New Method for the Determination of the Trialkylaluminum Content in Alumoxanes

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Summary: Alkylalumoxanes (such as methylalumoxane, MAO) can contain "free" trialkylaluminum (AlR_3). The relative ratio of the latter in any sample may be determined by ^{31}P NMR spectroscopy upon addition of excess PPh_3. The rapid exchange of free PPh_3 and $Me_3Al{\cdot}PPh_3$ results in the ^{31}P NMR signal being a weighted average from which an accurate determination of AlR_3 can be made, based on an external standard. This analysis method has been demonstrated for the determination of $AlMe_3$, $AlEt_3$, and Al^iBu_3 in methylalumoxane (MAO), ethylalumoxane (EAO), and isobutylalumoxane (IBAO) and bis(diisobutylaluminum oxide) (DBAO), respectively.

Introduction

Alumoxanes, $(RAlO)_n$, formed by the controlled hydrolysis of trialkylaluminum compounds, are used commercially as active catalysts and cocatalysts for the oligomerization and polymerization of olefins and epoxides. Although alumoxanes traditionally were proposed to be rings or chains containing three-coordinate aluminum, we have demonstrated that the primary species are cage compounds in which the aluminum is four-coordinate.[1-3] While we have isolated individual cage compounds for the *tert*-butylalumoxanes (e.g., $[(^tBu)AlO]_n$, $n = 6-9, 12$),[1,2] commercial alumoxanes, in particular methylalumoxane (MAO), are known to contain significant quantities of the parent trialkyl as a residue from the hydrolysis reaction.[4] Since the amount of $AlMe_3$ present has a significant effect on the catalytic activity of MAO,[5] it is of importance to determine accurately the quantity of $AlMe_3$ in any single sample of alumoxane.

There are at present a number of methods for the determination of content of $AlMe_3$ in MAO: (a) volatilization of $AlMe_3$, (b) ^1H NMR spectroscopy, and (c) titration of $AlMe_3$ with pyridine.[6] None of these methods give an accurate measure of $AlMe_3$ content due to a number of insurmountable issues.

The $AlMe_3$ present in commercial samples of MAO is present in two forms: *free* (i.e., Al_2Me_6) and *complexed* (i.e., $(MAO){\cdot}AlMe_3$). Removal of volatiles initially takes away the free $AlMe_3$. That more free $AlMe_3$ is observed on standing of a sample from which the $AlMe_3$ has been removed is due to the equilibrium between free and complexed trialkyl (eq 1).[7] Thus, the determination of

$$MAO + AlMe_3 \rightleftharpoons (MAO){\cdot}AlMe_3 \underset{-AlMe_3}{\overset{+Al^*Me_3}{\rightleftharpoons}} (MAO){\cdot}Al^*Me_3 \quad (1)$$

volatile aluminum content is highly dependent on the experimental conditions. The equilibrium between free and complexed $AlMe_3$ (eq 1) also precludes accurate integration of the ^1H NMR spectra, notwithstanding the pathological overlap of the $Al-CH_3$ peaks for $AlMe_3$ and $(MeAlO)_n$. Any methodology to determine $AlMe_3$ content must determine the total percentage of aluminum present as $AlMe_3$.

With respect to the pyridine titration method, the basic assumption is that complexation only occurs with the $AlMe_3$ and not the alumoxane. However, we have reported that the isolobal gallium sulfide cages react *via* cage cleavage with pyridine (eq 2),[8] and a similar

$$[(^tBu)GaS]_n + npy \rightarrow (n/3)[(^tBu)Ga(S)(py)]_3 \quad (2)$$

reaction is observed for alumoxanes.[1] The results of pyridine titration experiment are masked by side reactions. It is desirable, therefore, that any method for the determination of AlR_3 content should be specific for the trialkyl and preclude any reaction with the alumoxane.

Given the limitations of the analytical methods outlined above, we have developed a simple NMR method for the accurate determination of AlR_3 content in alumoxane solutions.

Results and Discussion

Rationalization of Method. Aluminum trialkyls react reversibly with triphenylphosphine to form a Lewis acid–base complex (eq 3).[9] While the equilibrium

$$AlR_3 + PPh_3 \rightleftharpoons R_3Al{\cdot}PPh_3 \quad (3)$$

constant for this reaction is dependent on the steric hindrance of the alkyl substituent, the reaction is sufficiently shifted to the right so that complexation is complete. This is true even if the parent trialkyl is dimeric, e.g., Al_2Me_6. In contrast to the cleavage of alkyl-bridged dimers, we have demonstrated that there is no reaction between PPh_3 and dimeric (or higher oligomeric) aluminum compounds where the bridging

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(5) Increased amounts of $AlMe_3$ in MAO have been shown to decrease the catalytic activity of MAO in a number of systems, including the ring-opening polymerization of β-lactones; see: Wu, B.; Lenz, R. W.; Harlan, C. J.; Barron, A. R. *Can. J. Biochem.*, in press.

(6) See: Jorden, D. E. *Anal. Chem.* **1968**, *40*, 2150 and references therein.

(7) It should be noted that the AlR_3 content in alumoxanes is also dependent upon the age of the sample.

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(9) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047.

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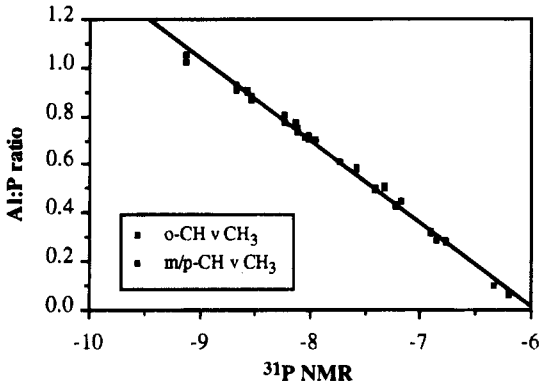

Figure 1. Plot of the ^{31}P NMR chemical shift of a mixture of $AlMe_3$ and PPh_3 in toluene-d_8 as a function of the Al:P ratio (R = 0.993).

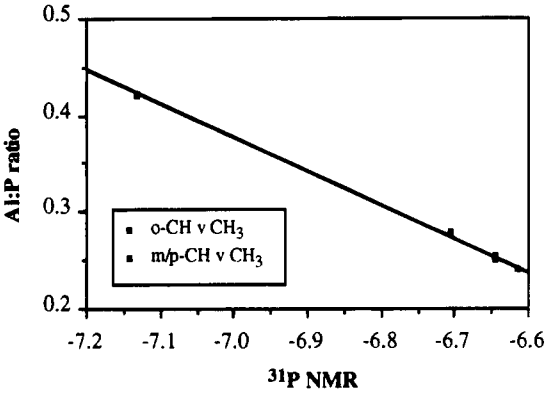

Figure 2. Plot of the ^{31}P NMR chemical shift of a mixture of $AlEt_3$ and PPh_3 in toluene-d_8 as a function of the Al:P ratio (R = 0.998).

ligand is an oxygen donor (e.g., oxide, alkoxide).[10] Thus, addition of PPh_3 to a mixture of $Al(^iBu)_3$ and $[(^iBu)_2Al(O^iBu)]_2$ results in complexation of the former and not the latter.

Addition of an excess of PPh_3 to a solution of $Me_3Al{\cdot}PPh_3$ shifts the equilibrium shown in eq 3. Thus, in the presence of an excess of PPh_3, essentially all the $AlMe_3$ will be complexed to the phosphine. An additional (concentration-independent) equilibrium between coordinated and free phosphine also is present (eq 4), such that the ^{31}P NMR spectrum of a sample

$$R_3Al{\cdot}PPh_3 + P^*Ph_3 \rightleftharpoons R_3Al{\cdot}P^*Ph_3 + PPh_3 \quad (4)$$

containing a mixture of $AlMe_3$ with an excess of PPh_3 will exhibit a single resonance whose shift is dependent on the $AlMe_3$:PPh_3 ratio. The relationship of the ^{31}P NMR spectral shift with respect to AlR_3:PPh_3 is shown in Figures 1 (R = Me), 2 (R = Et), and 3 (R = ^{i}Bu). The shift dependence was determined from a series of standard solutions (see Experimental Section). In each case, the absolute ratio was determined as an average from the integration of the phosphine *o*-CH signal versus the Al–alkyl signal and, independently, from the signal for the phosphine's *p*- and *m*-CH groups versus the aluminum–alkyl signal.[11] This assures the minimization of errors due to both partial hydrolysis and/or accuracy in integration of the ^1H NMR resonances. In

(10) Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949.

(11) The ^1H NMR signals for the triphenylphosphine *p*- and *m*-CH groups overlap and are observed as a broad unresolved multiplet.

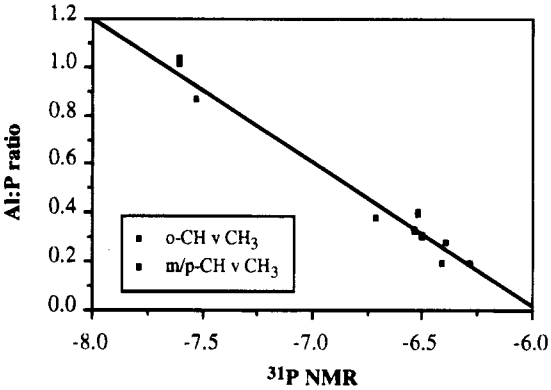

Figure 3. Plot of the ^{31}P NMR chemical shift of a mixture of $Al(^iBu)_3$ and PPh_3 in toluene-d_8 as a function of the Al:P ratio (R = 0.969).

each case, under conditions of excess PPh_3, there is a linear relationship between the Al:P ratio and the ^{31}P NMR shift. The relationships between the AlR_3 to PPh_3 ratio (Al:P) and the ^{31}P NMR shift (δ) are given in eqs 5–7. The concentration independence of these relationships was tested by the preparation of multiple samples of varying concentrations. Furthermore, there were found to be negligible differences with different solvents: hexane, heptane, benzene, and toluene.[12]

$$R = Me \quad Al{:}P = -2.0323 - 0.34148(\delta) \quad (5)$$

$$R = Et \quad Al{:}P = -2.0675 - 0.34921(\delta) \quad (6)$$

$$R = {}^iBu \quad Al{:}P = -3.5351 - 0.59143(\delta) \quad (7)$$

It should be noted that, unlike the complexation of group 13 alkyls with phosphine oxides,[13] the equilibrium shown in eq 3 is not frozen out at −80 °C, precluding the direct integration of free and complexed species.

Analysis of Alumoxanes. The relationships shown in Figures 1–3 have been used to determine the AlR_3 content of several commercial and synthesized alumoxane samples for which either the density and Al weight percent or the aluminum concentration was known.[14] A measured sample (5 mL) of alumoxane solution was added to an accurately weighed excess of PPh_3, and the mixture was allowed to reach equilibrium.[15] The ^{31}P NMR spectrum was obtained and the Al:P ratio determined. Since the total mass of PPh_3 is known and the proportion complexed to AlR_3 is calculated from eqs 5–7, then the mass (and/or molarity) of aluminum in the form of AlR_3 is readily calculated. The results for repeat runs of each sample are given in Table 1. From Table 2 it is clear that the internal precision of the technique is high: ±2% (R = Me).[16]

Two independent experiments are available to determine the validity of the phosphine approach. First, the

(12) Use of coordinating solvents, e.g., Et_2O and THF, should be avoided due to competing equilibria; see: Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830.

(13) Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1993**, *12*, 4908.

(14) The density and aluminum content, from which the total aluminum concentration can be calculated, are given for all commercial MAO samples. The aluminum concentration of "homemade" samples is readily calculated from the quantity of reactant employed.

(15) Separate NMR experiments indicate that equilibrium is reached within the mixing time of the solutions.

(16) Increased accuracy is obtained if an estimate of the Al:P ratio is made and the amount of PPh_3 added is proportioned to be *ca.* 1.5 greater.

Table 1. Analysis of AlR_3 in Samples of Alumoxanes

sample no.	alumoxane[d]	% Al as AlR_3
1[a]	MAO	43 ± 2
2[a]	MAO	48 ± 1
3[a]	MAO	36 ± 1
4[a]	MAO	52 ± 2
5[b]	MAO	25 ± 1
6[c]	MAO (no $AlMe_3$)	9.3 ± 0.1
7[b]	EAO	31 ± 1
8[a]	IBAO	5.4 ± 0.1
9[a]	DBAO	8.0 ± 0.1

[a] Commerical sample. [b] Synthesized by literature methods. [c] Volatiles removed from sample 2 under vacuum (10^{-3} Torr, 24 h). [d] Abbreviations: MAO = methylalumoxane, EAO = ethylalumoxane, IBAO = isobutylalumoxane, DBAO = bis(diisobutylaluminum oxide).

Table 2. Multiple Analysis of a Commercial MAO Sample[a]

run no.	vol of MAO soln[b] (mL)	amt of PPh_3 (g)	^{31}P NMR shift (ppm)	% Al as AlR_3
1	5.0	5.480	−7.013	46.9
2	5.0	5.108	−7.110	47.8
3	5.0	5.532	−7.045	48.8

[a] Sample 2 (see Table 1). [b] Conditions: toluene solution, 9.9 wt % Al, ϱ = 0.88 g cm^{-3}.

$Al(^iBu)_3$ content in a mixture with $[(^iBu)_2Al(O^iBu)]_2$ was determined using the ^{31}P NMR method described and direct integration of the ^1H NMR spectrum. On the basis of integration of the ^1H NMR spectrum, $Al(^iBu)_3$ was determined to be 45 ± 1% of the aluminum. A value of 45 ± 2% was obtained using the ^{31}P NMR spectral method. Second, an accurately measured additional quantity of $AlMe_3$ was added to a sample of a previously analyzed MAO sample prior to phosphine addition. The experimentally determined level of $AlMe_3$ was 55% of the total aluminum content, which compares favorably with the calculated "ideal" value of 54%.

The values in Table 1 are lower than those obtained for the same samples by the pyridine titration, consistent with our observation that pyridines readily cleave Al−O−Al moieties.[10] Furthermore, the values obtained for $AlMe_3$ content from the phosphine method are higher in comparison with those from the measurement of volatility, consistent with the observation of the incomplete removal of $AlMe_3$ from MAO solutions. The phosphine method may be used to determine the residual $AlMe_3$ in MAO from which the $AlMe_3$ has been "removed". A commercial sample of MAO was placed under vacuum (10^{-3} Torr) until no volatiles were collected in a liquid-N_2 trap. The sample was then analyzed by the phosphine method, and the $AlMe_3$ content was determined to be 9.3 ± 0.1% of the total aluminum content. The presence of $AlMe_3$ as opposed to another Lewis acidic species was confirmed by mass spectrometry.

It would appear, therefore, that the phosphine method for AlR_3 content determination is easier and more reproducible than previous methods. Furthermore, unlike previous methods, this is specific to AlR_3, is not affected by the presence of the alumoxane, and determines total (i.e., both "free" and "complexed") AlR_3 in an alumoxane solution.

Several additional points are worth making. First, it is clear that, unlike the *tert*-butylalumoxanes, samples of MAO contain varying quantities of $AlMe_3$. This obviously makes comparison of the catalytic activity of alumoxanes from different sources and/or batches difficult and further highlights the importance of accurately determining the AlR_3 content in alumoxanes. Second, the realtive AlR_3 content decreases with increased steric bulk of the aluminum alkyl (see Table 1), as exemplified by the absence of $Al(^tBu)_3$ in samples of TBAO (*tert*-butylalumoxane). Third, DBAO, which has been proposed to be a single species,[17] i.e., $[(^iBu)_2Al\{OAl(^iBu)_2\}]_2$, clearly contains residual $Al(^iBu)_3$.

Finally, note should be taken of two assumptions that must be made with regard to EAO, IBAO, and DBAO. First, EAO commonly contains a quantity of *n*-butyl groups. If $Al(^nBu)_x(Et)_{3-x}$ (x = 1−3) is formed, then substituent effects will cause a shift in the ^{31}P NMR from that expected for $Et_3Al{\cdot}PPh_3$. Second, the ethyl- and isobutylalumoxanes potentially contain Al−H groups. Since phosphines are known to cleave the $Al(\mu\text{-}H)_2Al$ unit,[18] the alkyl hydrides would complex to PPh_3 and cause a shift in the expected NMR resonance. However, given that these impurities are a minor constituent, they should not significantly change the accuracy of the analysis for AlR_3.

Experimental Section

All manipulation were carried out under an inert atmosphere of predried nitrogen or argon. Reference NMR spectra were recorded in toluene-d_8 on a Bruker WM-500. Shifts are reported in ppm relative to external $SiMe_4$ (^1H, ^{13}C) and external H_3PO_4 (H_2O) (^{31}P). Trimethylaluminum (TMA), isobutylalumoxane (IBAO), bis(diisobutylaluminum oxide) (DBAO), triisobutylaluminum (TBA), and triethylaluminum (TEA) were obtained from Akzo Nobel. Samples of methylalumoxane (MAO) were obtained from Akzo Nobel and Albemarle. Ethylalumoxane (EAO) and $Me_3Al(PPh_3)$ were prepared by following literature methods. PPh_3 (Aldrich) was recrystallized from EtOH prior to use.

Standard $AlMe_3/PPh_3$ samples were prepared in the drybox. $Me_3Al(PPh_3)$ (*ca.* 50 mg) was placed in a 5 mm NMR tube. To this was added PPh_3 (1−300 mg) and toluene-d_8 (*ca.* 1 mL). Standards with low PPh_3 were prepared by the addition of $AlMe_3$ to $Me_3Al{\cdot}PPh_3$.

Analysis of Alumoxane. In a typical experiment a measured sample of MAO solution (5.0 mL) with a known total aluminum content (sample 2, 9.9 wt %) is added to an excess of PPh_3 (5.108 g). The actual quantity of PPh_3 employed is not important; however, *ca.* 5.0 g measured to ±0.001 g is recommended. The resulting solution was stirred at room temperature for 2 h. An aliquot (*ca.* 1 mL) of the reaction mixture was then transferred to an NMR tube in which toluene-d_8 (*ca.* 0.2 mL) had already been added. The ^{31}P NMR spectrum was obtained at 25 °C. From the NMR spectral shift and the appropriate equation (R = Me; eq 5) the Al:P ratio was determined (0.395). Given the mass of PPh_3 used, the mass of PPh_3 complexed to $AlMe_3$ (2.0176 g) and, hence, mass of Al existing as $AlMe_3$ (0.2079 g) were determined. The percentage of the total aluminum content existing as $AlMe_3$ is thus obtained (47.8%).

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