements in toluene. The negative ion spectra are largely invariant to additive levels below 1 mol %. We have not detected ions higher in mass than ca. 3500 Da. Our results are in good agreement with earlier estimates of MW for MAO itself, while the predominant ions have compositions that are similar to the average composition of MAO determined by ¹H NMR spectroscopy (see Table 1).

Future work, which will be guided by these initial results, will focus on anion and cation speciation in reactions of MAO with metalloocene complexes under catalytically relevant conditions (i.e., nonpolar media). In particular, ESI-MS should provide useful information relating to the amount of available [AlMe₃]⁺ present per mole of MAO under various conditions.

ASSOCIATED CONTENT

S Supporting Information

Experimental details; additional MS and MS/MS spectra of all ions detected. This material is available free of charge via the Internet at http://pubs.acs.org.
AUTHOR INFORMATION

Corresponding Author
*E-mail: mcindoe@uvic.ca, scottcollins@shaw.ca.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.S.M. thanks the donors of the American Chemical Society Petroleum Research Fund (49195-ND3), NSERC (Discovery, Discovery Accelerator Supplement, and Research Tools and Infrastructure grants), the University of Victoria, BCKDF, and CFI for operating and infrastructure support. S.C. acknowledges support for a Visiting Scientist position from the University of Victoria.

REFERENCES

(20) At low Al/Zr ratios the dominant ion present is the dinuclear cation [(Cp2ZrMe)2](μ2-Me)− with m/z 485 (see Supporting Information), in agreement with other studies.3,11
(25) There is no compelling evidence for facile halide abstraction from [Bu4N]Cl by a neutral species in these spectra. We thus believe that the ionization process does not involve direct methide abstraction from AlMe3 by MAO.
(26) The use of lipophilic ionic additives allows ESI-MS experiments to be conducted in apolar media such as toluene and hexane; however, of those previously reported,21 none are compatible with MAO.