

²⁷Al NMR spectroscopy of triethylaluminum. A direct method to the determination of the proportion of monomer in solution

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Abstract

The sole ²⁷Al NMR signal of triethylaluminum (TEA) is shifted significantly to lower field with: (1) decreasing concentration; (2) increasing temperature; and (3) increasing polarity of the solvent; that is, in each case with an increase in the amount of the monomeric form. ²⁷Al NMR chemical shifts of Al₂Et₆ and AlEt₃ are estimated as 153 ± 2 and 265 ± 10 ppm, respectively. By use of these and observed values, thermodynamic data *K*_d, Δ*H*_d and Δ*S*_d were calculated for the dissociation of Al₂Et₆. The dependence of the monomer-dimer equilibria on the concentration of TEA in the solvents used indicated the participation of an "intermolecular" process in the exchange of bridging and terminal ethyl groups not only in aromatic solvents but also, in contrast to previous reports, in aliphatic hydrocarbons.

Introduction

Monomeric trialkylaluminum compounds, AlR₃, are strong Lewis acids. This property is a reason for their self complexation, the extent of which is greater the more sterically accessible the central Al atom is; the strongly dimeric character of trimethylaluminum [1,2] and largely monomeric character of tri-*sec*-butylaluminum [2] in hydrocarbon solvents illustrate this. An important member of the trialkylaluminum series is triethylaluminum (TEA), which can be expected to show less association than trimethylaluminum [1,2]. Since only the monomeric form of TEA is catalytically active in the polymerization of ethylene or α-olefines, detailed information on its dissociation under various conditions is important. The available data for the heat of dissociation (Δ*H*_d) of Al₂Et₆ to AlEt₃ are somewhat at variance [3,4], yet such data had an influence on proposals for the mechanism of terminal-bridge exchange of ethyl groups in TEA [5].

NMR spectroscopy is a useful technique for monitoring structural and dynamic properties of TEA in solutions [5-13]. A fast exchange of terminal and bridging

ethyl groups at ambient temperature and its decrease in rate with decreasing temperature was detected by ^1H NMR spectroscopy [6,7]. A mechanism for this exchange was discussed on the basis of an analysis of proton-decoupled ^{13}C NMR spectra [5]. Use of ^{27}Al NMR spectroscopy has led to determination of the dominant relaxation mechanism of ^{27}Al nuclei in TEA [8–10]. A comparison of effective correlation times calculated from ^{13}C and ^{27}Al NMR spectra for various centres of the TEA molecule allowed characterization of the molecular motion of TEA as well as that of its ethyl groups [11].

The fact that the chemical shift of ^{27}Al NMR signals gives information about the coordination of appropriate Al atoms [12,13] prompted us to study measurement of the extent of association of AlEt_3 , and related problems, by this direct method.

Results and discussion

The chemical shift of the ^{27}Al NMR signal of TEA has appeared several times in publications, as reported in a survey covering reports up to 1978 [12], and in a paper that appeared in 1983 [13]. The various values were very different, ranging from 142 to 171 ppm, but the discrepancies were not discussed.

In this study, in order to reduce errors and inaccuracies to an acceptable measure, TEA was prepared in two different ways, the absence of alkoxy derivatives was rigorously ensured, and the main measurements were repeated three times. The results (Table 1) reveal that the ^{27}Al NMR signal of TEA is shifted to lower magnetic field (to higher frequencies) with: (a) decreasing concentration of TEA in solutions; (b) increasing temperature, and (c) increasing polarity of the solvent in the order n-heptane < xylene < chlorobenzene (as indicated by the relative permittivities, ϵ_r^{20} , of 1.92, 2.52, and 5.71, respectively).

The presence of only one ^{27}Al NMR signal from TEA and its observed variation, especially the dependence of $\delta(^{27}\text{Al})$ on concentration, unambiguously indicate the existence of equilibrium 1, the right to left hand reaction of which is bimolecular. In this reversible process an increase in the degree of dissociation causes a decrease in the number of four-coordinated Al atoms (with $\delta 153 \pm 2$ ppm, see below), present in dimeric TEA and consequent increase in the number of three-coordinated Al atoms, present in AlEt_3 (with $\delta 265 \pm 10$ ppm), and thus there is a monotonic shift of the ^{27}Al signal to lower field:



The dissociation constant K_d for equilibrium 1 is given by the eq. 2:

$$K_d = \frac{4 a^2 c_0}{(1 - a)} \quad (2)$$

where a is the degree of the dissociation of the TEA dimer into the monomer, and c_0 refers to the concentration of TEA in moles of Al_2Et_6 /litre. For a system with a fast chemical exchange reaction 1, eq. 3 can be written:

$$\delta = P_{\text{A}}\delta_{\text{A}} + P_{\text{B}}\delta_{\text{B}} \quad (3)$$

Table 1

²⁷Al NMR spectral data for solutions of triethylaluminum in chlorobenzene (A), xylene ^c (B) and heptane (C)

Concentration (%)	Temperature (°C)	δ^a (ppm)	$W_{1/2}^b$ (Hz)	Temperature (°C)	δ (ppm)	$W_{1/2}$ (Hz)	Temperature (°C)	δ (ppm)	$W_{1/2}$ (Hz)				
A	53.1	25	154.3	3310	60	156.1	2165	80	157.7	1920	100	159.4	1600
	25.2		154.8	3000		158.1	2350		159.6	2070		161.8	1535
	15.9		155.0	2970		160.1	2300		164.1	2070		167.3	1580
	5.3		157.5	3190		165.5	2220		169.3	1900		175.5	1840
	2.6		159.8	3230		169.0	2415		176.0	2020		183.8	1820
B	29.4	25	155.3	3000	60	158.3	2060	80	160.2	1690	100	162.8	1380
	12.6		156.1	2940		159.4	2040		163.5	1680		166.9	1450
	7.0		157.6	2940		162.5	1980		166.2	1680		171.8	1480
	3.5		158.2	2920		165.9	2100		170.0	1620		179.2	1560
	1.3		160.0	3090		169.5	2240		179.1	1790		187.1	1890
C	45.0	25	154.5	2320	60	156.6	1590	80	157.3	1320	100	159.4	1150
	23.4		154.6	2030		156.9	1430		158.6	1080		161.2	990
	9.1		155.3	1820		158.2	1320		160.9	1060		165.7	950
	3.8		156.0	1760		158.7	1340		162.7	1080		169.2	940

^a Chemical shifts $\delta(^{27}\text{Al})$ are relative to external aqueous $(\text{Al}(\text{OH})_2)_3^{3+}$ ($\delta(\text{Al})$ 0.0 ppm). The δ values shown are the average of three measurements. The accuracy of δ for $W_{1/2} < 2000$ Hz = ± 1 ppm and for $W_{1/2} > 3000$ Hz = ± 2 ppm. ^b Line width at half height (Hz), the accuracy for $W_{1/2} < 2000$ Hz = ± 10 Hz, for $W_{1/2} > 3000$ Hz = ± 30 Hz. ^c Composition: 60% *m*-, 20% *p*- and 20% *o*-xylene.

where δ is the observed chemical shift of the ^{27}Al NMR signal, P_A is the proportion of four-coordinated Al atoms (in the dimeric species) and P_B the proportion of three-coordinated Al atoms (in the monomeric form), and δ_A , δ_B are their respective chemical shifts. By use of these chemical shifts, values of P_B and $P_A (= 1 - P_B)$ can be calculated from eq. 3 and the degree of dissociation a from eq. 4:

$$a = \frac{P_B}{(2 - P_B)} \quad (4)$$

The ^{27}Al NMR chemical shifts of the separate dimeric and monomeric forms of TEA, δ_A and δ_B , respectively, are unknown, but they may be estimated with sufficient accuracy for the calculations, as follows:

To the completely dimeric Al_2Et_6 form we assign the ^{27}Al NMR shift 153 ± 2 ppm on the basis of the following observations:

(a) The ^{27}Al signal of Al_2Et_6 converges under conditions that promote the association (i.e. decreasing temperature, increasing concentration, and decreasing polarity of solvent) to the limiting value 153–154 ppm (Table 1).

(b) Similar values were found for largely dimeric Al_2Me_6 , namely 153 ppm (20–50% in toluene) at 27°C [13] and 156 ppm in the pure state at 25°C [14]. (The change in alkyl groups has a negligible effect.)

(c) Almost identical values were found for tetraalkylaluminates, for which the nature of the alkyl group or the solvent again is of negligible influence; for example for NaAlMe_4 δ 154 ppm and for NaAlEt_4 155 ppm, both in THF, at 20°C [15].

The shift for the ^{27}Al resonance in monomeric AlEt_3 was estimated as 265 ± 10 ppm as follows:

(a) The chemical shift of the ^{27}Al nuclei in practically all monomeric trialkylaluminum species are very similar; e.g. *i*- Pr_3Al (256 ppm), *i*- Bu_3Al (276 ppm) and *t*- Bu_3Al (255 ppm) (all in 20–50% toluene solutions at 27°C [13]).

(b) It was assumed that the identity of the alkyl group has only a minimum influence on the chemical shift of planar AlR_3 ; this assumption is based on the observation that the structurally analogous BR_3 compounds show a remarkable insensitivity of $\delta(^{11}\text{B})$ shifts to the alkyl change; e.g. for BMe_3 δ 85 ± 1 ppm, BEt_3 85 ± 1 ppm, *i*- Pr_3B 85 ± 1 ppm, and *t*- Bu_3B 83 ppm [16].

The values of the degree of dissociation a and the dissociation constants K_d (Table 2) were calculated from eqs. 1, 2 and 3 by using these estimated shifts δ_A , δ_B and the chemical shift δ of TEA solutions observed under various conditions (see Table 1). Table 2 also shows the changes in ΔH_d and ΔS_d of the dissociation process represented by equilibrium 1, and calculated from the temperature dependence of the mean values K_d in the range of 60–100°C. Over such a narrow temperature range the ΔH_d values were considered to be constant for a particular solvent. This calculation of ΔH_d was based on an assumption that most of the three-coordinated Al atoms in the equilibrium TEA autocomplexes are presented in the AlEt_3 monomer, and only a very small fraction, if any, present as a linear dimeric species I (see Scheme 1) having only one three-coordinated Al atom.

The dissociation of TEA represented by equilibrium 1 is also reflected in the dependence of the width of the ^{27}Al signal in the half-height ($W_{1/2}$) on the concentration of TEA, on the temperature and on the polarity and the viscosity of the solvent (decreasing in the order *n*-heptane < xylene < chlorobenzene; values of μ^{25} are 0.041, 0.066, and 0.073 Pa s, respectively. The changes in $W_{1/2}$ are more

Table 2

Equilibrium constants ${}^a K_d$ and degrees of dissociation ${}^b a$ for solutions of triethylaluminum in chlorobenzene (A), xylene c (B) and heptane (C)

Concentration (%)	Temperature (°C)	$K_d \times 10^3$ (mole/l)	Temperature (°C)	$K_d \times 10^3$ (%)	Temperature (°C)	$K_d \times 10^3$ (%)	Temperature (°C)	$K_d \times 10^3$ (%)	ΔH_d^d (kcal/mol)	ΔS_d^e (cal/mol deg)
A	25	0.4	60	1.4	80	2.1	100	2.9		
	53.1	0.1		1.7		4.0		7.3		
	25.1	0.15		2.4		4.1		7.4		
	15.9	0.1		3.3		3.25		6.8		
	5.3	0.3		5.9		3.7		11.2		
	2.6	0.4		7.7		3.1		15.9		
		$\bar{K}_d = 0.2 \times 10^{-3}$		$\bar{K}_d = 2.9 \times 10^{-3}$		$\bar{K}_d = 6.0 \times 10^{-3}$		$\bar{K}_d = 11.3 \times 10^{-3}$		8.6
		$(\sigma = 0.1 \times 10^{-3})$		$(\sigma = 0.7 \times 10^{-3})$		$(\sigma = 1.7 \times 10^{-3})$		$\sigma = 3.3 \times 10^{-3}$		$(\sigma = 0.8)$
B	25	0.8	60	2.4	80	3.3	100	4.6		
	12.6	0.3		2.9		4.6		6.6		
	7.0	0.4		4.4		4.2		9.2		
	3.5	0.25		6.1		3.7		13.2		
	1.3	0.2		8.0		3.7		18.0		
		$\bar{K}_d = 0.3 \times 10^{-3}$		$\bar{K}_d = 1.9 \times 10^{-3}$		$\bar{K}_d = 4.2 \times 10^{-3}$		$\bar{K}_d = 8.6 \times 10^{-3}$		9.5
		$(\sigma = 0.1 \times 10^{-3})$		$(\sigma = 0.4 \times 10^{-3})$		$(\sigma = 0.4 \times 10^{-3})$		$(\sigma = 0.9 \times 10^{-3})$		$(\sigma = 0.6)$
C	25	0.4	60	1.6	80	2.0	100	2.9		
	23.4	0.1		1.8		1.8		3.8		
	9.1	0.1		2.4		0.6		6.0		
	3.8	0.1		2.6		0.4		7.8		
		$\bar{K}_d = 0.1 \times 10^{-3}$		$\bar{K}_d = 0.8 \times 10^{-3}$		$\bar{K}_d = 1.6 \times 10^{-3}$		$\bar{K}_d = 3.8 \times 10^{-3}$		10.5
		$(\sigma = 0.4 \times 10^{-3})$		$(\sigma = 0.4 \times 10^{-3})$		$(\sigma = 0.4 \times 10^{-3})$		$(\sigma = 0.7 \times 10^{-3})$		$(\sigma = 1.3)$

a,b Calculated from δ_A 153 ppm and δ_B 265 ppm. c Composition 60% *m*-, 20% *p*-, and 20% *o*-xylene. d,e Calculated from δ_A 151–155 ppm and δ_B 265 ppm, (60°C–100°C).

complex than those of $\delta(^{27}\text{Al})$, because of the operation of two opposing effects, viz.:

(a) Narrowing of the ^{27}Al NMR signal owing to an increase in mobility of TEA molecules as a result of increase of temperature and of lowering of the viscosity of the medium by dilution [9,10].

(b) A considerable broadening of the signal caused by an increase of electric gradient around the ^{27}Al nuclei due to the dissociation of TEA, i.e. to a transformation of a symmetrical tetrahedral (AlR_4) arrangement in Al_2Et_6 into a less symmetrical planar arrangement of the AlR_3 monomer.

An example of the influence of the two factors is the dependence of $W_{1/2}$ on concentration of TEA at a given temperature and solvent (see Table 1). This dependence is not monotonic, the $W_{1/2}$ values showing a minimum.

Inspection of the results in Table 2 reveals that the ΔH_d values decrease from heptane to chlorobenzene, reflecting promotion of the dissociation of TEA to the AlEt_3 monomer by an exothermic solvation by aromatic solvents. A similar trend with ΔS_d indicates an increase in ordering of molecules on solvation.

The published temperature expressions for equilibrium constants K_d of reaction 1 and ΔH_d and ΔS_d values can be divided into two categories. In the first, frequently used in the literature [e.g. 5, 17], $\ln K_d = -820/T + 16.2$ and $\ln K_d = -6696/T + 12.1$ in n-hexadecane (60–150 °C) and mesitylene (40–100 °C), respectively were obtained [18,19] with corresponding $\Delta H_d = 16.9$ and 13.3 kcal/mole of Al_2Et_6 . In the second, the temperature expression $\ln K_d = -4823/T + 7.45$ was found from the vapour pressure of TEA measured in the temperature range 60–120 °C [20]. By this method, ΔH_d was estimated to be 10.2 ± 1 kcal/mole of TEA, in excellent agreement with a value for ΔH_d of 11 ± 2 kcal/mole calculated from the data of Laubengayer and Gilliam [20,21]. These values of ΔH_d were used with good results to evaluate the Arrhenius parameters for the reaction of the TEA monomer with α -alkenes in the liquid phase [3,20,22].

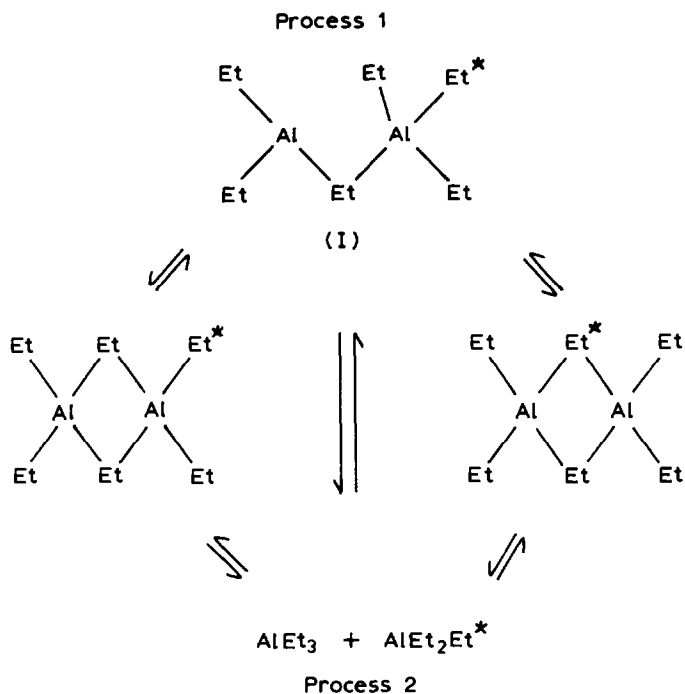
The data obtained independently in the present study support those obtained by the second approach above. For the equilibrium constants K_d in n-heptane (60–100 °C) we obtained $\ln K_d = -5284/T + 8.3$ and $\Delta H_d = 10.5$ kcal/mol Al_2Et_6 . Comparison of these data with those obtained in the gas phase is allowable since the heat of association of TEA with n-heptane and other aliphatic hydrocarbons is very small [18,19], and the enthalpies of the dissociation of TEA in the vapour phase and in aliphatic hydrocarbons can be assumed to be very similar.

ΔH_d values have played a great part in the discussion of the mechanism of the bridge-terminal exchange of the ethyl groups in TEA (Scheme 1).

A comparison of the activation energy for this exchange process $\Delta H_d^* = 15.5$ kcal/mol (valid in the interval -70 °C to -30 °C) [5] with the above-mentioned values of ΔH_d of 13.3 and 16.9 kcal/mol TEA for mesitylene and n-hexadecane, respectively, [18,19], led the authors concerned to conclude that different mechanisms of alkyl exchange within TEA predominate in aromatic and aliphatic hydrocarbon solutions [5]. For the former, predominant "intermolecular" mechanism, i.e. process 2 was favoured, while for the latter splitting and reorganization by an "intramolecular process", Process 1, was considered dominant.

Our results (obtained for the range 25 to 100 °C), in contrast, indicate that:

(1) There is sufficient monomeric AlEt_3 in aromatic as well as in aliphatic solvents to conclude that the "intermolecular" mechanism, process 2, must dominate in both types of solvent.



Scheme 1

(2) The enthalpy of reaction 1, ΔH_d , in both aromatic and aliphatic solvent is substantially less than the total activation energy ΔH_d^* [5]; this also favors the "intermolecular" alkyl exchange mechanism (process 2).

In the light of these facts, the ΔH_d^* and ΔH_d values and, especially, their temperature dependence, should be further investigated.

TEA is exceptionally sensitive towards oxygen. Inadequate care in manipulation can lead to its oxidation according to eq. 5:



The ^{27}Al NMR signal of the ethoxydiethylaluminum (II) appears in the region of 151 ppm [13], and so may interfere with the signal from TEA, and confuse the interpretation of the spectra. To throw light on the extent of errors which can arise from the presence of this compound, some TEA solutions were shaken with known amounts of dry air. The ratios of the amounts of atmospheric oxygen, and of TEA, and signals obtained are shown in Table 3. (The new ^{27}Al NMR signal is marked with an asterisk). It will be seen that at lower temperatures the signal from II is hidden by the strong signal from TEA. When the temperature is raised, an asymmetrical signal, made up of the signals from both TEA and II appears. The chemical shift of II is independent of temperature, and the presence of II does not influence the chemical shift of TEA. This indicates that II does not participate in the fast monomer-dimer exchange, but lowers the initial concentration of TEA. All

Table 3

^{27}Al NMR spectral data for solutions of triethylaluminum in xylene ^b (A) and heptane (B) after treatment with oxygen of the air

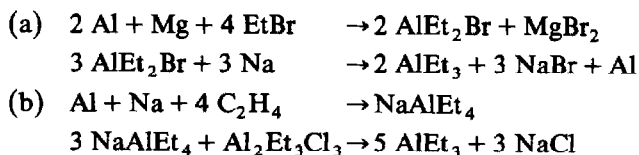
	Concentration (%)	TEA/O ₂ (mole ratio)	Temperature (° C)	δ^a (ppm)	$W_{1/2}$ (Hz)	I (%)
A	10	3.5/1	25	158.8	2850	100
			60	161.4	2260	100
			100	151.5*	1750	11
		2/1	25	169.7	1620	89
			60	156.0	2020	100
			100	150.7*	1320	17
	B	3.5/1	25	163.0	2380	83
			60	149.7*	1440	32
			100	172.7	1790	68
		2/1	25	156.0	2020	100
			60	158.3	1560	100
			100	150.7*	1200	19
B	3.5/1	25	163.9	1190	81	
		60	156.1	2240	100	
		100	152.4*	1290	38	
	2/1	25	160.3	1700	62	
		60	151.5*	1060	40	
		100	165.0	1220	60	

^a The ^{27}Al NMR signal marked with an asterisk is assumed to be from the ethoxydiethylaluminum produced by the reaction of triethylaluminum (TEA) with O₂. ^b Composition 60% *m*-, 20% *p*-, and 20% *o*-xylene.

the solutions used for the monomer–dimer equilibrium study described in this paper gave no Et₂AlOEt (II) signal.

Experimental

TEA was prepared in two ways, (a) and (b):



The yields based on the Al content from the two routes were 98.2 and 98.7%, respectively, and the ^{27}Al NMR spectra of the two products were identical. The samples were sealed under argon in 10 mm diameter tubes along a capillary containing an aqueous solution of (Al(OH₂)₆)Cl₃, $\delta(^{27}\text{Al})$ 0 ppm.

^{27}Al NMR spectra were recorded at 52.13 MHz with a Varian XL-200 spectrometer. To ensure the reproducibility of the values of $\delta(^{27}\text{Al})$ and $W_{1/2}$, optimum values of alpha delay, acquisition time (0.01 to 0.1 sec), and receiver gain (relatively low) were carefully selected. The transmitter offset was always adjusted so that ^{27}Al signal appeared in the centre of the recorded spectrum.

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