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SOLVENT EFFECTS ON THE PMR SPECTRUM OF LITHIUM TETRAMETHYLALUMINATE*

JOHN F. ROSS AND JOHN P. OLIVER
Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)

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SUMMARY

The PMR spectrum of $LiAl(CH_3)_4$ has been investigated in a series of different solvents as a function of concentrations and temperature. These studies suggest that in 1,2-dimethoxyethane (DME) the compound is highly dissociated while in non-polar solvents it is sparingly soluble and strongly associated. In tetrahydrofuran (THF) solution, which has intermediate solvating ability, the PMR spectrum is highly dependent upon both concentration and temperature. This is interpreted in terms of a solvent separated–contact ion pair equilibrium and the quadrupolar effects of the ^{27}Al nucleus.

$LiAl(CH_3)_4$ has also been shown to form a stable 1/1 complex with DME. When this adduct is dissolved in benzene solution the $[LiDME]^{+1}$ complex becomes associated with a benzene molecule as indicated by the PMR spectrum of the complexed DME which exhibits magnetic shielding from the benzene ring

INTRODUCTION

The simple Group IIIA "ate" complexes of the form $MM'R_4$ (M = Li, Na, K, Rb, Cs; M' = B, Al, Ga, In, Tl) have been known for some time. A number of studies dealing particularly with the chemistry of the boron and aluminum derivatives have been reported**. The structures of many of these compounds, including the aluminum derivatives of interest in this paper, have been determined by X-ray techniques[3,4], but only limited studies concerning their other physical properties have been reported. The structure of $LiAl(C_2H_5)_4$ may be interpreted in terms of an interaction or electron deficient bridge bonding between the Li^+ and ethyl group[3], whereas it is suggested that with larger alkali metal ions no tendency for metal–carbon–metal bridging exists[4]. Some interaction between the Li^+ and $Al(CH_3)_4^-$ (ref. 5) has been inferred from IR studies and confirmed by a measurable ^6Li–^7Li isotope shift on the C–H deformation modes in the IR spectrum[6].

Several PMR studies have been reported which show only line broadening

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** For reviews of some of these studies see refs. 1 and 2.

due to ^{27}Al–^{1}H coupling in poorly coordinating solvents such as diethyl ether[7,8] while in strongly coordinating solvents, such as DME, ^{27}Al–^{1}H coupling is observed[9]. These differences appear to be the result of the solvent's ability to coordinate and remove the lithium ion from the vacinity of the $Al(CH_3)_4^-$. When strong coordination occurs the symmetry around the ^{27}Al nucleus is high and ^{27}Al–^{1}H coupling is observed. As the symmetry is reduced by ion–ion interaction quadrupole induced relaxation occurs.

The current studies extend the investigation of the NMR spectrum to determine additional effects of solvent and temperature on the degree of solvent interaction and also provide evidence for Li^+–DME and Li^+–DME–benzene complex formation.

EXPERIMENTAL

$LiAl(CH_3)_4$ was prepared by two methods, first by the direct reaction of lithium metal with $Al_2(CH_3)_6$ either neat or in hexane solution similar to the reactions reported by Hein[10] and by von Grosse and Mavity[11] and discussed by Lehmkuhl[12]; or second, by addition of $LiCH_3$ to $Al_2(CH_3)_6$ as described by Hurd[13] and by Baker and Sisler[14]. The direct route involved the reaction

$$3\,Li+2\,Al_2(CH_3)_6 \rightarrow 3\,LiAl(CH_3)_4+Al$$

and was found to proceed slowly at room temperature yielding only 10–15% product after four days when hexane solvent was used. A poorer yield was obtained for the neat reaction with many side products. The material prepared by either of these reactions was purified by dissolution in DME, filtration and then removal of the DME under vacuum. $LiAl(CH_3)_4$ obtained in this way is a translucent solid. Solution in benzene and removal of this solvent under vacuum resulted in a product which retained one mole of DME per mole of lithium.

The second method proceeds quantitatively in diethyl ether to yield a white amorphous powder of high purity. Excess $Al_2(CH_3)_6$ was used to insure that no CH_3Li remained. The product was purified by removal of all solvent and excess $Al_2(CH_3)_6$ under vacuum, redissolving in ether and removal of most of this to yield a white powder which was filtered off and dried under 10^{-5} mm.

Trimethylaluminum was obtained from Ethyl Corporation, CH_3Li from Alfa Inorganics, and lithium from Lithium Corporation of America. All were used without further purification. Cyclopentane and benzene were dried over $Mg(ClO_4)_2$, methylene chloride over barium oxide, and all other solvents over sodium/potassium alloy.

Standard high vacuum techniques were used throughout except for sample transfer of solid materials which were accomplished in an argon filled drybox with a sodium/potassium alloy scavenger. PMR studies were made on a Varian A-60A spectrometer with a variable temperature probe and a Jeolco JNM 4H-100 MHz spectrometer. Chemical shifts were determined by standard audiofrequency sideband techniques from internal benzene or cyclopentane and are reported relative to TMS which is -7.07 or -1.50 ppm from the respective internal standards. The chemical shifts in tetrahydrofuran (THF), methylene chloride and benzene are concentration dependent. Shifts obtained by extrapolation to infinite dilution in these solvents are $+1.50$, 1.15 and 0.36 ppm respectively. For the $Al(CH_3)_4^-$ group the concentrations were determined in two ways, by direct weight of the solid $LiAl(CH_3)_4$

and by integration of the $Al(CH_3)_4^-$ resonance lines and comparison of this integral with that of a known concentration of benzene or cyclopentane present in the sample. They were also checked in some instances by integration of the solute and solvent and comparison of these values.

RESULTS AND DISCUSSION

The results previously obtained for $LiAl(CH_3)_4$ in both diethyl ether[7,8] and DME[6] were duplicated. Additional studies in DME also indicate that the spectrum collapses to one having four very broad maxima in saturated solutions. Studies on the ether solution from −75° to 36° showed only a single line with $\nu_{\frac{1}{2}}$ increasing from approximately 2 Hz to 3 Hz over this temperature range for a 1 molar solution.

In THF solution the PMR spectrum is highly concentration and temperature dependent. Fig. 1 shows some typical spectra with varying concentrations of $LiAl(CH_3)_4$. As can be seen the well resolved sextuplet merges and collapses to a single line with increasing concentration. The sextuplet shows coupling of 6.2 Hz while the line collapses to a $\nu_{\frac{1}{2}}$ of 3.6 Hz in a 2.7 molar solution. The line shapes are also quite temperature-dependent as seen in Fig. 1 for the 1.6 molar sample. All samples appear to collapse at low temperature, *i.e.*, −50 or below and undergo considerable modification in line shape at elevated temperatures.

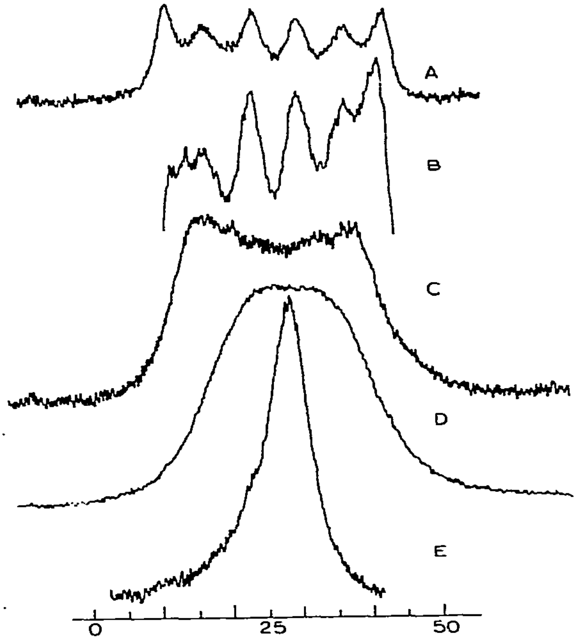

Fig. 1. The 60 MHz spectra of $LiAl(CH_3)_4$ in THF solutions as a function of concentration. The spectra were taken at ambient temperature (~37°) unless otherwise noted. A, 0.3 molal; B, 1.3 molal; C, 1.6 molal; D, 1.6 molal, −50°; E, 2.21 molal.

Two possible explanations must be considered for these observed variations in the PMR spectra. These are:

(1). Group exchange between different molecular or ionic species;

(2). Quadrupolar induced relaxation effects.

The first of these was discounted as a major factor for two reasons. The temperature dependence observed, *i.e.*, the decrease in line width with decreasing temperature, is opposite from that expected for an exchanging system. Secondly, observation of the same sample at both 60 and 100 MHz under the same conditions made no significant change in the appearance of the spectrum which again is contrary to the behavior of an exchanging system.

Quadrupolar relaxation does, however, account for both the temperature and concentration dependence of the THF solutions of $LiAl(CH_3)_4$ as shown by Pople[15]. A detailed calculation of line shapes and quadrupolar lifetimes will not be presented here, since Gore and Gutowsky[16] have dealt with this problem in detail. It is interesting to note, however, that the calculated intensities for the interaction of a spin $\frac{1}{2}$ nucleus interacting with one of spin $\frac{5}{2}$ made by Pople[15], for a system in which quadrupolar relaxation is slow, are fit relatively well by both the DME solution and dilute THF solutions of $LiAl(CH_3)_4$ as seen in Table 1.

TABLE 1

CALCULATED AND OBSERVED LINE INTENSITIES FOR A $I=\frac{1}{2}$—$I=\frac{5}{2}$ SYSTEM WITH SLOW QUADRUPOLAR RELAXATION

	Relative line intensities for $I=$					
	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
Dilute DME[a]	45	56	47	47	56	45
Dilute THF[a]	45	59	51	51	59	45
Calculated	45	69	54	54	69	45

[a] Observed lines were adjusted so that the outside lines were of equal intensity for all cases.

The line broadening and observed spectral changes in the more concentrated THF solutions are the result of the interaction between the ^{27}Al nucleus and an electric field gradient must be produced by the interaction between the Li^+ and $Al(CH_3)_4^-$ species. It has been suggested that this interaction arises upon the formation of contact ion pairs[8,16] through the equilibrium:

$$\begin{array}{lcl} Li^+, Al(CH_3)_4^- & \rightleftharpoons & Li^+ \| Al(CH_3)_4^- \\ \text{Contact ion pair} & & \text{Solvent separated ion pair} \end{array}$$

similar to that described for fluorenyllithium[18],*. The equilibrium constant for this defined as the ratio of solvent separated to contact ion pairs has been estimated as 100 in THF solutions[16].

The exact nature of the contact ion pair formed between Li^+ and $Al(CH_3)_4^-$ has not been determined by Williams and Brown[8] or Gore and Gutowsky[16], but from their data and that of Dixon[18] it appears that the lithium ion is coordinated if base is present. It has also been shown from IR studies [including observation of ^6Li–^7Li isotope isotope effects on the CH deformation modes in $Al(CH_3)_4^-$] that a direct interaction between the Li^+ and $Al(CH_4)^-$ in the solid, in hydrocarbon solution and in ether solution[5,6].

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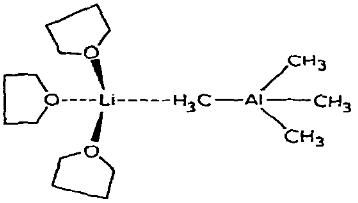
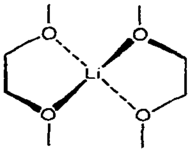
* A comprehensive discussion of contact ion pairs and solvent separated ion pairs is included in ref. 17.

It is proposed that the contact ion pair take the form:



in THF solution, including both coordination of the lithium ion by THF and the formation of a "very weak Li–C–Al bridge bond". In less effectively coordinating solvents fewer coordination sites might be occupied, resulting in still stronger interactions between the Li^+ species and the $Al(CH_3)_4^-$ ion which would further increase quadrupolar relaxation. The solvent separated ion pair could easily be accounted for by noting that if a fourth position is occupied on the Li^+ ion the distance between the Li^+ and $Al(CH_3)_4^-$ will be greatly increased and the field gradient decreased. Four coordination is even more likely when a chelating agent such as DME is present since it should readily form the complex:



Thus one can account for the sharp difference in the ability of the solvents to permit or prevent quadrupolar induced relaxation.

Further evidence for strong lithium coordination was found on examination of the $LiAl(CH_3)_4$ recrystallized from DME. This material, after drying at 50° under 10^{-5} mm for two days, has substantially different properties from that obtained from ether solution. It is a transparent, crystalline appearing material, soluble in benzene unlike pure $LiAl(CH_3)_4$. Integration of the PMR spectrum of both benzene and methylene chloride solutions showed that his material retained 1 mole of DME per mole of $LiAl(CH_3)_4$ (Table 2).

TABLE 2

PMR DATA ON THE COMPLEX OF DME WITH $LiAl(CH_3)_4$

Concn. (mole/l)	Solvent	Ratio DME/$LiAl(CH_3)_4$	Chemical shift (ppm)[a] of		
			CH_2	$CH_3(-O-)$	$Al(CH_3)_4$
0.862	C_6H_6	1.09	−2.89	−2.96	+0.568
0.766	C_6H_6	1.16	−2.83	−2.94	+0.483
0.105	C_6H_6	1.10	−2.75	−2.92	+0.400
0.0593	C_6H_6	1.20	−2.74	−2.92	+0.375
0[b]	C_6H_6		−3.40	−3.19	
0[c]	DME		−3.44	−3.26	
Saturated	DME	6.87	−3.61	−3.38	+1.32
0.290	CH_2Cl_2	1.25	−3.70	−3.55	+1.06
0.1	CH_2Cl_2	1.20	−3.69	−3.53	+1.06

[a] Relative to TMS, + indicates higher field; converted from internal standard C_5H_{10}. [b] Contains about 0.1 mole/l of DME in C_6H_6. No $LiAlMe_4$ present. [c] Pure DME containing about 0.1 mole/l of C_5H_{10}.

Table 2 also shows that the methyl and methylene groups of the complexed DME are shifted down field in a methylene chloride solution as expected for a complex or addition compound, but that in benzene solution they are both shifted upfield substantially and in fact now occur in reversed order with the methylene group at higher field.

In order to account for this behavior it is proposed that complex ion $[Li \cdot DME]^+$ undergoes further complex formation with a benzene ring as shown in Fig. 2. Since it has been shown that protons situated near the center of the ring are shielded while those near the plane of the ring are deshielded[19] this may be used to account for the observed upfield shift of the DME protons.

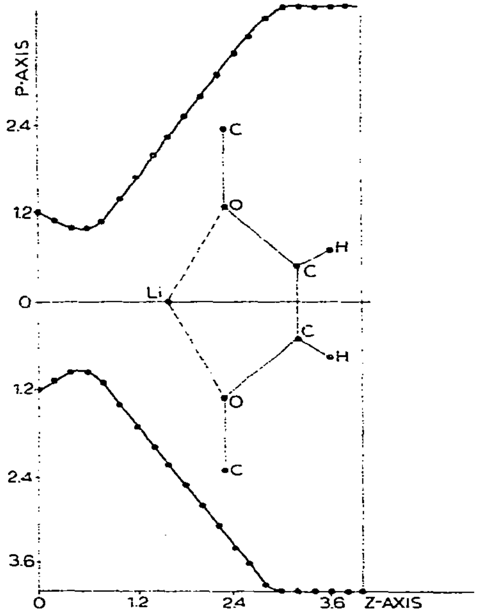


Fig. 2. Proposed structure and magnetic shielding effects in the $LiAl(CH_3)_4 \cdot DME \cdot$Benzene complex.

Johnson and Bovey[20] have tabulated these effects for a proton at any position relative to a benzene ring and these values have been used in the construction of Fig. 2, to demonstrate the effect of the formation of the benzene complex on the chemical shifts of the DME. In this figure, the P-axis represents distance from the center of the ring in a plane parallel to the ring. The Z-axis measures the perpendicular distance from the plane of the ring. Each unit is one benzene radius, 1.39 Å. The graph is drawn in such a fashion that the benzene is seen on edge, with the C_6 axis at $p=0$; *i.e.*, the diameter of the benzene ring (excluding the hydrogens) is projected on the P-axis from $p=+1.0$ to $p=-1.0$. For a given "z-value", the plot gives the maximum "p-value" for which a given proton will be shifted toward a higher field. It does not show the magnitude, but merely gives the direction of the shift.

For the sake of simplicity in the projection of the complex on this figure, assumptions have been made: (1) there is no distortion of bond angles, and (2) the DME group is exactly centered over the C_6 axis of benzene and is symmetric with respect to that axis.

The lithium–benzene and lithium–oxygen distances, each about 2 Å in Fig. 2, are arbitrary to be sure but fall reasonably within the limits of other well known benzenoid–metal complexes[21], and the known structures for DME metal complexes[22]. The nature of the ring current effect, however, places certain limitations on the total distance from benzene to the CH_2–CH_2 bond of DME. If this distance is appreciably greater than 3.2 z (4.5 Å), the upfield shift of the methylene protons becomes too small for the experimentally observed value. If the distance is made shorter, the methyl protons will actually be shifted downfield. The methyl protons, not shown in Fig. 2, experience some average shift as a result of the rotation of the methyl group.

The magnitude of the shift decreases more rapidly for increasing p values than for increasing z values. Thus, although the methylene protons are further away (have a greater z value) from benzene, they are closer to the center of the ring (smaller p value) than the methyl protons. The methylene protons will be shifted further upfield than the methyl protons.

To futher substantiate this, interpretation studies were carried out on methylene chloride solutions of the $LiAl(CH_3)_4 \cdot DME$. In this instance the spectrum of the $Al(CH_3)_4^-$ moiety was essentially the same as that observed in diethyl ether. At room temperature the half-width of the $Al(CH_3)_4^-$ peak was 4.0 Hz and at $-75°$ it decreased to 1.6 Hz. Examination of the downfield region (Table 2) showed the methyl and methylene protons of the DME shifted downfield from the position observed for free DME, as would be expected for a complexed ether. This suggests the DME is strongly complexed to the lithium ion in this solvent, and in the absence of benzene behaves in a "normal" fashion.

On the basis of these studies it may be concluded that $LiAl(CH_3)_4$ exists in a complex equilibrium of solvated contact ion pairs and solvated solvent separated ion pairs:

$$\text{Solvent}\cdot Li^+,\ Al(CH_3)_4^- \rightleftarrows Li(\text{solvent})_n^+ \| Al(CH_3)_4^-$$

with the equilibrium constant determined by the basicity of the solvent. With benzene present the $Li(DME)Al(CH_3)_4$ further interacts to give a Li·DME·benzene complex of the type indicated in Fig. 2. This system also indicates a strong concentration dependence for the $Al(CH_3)_4^-$ ion which indicates some additional solvent interaction with this ion.

REFERENCES

1 G. Wittig, *Quart. Rev. (London)*, 20 (1966) 191.
2 G. E. Coates and K. Wade, in *Organometallic Compounds*, Vol. 1, Methuen, London, 3rd ed., 1967, pp. 193–374.
3 R. L. Gerteis, R. E. Dickerson and T. L. Brown, *Inorg. Chem.*, 3 (1962) 872.
4 R. Wolfrum, G. Sauermann and E. Weiss, *J. Organometal. Chem.*, 18 (1969) 27.
5 K. Mach, *J. Organometal. Chem.*, 2 (1964) 410.
6 C. A. Wilkie and J. P. Oliver, unpublished observations.
7 D. J. Pasto and R. Snyder, *J. Org. Chem.*, 30 (1965) 1634.
8 K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 4134.
9 J. P. Oliver and C. A. Wilkie, *J. Amer. Chem. Soc.*, 89 (1967) 163.
10 F. Hein, E. Petzchner, K. Wagler and F. A. Seglitz, *Z. Anorg. Allg. Chem.*, 141 (1924) 161.
11 A. v. Grosse and J. M. Mavity, *J. Org. Chem.*, 5 (1940) 106.

12 H. Lehmkuhl, *Tetrahedron Lett.*, (1966) 2811.
13 D. T. Hurd, *J. Org. Chem.*, 13 (1948) 711.
14 E. B. Baker and H. H. Sisler, *J. Amer. Chem. Soc.*, 75 (1953) 5193.
15 J. A. Pople, *Mol. Phys.*, 1 (1958) 168.
16 E. S. Gore and H. S. Gutowsky, *J. Phys. Chem.*, 73 (1969) 2515.
17 (a) L. L. Chan and J. Smid., *J. Amer. Chem. Soc.*, 90 (1968) 4654.
(b) L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, 89 (1967) 4547.
(c) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.* 88 (1966) 318.
(d) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 88 (1966) 307.
18 J. A. Dixon, P. A. Gwinner and D. C. Lini, *J. Amer. Chem. Soc.*, 87 (1967) 1381.
19 J. W. Emsley, J. Feeney and L. H. Sutcliff, *High Resolution Magnetic Resonance Spectroscopy*, Vol. 1, Pergamon, London, 1965, pp. 140–145.
20 C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 29 (1958) 1012.
21 H. Zeiss, P. J. Wheatley and H. J. S. Winkler, *Benzenoid Metal Complexes*, Ronald, New York, 1966, p. 4.
22 G. W. A. Fowles, T. E. Lester and J. S. Wood, *J. Inorg. Nucl. Chem.*, 31 (1969) 657.