

^{27}Al NMR study of the trimethylaluminum monomer–dimer equilibrium

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Abstract

The ^{27}Al NMR signal from trimethylaluminum (TMA) in solution is shifted to lower field with: (i) increasing temperature; (ii) decreasing concentration of TMA; and (iii), more markedly, the increasing solvating power of the solvent. This shift reflects an increase in the degree of dissociation of the dimer to the monomer. Thermodynamic data (K_d , ΔH_d , ΔS_d) of the TMA dissociation have been calculated from the observed values of the NMR chemical shift by use of the shifts estimated for the separate dimeric (Al_2Me_6) and monomeric (AlMe_3) species. In both solvents employed (n-heptane and mesitylene) the derived ΔH_d values lie between 11.2 and 14.7 kcal/mol for Al_2Me_6 , values in good agreement with the ΔH_d value of 13.4 kcal/mol previously determined experimentally. (These experimental values are lower than previously estimated ΔH_d values, which lay between 14.2 and 19.7 kcal/mol.) The ^{27}Al NMR spectra of TMA solutions recorded over the range of 25–100°C unambiguously proved the exchange of methyl substituents between bridge and terminal positions in the TMA dimer. In both aromatic and aliphatic solvents, this exchange occurs via the “intermolecular mechanism”, i.e. via the separated monomeric form of TMA; experimentally determined ΔH_d values are in accord with this mechanism.

Introduction

In spite of considerable attention paid to the study of trimethylaluminum (TMA), anomalies still exist in respect of the reversible dissociation of the dimeric to the monomeric form (eq. 1).



Accepted thermodynamic data, viz. $K_d = k_1/k_{-1}$, ΔH_d and ΔS_d , are available for equilibrium 1 in the gaseous phase [1,2], but, the equilibrium constants K_d had not until now been experimentally determined for solutions [3], and ΔH_d values have been estimated to be in the wide range of 14.2–19.7 kcal/mol [3–5]. The lower values in this range were estimated from the thermodynamic data associated with the temperature dependence of the saturated vapor pressure of TMA [4], and were found to be consistent with the ΔH_d values estimated [5,6] from ^1H NMR data for the exchange of methyl substituents between TMA and trimethylgallium, which were less than 15–16 kcal/mol. One of the higher values in the range, viz. ΔH_d ca. 19.4 kcal/mol, was derived by application of the thermodynamic “dissociation-vaporization” rule [3]. A similarly high value of ΔH_d was derived from ΔH_d for triethylaluminum (TEA), a questionable value of $\Delta H_{d(\text{TEA})}$ 16.9 kcal/mol being used to give an estimate for $\Delta H_{d(\text{TMA})}$ [3].

These estimated ΔH_d values have been adopted in the literature [7–10] and employed in further analysis [9–13], and the sole ΔH_d value, of 13.4 kcal/mol, experimentally determined up to now was thereby assumed to be anomalously low. This value was obtained by Hoffman [14] from a calorimetric investigation of the interaction of TMA with $(i\text{-Bu})_3\text{Al}$ in decalin. He concluded that monomeric $(i\text{-Bu})_3\text{Al}$ is changed (as a result of substituent-exchanges) on progressive addition of predominantly dimeric TMA into the predominantly dimeric mixed trialkylaluminums. Upon formation of the new associative $\text{Al}-\text{CH}_3-\text{Al}$ bond, the energy of 6.7 kcal/mol of these bonds is released, and this corresponds with the above mentioned ΔH_d value of 13.4 kcal/mol.

Recently, an ^{27}Al NMR spectroscopic study of triethylaluminum (TEA) allowed calculation of ΔH_d and other thermodynamic data for its dissociation [15]. We thought it likely that a similar approach to TMA would resolve the ambiguities in the thermodynamic data for this species and we present below the results of the investigation.

The values of ^{27}Al NMR parameters for TMA reported to date are as follows: (a) $\delta(^{27}\text{Al})$ 156 ppm, with $W_{1/2}$ 440 Hz for pure TMA [16], and (b) $\delta(^{27}\text{Al})$ 153 ppm with $W_{1/2}$ 850 Hz for 20–50% solution of TMA in toluene [17], both values being determined at ambient temperature.

Results

The ^{27}Al NMR spectra of two series of solutions of varying concentrations of TMA in n-heptane or mesitylene were recorded at various temperatures. The results (Table 1) show that (as for the TEA signal [15]) the TMA signal is shifted to lower field with: (i) decreasing concentration of TMA in both solvents; (ii) increasing temperature; and (iii), more markedly, increase in the solvating power of the solvent. These changes in the shift can be interpreted in the same way as those observed for TEA signal [15]; that is, with increasing dissociation of equilibrium 1, the number of four-coordinated Al atoms in Al_2Me_6 (resonating in the region δ_A ca. 155 ppm, see below) falls as the number of three-coordinated atoms in the monomeric form AlMe_3 (resonating in the region of δ_B ca. 265 ppm, see below) increases. These factors lead to a smooth downfield shift of the ^{27}Al NMR signal of TMA, from δ_A ca. 155 ppm to δ_B ca. 265 ppm, upon increased dissociation.

Table 1
 ^{27}Al NMR spectral data for solutions of trimethylaluminum (TMA) in mesitylene and heptane

Solution	Concentration (%)	Temperature ($^{\circ}\text{C}$)	δ^a (ppm)	$W_{1/2}^b$ (Hz)	Temperature ($^{\circ}\text{C}$)	δ (ppm)	$W_{1/2}$ (Hz)	Temperature ($^{\circ}\text{C}$)	δ (ppm)	$W_{1/2}$ (Hz)
mesitylene	44.2	23	154.5	1135	60	155.1	715	80	155.6	595
	21.4		154.5	1170		155.1	795		155.9	650
	11.4		154.6	1260		155.4	830		156.4	690
	3.1		154.7	1350		156.5	920		157.9	770
	1.5		156.0	1370		157.5	950		159.0	810
heptane	51.0	23	155.1	690	60	155.4	485	80	155.8	415
	36.0		155.2	680		155.5	480		155.8	420
	24.5		155.3	675		155.8	475		156.1	415
	7.4		155.5	665		155.9	480		156.4	425
	3.1		155.5	665		156.3	570		156.7	485

^a Chemical shifts δ (^{27}Al) are relative to external aqueous $\text{Al}(\text{OH})_3^{3+}$ (δ (^{27}Al) 0.0 ppm). The δ values shown are the average of at least three measurements. The estimation of the accuracy of δ is ± 0.1 ppm for 60–100 $^{\circ}\text{C}$, see Experimental part. ^b Line width at half height (Hz). The estimate of the accuracy of $W_{1/2}$ is ± 10 Hz for 60–100 $^{\circ}\text{C}$.

Within the concentration range used for both TMA and TEA [15] (approx. 1–50%) at the given temperature, the value of the ^{27}Al chemical shift quantitatively reflects the degree of dissociation (a), which decreases in the series: TEA(I) > TEA(II) > TMA(I) > TMA(II), where I denotes a solution in an aromatic and II that in an aliphatic solvent.

The results summarized in Table 1 reveal a rather complicated dependence of the halfwidth of the ^{27}Al NMR signals ($W_{1/2}$) upon the solvent, temperature, and the concentration of TMA. As suggested for TEA [15], this dependence presumably results from two competing processes: (a) a narrowing of the observed signal resulting from physical effects, principally an increase in the relaxation time arising from an increase of molecular movement of the solute with increasing temperature and decreasing viscosity of the medium [18,19]; and (b) a broadening of the signal resulting from a chemical effect, viz. the shift of the position of equilibrium 1 in favour of the monomeric form. This change is associated with a decrease in the number of species with a symmetrical tetrahedral arrangement of the Al nucleus, in the Al_2Me_6 dimer, in favour of species of lower symmetry of the planar environment of the Al nucleus, in the monomeric AlMe_3 form. During the rapid exchange of the positions of Al nuclei between the two forms, there is overall increase in the electrical gradient in the vicinity of Al nuclei and so of the signal broadening.

Calculation of thermodynamic data of equilibrium 1

The theoretical basis of the method used for calculation of the thermodynamic data for equilibrium 1 from the ^{27}Al NMR spectral data for TMA is that previously described for TEA [15]. In this treatment it is assumed that the appearance of a single ^{27}Al NMR signal for TMA is a result of rapid exchange between the monomeric and dimeric forms, so that equation 2 may be written

$$\delta = \delta_A P_A + \delta_B P_B \quad (2)$$

where δ is the observed chemical shift, δ_A and δ_B are the chemical shifts of the dimeric and monomeric forms, respectively, of TMA, and P_A and P_B are their respective populations. If δ_A and δ_B are known (see below), then $P_A (= 1 - P_B)$ may be calculated from eq. 2. Further, the equilibrium degree of dissociation (a) can be calculated from eq. 3:

$$a = \frac{P_B}{(2 - P_B)} \quad (3)$$

The equilibrium dissociation constant K_d can be calculated from the degree of dissociation by use of eq. 4:

$$K_d = \frac{4ac_0}{(1 - a)} \quad (4)$$

where c_0 (mol/l of Al_2Me_6) is the initial concentration of TMA.

Determination of values δ_A and δ_B

The unknown δ_A and δ_B values can be determined with sufficient accuracy for the calculation of a and K_d (eq. 2, 3 and 4) in the following way.

Table 2
Equilibrium constants ^a K_d and degrees of dissociation ^b α for solutions of trimethylaluminum in mesitylene and heptane

Solvent	Concentration (%)	Temperature (°C)	α (%)	$K_d \times 10^5$ (mol/l)	Temperature (°C)	α (%)	$K_d \times 10^5$ (mol/l)	Temperature (°C)	α (%)	$K_d \times 10^5$ (mol/l)	ΔH_d^c (kcal/mol)	ΔS_d^d (cal/mol.deg)
mesitylene	44.2	40	0.0	0.2	60	0.3	8.3	80	0.5	25.7		
	21.4		0.1	0.4		0.3	3.5		0.6	19.1		
	11.4		0.1	0.5		0.4	4.3		0.8	18.2		
	3.1		0.5	1.5		0.9	5.6		1.6	17.1		
	1.5		0.8	2.3		1.4	6.5		2.1	14.2	13.1	19.3
heptane			$\bar{K}_d = 1.0 \times 10^{-5}$ ($\sigma = 0.9 \times 10^{-5}$)			$\bar{K}_d = 5.7 \times 10^{-5}$ ($\sigma = 1.9 \times 10^{-5}$)			$\bar{K}_d = 18.9 \times 10^{-5}$ ($\sigma = 4.2 \times 10^{-5}$)		$\bar{K}_d = 35.9 \times 10^{-5}$ ($\sigma = 13.8 \times 10^{-5}$)	
	51.0	40	0.0	0.2	60	0.1	1.8	80	0.3	8.3		
	36.0		0.1	0.6		0.2	2.2		0.3	6.7		
	24.5		0.1	0.9		0.3	4.6		0.5	9.2		
	7.4		0.2	0.7		0.4	1.8		0.6	4.7		
	3.1		0.3	0.6		0.5	1.6		0.7	3.1	12.9	17.6
			$\bar{K}_d = 0.6 \times 10^{-5}$ ($\sigma = 0.2 \times 10^{-5}$)			$\bar{K}_d = 2.4 \times 10^{-5}$ ($\sigma = 1.3 \times 10^{-5}$)			$\bar{K}_d = 6.4 \times 10^{-5}$ ($\sigma = 2.5 \times 10^{-5}$)		$\bar{K}_d = 16.8 \times 10^{-5}$ ($\sigma = 4.1 \times 10^{-5}$)	
											(11.2–14.7) ^e	(13.0–22.3) ^e

^a Calculated from δ_A 154.5 ppm for mesitylene. ^b Calculated from δ_A 155.1 ppm for heptane. ^c Calculated from the interval of δ_A 154.4–154.6 ppm for mesitylene.

^d Calculated from the interval of δ_A 155.0–155.2 ppm for heptane. ^e Limiting values.

The assumption of the non-dependence on the solvent of the chemical shifts of pure monomeric and dimeric forms of trialkylaluminum, which was found to be suitable for TEA [15], needs modification for TMA. The reason is evident. The greater predominance of the dimeric form of TMA compared with that for higher trialkylaluminums [20], means that the observed δ (^{27}Al) values for the TMA signal are close to the value for the pure TMA dimer, i.e. δ_{A} . The calculations of the equilibrium data depend substantially on this δ_{A} value, which must therefore be determined separately for each solvent. Under the conditions favouring TMA association (lower temperatures and higher concentrations, i.e. tending towards 0°C and ca. 50% solution) the δ (^{27}Al) values fall asymptotically toward the limiting δ_{A} value for the dimeric form of TMA. Taking into account the errors in chemical shift determination (ca. ± 0.1 ppm), the limits of the initial δ_{A} values thus estimated are as follows: 154.4 ppm to 154.6 ppm for solutions in mesitylene, and 155.0 ppm to 155.2 ppm for those in n-heptane. The ca. 0.5 ppm upfield shift in mesitylene is consistent with the increased shielding of ^{27}Al nuclei in the TMA dimer caused by its solvation by aromatic compared with aliphatic solvents. (Interestingly, this contrasts with the behaviour of δ (^{27}Al) for $\text{Bu}_4\text{NAlEt}_4$, which does not significantly change on variation of the solvating ability of the solvent [21]). The mean values of the limits of δ_{A} values, i.e. 155.1 ppm in heptane and 154.5 ppm in mesitylene, were used for calculating the value of a and K_{d} listed in Table 2.

Because of the high degree of association mentioned above, the calculations of a and K_{d} are much less dependent on the initial δ_{B} value for the pure monomeric form of TMA. Consequently, the δ_{B} value of 265 ppm [15] (derived from the chemical shifts for predominantly monomeric AlR_3 trialkylaluminium compounds [17]) could be used for calculations in both solvents.

Calculation of ΔH_{d} and ΔS_{d} values

ΔH_{d} and ΔS_{d} values were calculated from the temperature dependence of K_{d} between 60 and 100°C in n-heptane and between 60 and 120°C in mesitylene. The ΔH_{d} and ΔS_{d} values listed in Table 2 represent the mean values of a set of ΔH_{d} and ΔS_{d} values calculated from eq. 2 by use of a series of initial δ_{A} values that varying by 0.02 increments within the limits of 154.4–154.6 ppm for mesitylene, and 155.0–155.2 ppm for n-heptane.

In addition to the mean values of ΔH_{d} and ΔS_{d} , the respective limiting values (i.e. maximum and minimum) are also listed in Table 2. These values were derived from the limiting values of the δ_{A} ranges used, thus illustrating the potential of ^{27}Al NMR spectroscopy as a technique for the calculation of thermodynamic data for equilibrium 1. Although it is generally assumed that ΔH_{d} in an aromatic solvent should be lower than that in an aliphatic solvent by the amount of heat released by solvation of the TMA monomer formed, we find comparable mean values for ΔH_{d} for both solvents, viz. 12.8 kcal/mol for n-heptane and 13.1 kcal/mol for mesitylene. However, the range of ΔH_{d} values calculated for heptane solutions (11.2–14.7 kcal/mol) is notably larger than that for these in mesitylene (12.2–13.9 kcal/mol).

Discussion of ΔH_{d} values

The ΔH_{d} values of ca. 13 kcal/mol calculated in this work are in good agreement with the only other experimentally determined of ΔH_{d} value of 13.7 kcal/mol [14]. These experimental ΔH_{d} values are lower than estimated high ΔH_{d} values of

14.2–19.7 kcal/mol [3–5]. Comparison of these estimated ΔH_d values with the activation enthalpy ΔH^* (ca. 15–16 kcal/mol [5,6,12,22]) for terminal-bridging methyl group exchange in the TMA dimer [23] previously led [12,13] to the conclusion that the exchange could proceed via two distinct processes: (a) an intermolecular mechanism occurring via the reversible process shown in eq. 1, which should dominate in aromatic solvents, for which the ΔH_d values of ca. 15–16 kcal/mol [4,5,13] (i.e. towards the lower limit of the range of the estimated ΔH_d values) is comparable with ΔH^* ; and (b) an intramolecular mechanism, occurring either (i) by the rupture of only one bridge bond in the TMA dimer with subsequent rotation and recombination of that dimer [22,23], or (ii) via a transition state with a looser structure described in terms of “solvent-caged monomers” or “monomer pairs” [5,6,9,12]. These mechanisms would proceed in aliphatic solvents, for which the ΔH_d values of ca. 19 kcal/mol [3] are higher than ΔH^* .

From this viewpoint, the range of “low” experimental ΔH_d values (i.e. 11.2–14.7 kcal/mol) now indicates the dominance of an intermolecular mechanism for the exchange of substituents in both solvent types. It is also evident that only these experimental ΔH_d values are in accord with the observed dependence of δ (^{27}Al) for TMA (in a given solvent and at a given temperature) on the initial TMA concentration c_0 shown in eq. 4. This suggests that the reversible reaction 1 is responsible for the intermolecular type of exchange, which was assumed by Ziegler [24] and Poole [18] to be the only mechanism operating. The findings also agree more satisfactorily with the interpretation of ^1H NMR kinetic data [5,6,9,10] for methyl groups exchange reported by Matteson [25,26] and by Brown and Murrell [10] than with the interpretation advanced by Jeffery and Mole [6,9]. The former authors assumed that wholly separated TMA monomers are involved both in bridge-terminal exchange of methyl substituents and in exchange of methyl groups between TMA and GaMe_3 , while the latter authors assumed that the “monomer pairs” in the solvent cage are responsible for the exchange. In view of the observation that ΔH_d is less than ΔH^* in all the solvents used, it is not necessary to limit the extent to which the rate of the GaMe_3 –TMA methyl exchange is controlled by the dissociation reaction in eq. 1 [26]. Thus, reaction 1 may be regarded as the wholly rate-determining step, as originally assumed in all the kinetic studies [5,6,9,10,25].

Comparison of the ΔH_d and ΔH^* values for TMA and TEA [15] leads to the conclusion that both the dissociation of dimer and the association of monomers (equilibrium 1) are activated processes with non-zero activation energy, i.e. $\Delta H^* = \Delta H_d + E'$, where E' is an activation energy of association process. It can evidently be assumed that dissociation of the TMA or TEA dimer is accompanied or quickly followed by solvation of the monomers, and so the reverse process (association) must be connected with desolvation of the monomers, which requires the activation energy E' .

On the other hand, there still remain discrepancies in respect of: (i) the precise nature of the rate determining process [5,6,9,10,25]; (ii) the values of the forward rate constant k_1 [5,6]; and (iii) the values of the equilibrium constants K_d ($= k_1/k_{-1}$, eq. 1), together with their temperature dependence. Like Jeffery and Mole [6,9], we can calculate k_{-1} at -50°C . Thus, from the expression $\ln K_d = -6490/T + 8.7$, obtained from our NMR data in heptane, it follows that $K_d(-50^\circ\text{C}) = 1.5 \times 10^{-9} \text{ mol l}^{-1}$. The forward rate constant k_1 determined from ^1H NMR data has been reported to be 10 s^{-1} at -50°C in cyclopentane [6]. Thus the reverse rate constant

Table 3

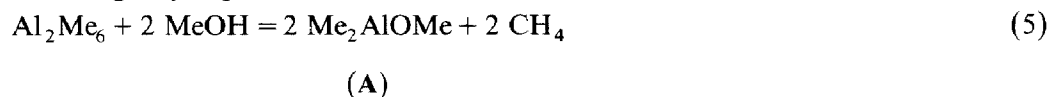
²⁷Al NMR spectral data for trimethylaluminum solutions in mesitylene and heptane after the addition of MeOH

Solvent	Concentration (%)	TMA/MeOH (mol ratio)	Temperature (°C)	δ (ppm)	<i>W</i> _{1/2} (Hz)	Rel. intensity (%)
mesitylene	9.0	1.8/1	25	154.1	1530	100
			100	152.1 ^a	740	45
				159.1	615	55
heptane	9.0	2.2/1	25	154.8	820	100
			100	153.0 ^a	470	43
				158.6	400	57

^a Signal assigned to methoxydimethylaluminum (A) formed according to eq. 5.

k_{-1} ($=k_1/K_d$) has a value of $5 \times 10^{12} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1}$. For comparison with this value of k_{-1} , the $k_{-1}(\text{max})$ value can be calculated (where $k_{-1}(\text{max})$ is the rate constant for association of monomers when this is controlled by diffusion). For this maximum rate we can write $r = 4DRc^2$ [28], where D is the diffusion coefficient ($D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [28]), R is the distance at which the monomers just react (a typical value of R being $4 \times 10^{-8} \text{ cm}$ [28]), and c is the monomer concentration. From this expression it follows that $k_{-1}(\text{max}) = 4DRN_A$ (where N_A is Avogadro number) and hence that $k_{-1}(\text{max}) = 7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This $k_{-1}(\text{max})$ value is, surprisingly, the same as k_{-1} calculated above from the K_d and k_1 values. These findings are thus at variance with our suggestion that association of the monomers is an activated process, in which k_{-1} can be expected to be much smaller than $k_{-1}(\text{max})$. Clearly further information in thermodynamic data and a detailed kinetic analysis, are required.

In order to avoid the possibility of erroneous interpretation of the ²⁷Al NMR data for the TMA solutions (which might give signals arising from oxidation products of the air-sensitive TMA), control samples were prepared in which the expected oxidation product, methoxydimethylaluminum (A), was generated purposely in the following way, eq. 5:



The results of these experiments are listed in Table 3. It is evident that corresponding low temperature ²⁷Al NMR spectra (ca. 25°C) show only one signal, but at higher temperatures the signals of both components (i.e. unchanged TMA and A) can be seen. The observed chemical shift $\delta(^{27}\text{Al})$ for A lies around 152–153 ppm, which is in good agreement with the value reported for the trimer of A [27] ($\delta(^{27}\text{Al})$ 152 ppm, in toluene at 37°C). It is also evident that the chemical shift of signal for A is temperature independent, and that the presence of A in the sample does not significantly affect the NMR behaviour of the TMA signal. All samples of TMA solutions employed in this study for investigating the equilibrium 1 gave no detectable signal for A.

Experimental

TMA was prepared by reaction of AlCl_3 with a 3 molar proportion of MeMgBr . The yield based on the Al content was 99%. The samples were sealed under argon in

10 mm diameter tubes along with a capillary containing an aqueous solution of $(\text{Al}(\text{OH})_2)_6\text{Cl}_3$, δ (^{27}Al) 0 ppm.

The ^{27}Al NMR spectra were recorded at 52.13 MHz with a Varian XL-200 spectrometer. The accuracy in the determination of the parameters of the broad ^{27}Al NMR signals (the range of linewidths reported in this paper varies from 400 to 1400 Hz) depends on the phasing of spectra, the base-line correction, and on the way in which the position of the peak is determined. Thus: (i) the transmitter offset (always adjusted so that ^{27}Al NMR signal would appear in the centre of the recorded spectrum); (ii) pulse width (α 15–20°); (iii) acquisition time (0.1–0.01 s); (iv) receiver gain (relatively low); (v) number of transients (no more than 2/3 of maximum); and (vi) preacquisition time (5–7 μs), were carefully selected to prevent distortion of the base-line. Under these conditions, the single TMA signal can be well represented by a Lorentz-type curve (the parameters of which were calculated by the non-linear least-squares method), and it was possible to observe the concentration and the temperature changes of δ (^{27}Al) NMR of the TMA signal with an estimated reproducibility of ± 0.1 ppm. This estimate was made for the temperature range 60–100°C for which thermodynamic data were calculated.

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