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ION-SOLVENT EFFECTS ON THE PMR SPECTRUM OF SODIUM TETRAETHYLALUMINATE

A NOVEL, LONG-RANGE, ALUMINUM–PROTON COUPLING*

T. D. WESTMORELAND, JR., N. S. BHACCA, J. D. WANDER and M. C. DAY**
Coates Chemical Laboratory, Louisiana State University, Baton Rouge, Louisiana 70803 (*U.S.A.*)

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SUMMARY

The PMR spectrum of $NaAlEt_4$ has been investigated in a number of solvents at the ambient temperature, and in THF as a function of temperature and concentration. In coordinating solvents, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), or 1,2-dimethoxyethane (DME), the PMR spectrum of $NaAlEt_4$ consists of an evenly spaced, 9-line pattern at high field and a more complex multiplet at somewhat lower field, assigned to the methylene and methyl resonances, respectively, of the ethyl groups. In a non-coordinating solvent (benzene) this spectrum appears as a broadened quartet and triplet, respectively, indicating that the two- and three-bond couplings of these protons to the aluminum nucleus have collapsed, leaving only the normal proton–proton splitting of the ethyl group pattern. By analogy to earlier studies, this solvent dependence is interpreted as resulting from a solvation equilibrium in which one observes a predominance of symmetric, solvent-separated anions in coordinating solvents, and of contact ion pairs (of lower symmetry) in the hydrocarbon. The pattern shapes in the PMR spectrum of $NaAlEt_3H$ in DME (which is thought to support solvent separation) are similar to those recorded for $NaAlEt_4$ in benzene, as expected on the basis of the effect of the degradation of symmetry about the aluminum nucleus.

K_{eq} for the dissociation of $NaAlEt_4$ into separated ion pairs in THF is smaller than for the corresponding dissociation of $LiAlMe_4$, but apparently larger than for $NaAlMe_4$. PMR signals observed for $NaAlEt_4$ in Et_2O exhibit the same pattern width as seen in DME but are of inferior definition and thus suggest that this solvent also supports solvent separation, although to a somewhat lesser degree than the other coordinating solvents.

INTRODUCTION

In principle, two approaches can be made to the study by NMR of solvation

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** To whom correspondence should be addressed.

processes[1]. To wit, one may examine the behavior of the solvent or of the solute. Study of the solvent (generally present in an overwhelming excess) is a convenient[2] but indirect method, whereas direct examination of the solute generally provides a more demanding but more incisive approach. One direct attack for investigating the solvation of alkali metal salts in nonaqueous media is to examine the nuclear magnetic resonances of the cationic species. Despite the complications that make the NMR study of such quadrupolar nuclei less attractive, researchers have reported results[3] obtained in this way. In favorable circumstances, however, the magnetic properties of protons of an organic or organometallic anion may reflect[4] the extent of interaction of solvent with the cation, and provide a more conventional alternative route for investigation of the solvation interactions.

Several authors have reported that a two-bond, ^{27}Al–^{1}H spin–spin coupling (^{2}J(Al, H)) observed in the PMR spectrum of alkali metal tetramethylaluminate salts is influenced by the nature of the solvent[4]. In solvents that function poorly as Lewis bases (*i.e.*, solvents that do not coordinate effectively with cations), the methyl proton resonance is observed as a broad ($\sim$2–4 Hz) singlet, whereas in a good coordinating agent (DME) it appears as a six-line pattern due to the spin–spin interaction of ^{1}H and ^{27}Al (^{27}Al has $I = 5/2$). The presence of this coupling has been interpreted[4b,c] as signifying at least a minimal condition of symmetry (T_d) on the NMR time scale ($\sim$1 s) about the aluminum nucleus. The ^{2}J(Al, H) interaction of $LiAlMe_4$ in THF is enhanced by dilution and, in an uncertain[4b,c] manner, by cooling. Solvent-separated ion pairs were, therefore, identified[4b] as the species having this symmetry.

The alkali metal tetramethylaluminate salts are, however, not ideal substrates for such studies, in that they require careful manipulative techniques and exhibit only modest solubility in nonethereal solvents. Sodium tetrabutylaluminate ($NaAlBu_4$) is more convenient to handle and is miscible in all proportions with hydrocarbon solvents, which would be suitable as noncoordinating bulk solvents for quantitative studies of the effect of added coordinating agents. Unfortunately, however, the PMR spectrum of $NaAlBu_4$ is too complex to permit the extraction of useful information. The corresponding tetraethylaluminate salt ($NaAlEt_4$) exhibits stability and solubility properties superior to those of $AlMe_4^-$ salts. Further, its PMR spectrum consists of two, well-separated patterns[5], which could provide structural information from ^{1}H–^{1}H or ^{27}Al–^{1}H couplings, as well as from chemical shifts.

Accordingly, we have extended our PMR studies on the solvation of the sodium cation in nonaqueous solvents[2b,6] by examining the influence of solvent properties on the NMR spectra of $NaAlEt_4$ and $NaAlEt_3H$. The latter compound was prepared in order to examine the importance of T_d symmetry in the anion because of its inability to exhibit tetrahedral symmetry about the ^{27}Al nucleus.

EXPERIMENTAL

The preparation of $NaAlEt_4$ was accomplished by adding commercial aluminum triethyl (114 g, Ethyl Corporation) to a dispersion of sodium (23 g, a slight excess) in toluene, according to the procedure of Frey *et al.*[7]. After 3 h, the reaction mixture was taken into a nitrogen atmosphere dry box, filtered free of residual solids, and cooled to induce crystallization of $NaAlEt_4$ as white needles. The solid was isolated by filtration, recrystallized from toluene, and dried *in vacuo*, giving $NaAlEt_4$, m.p. 125° (lit.[7] 123–124°; an alternative preparation gave[8] m.p. 125°).

$NaAlEt_3H$ was prepared in a dry box by addition of 2.4 g of NaH (53% by weight in mineral oil,Metal Hydrides, Beverly, Mass.) to a solution of 11.7 g (a slight excess) of aluminum triethyl in 200 ml of hexane, after the method of Zakharkin and Gavrilenko[9]. The solid $NaAlEt_3H$, which separated spontaneously upon mixing of the reactants, was filtered off and washed with hexane. The resulting fluffy white flakes melted over a narrow range near 64° (Zakharkin and Gavrilenko[9] reported m.p. 64°) and were used without further purification.

Manipulations were performed in a nitrogen atmosphere dry box according to techniques described previously[10]. Prior to use, all solvents were distilled over CaH_2 in a nitrogen atmosphere. Samples were prepared gravimetrically. PMR studies were performed on Varian A-60A and HA 100 spectrometers fitted with a V–6040 variable temperature accessory. All spectra are referenced to internal $SiMe_4$. Parallel determinations were employed for cases in which the $SiMe_4$ resonance obscured spectral information.

RESULTS AND DISCUSSION

The PMR spectrum of $LiAlEt_4$ in the noncoordinating solvent benzene has been reported to consist of two patterns of unspecified multiplicity, separated by 1.3 ppm, with the methylene resonance appearing at higher field[5]. We observed substantially similar results for the sodium analog. The methyl and methylene protons appear 1.18 and 0.14 ppm downfield from $SiMe_4$, as a broadened triplet and quartet, respectively, at 51°. (See Fig. 1b.) The PMR spectrum of $NaAlEt_4$ in other solvents (DME, DMSO, THF) exhibits signals having the same general separation, but displaced approximately 0.5 ppm to higher field, as observed by Ross and Oliver[4d] for solutions of alkali metal tetramethylaluminate salts.

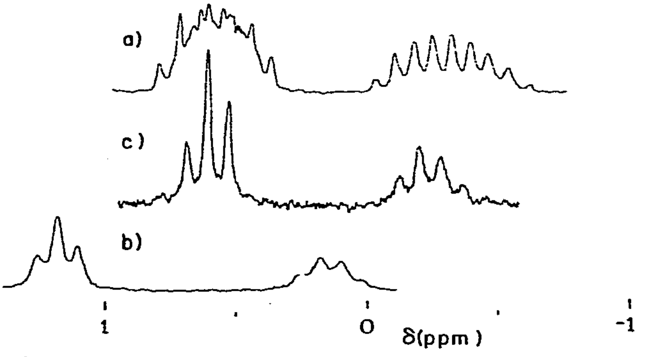

Fig. 1. 60-MHz NMR spectra of 0.69 *M* solutions of (*a*) $NaAlEt_4$ in DME (35°); (*b*) $NaAlEt_4$ in benzene (53°); (*c*) $NaAlEt_3H$ in DME (35°). Chemical shift values were determined in parallel samples to which TMS had been added.

In the strongly coordinating solvent DME, the PMR spectrum of $NaAlEt_4$ (Fig. 1a) exhibits a nine-line pattern at higher field (δ −0.33), representing the methylene protons, which are split (fortuitously) equally (7.3 ± 0.1 Hz) by the three equivalent protons ($^3J(H, H)$) on the adjacent methyl group, and by the aluminum nucleus

(^2J(Al, H); ^{27}Al has $I=5/2$). At lower field (δ 0.58), the methyl resonance is seen as a complex multiplet in which ^3J(H, H) (7.3±0.3 Hz) and ^3J(Al, H) (5.8±0.3 Hz) are in evidence; the observed pattern width (51.2 Hz) is in agreement with the value calculated ($3\times 7.3+5\times 5.8=50.9$ Hz) for these coupling parameters. Although three-bond heteronuclear couplings to protons are well known[4a,5,11], this is the first documented[4a] example of such a long-range interaction involving the aluminum nucleus.

The observation of these long-range couplings suggests that the tetraalkylaluminate species occur primarily in the form of tetrahedrally symmetric, solvent separated ion pairs[4d] in this solvent. By way of providing an experimental test of this inference, we prepared an analogue ($NaAlEt_3H$) that can under no conditions exhibit tetrahedral symmetry (the $AlEt_3H^-$ ion is limited to no higher than C_{3v} symmetry). The PMR spectrum (Fig. 1c) of $NaAlEt_3H$ in DMSO (or in benzene or DME) exhibits the anticipated, slight broadening due to interaction of the quadrupolar aluminum nucleus with the protons but no evidence of simple aluminum–proton spin spin coupling, despite the fact that one would expect a significant contribution by solvent separated ion pairs to the equilibrium distribution of species in DME, and by free ions in DMSO. This illustrates the necessity for some region of symmetry of order higher than C_{3v} at the ^{27}Al nucleus in order for the aluminium–proton coupling interaction to appear. Further experiments are in progress in this laboratory to test whether (*a*) the observation of J(Al, H) requires T_d symmetry throughout the entire anion (and possibly its solvation sphere), or (*b*) more local conditions of symmetry (as in methyltriethylaluminate ions, which are pseudotetrahedral to only the first position away from the aluminum atom) are sufficient to prevent decoupling by the quadrupole.

The predominance of solvent-separated ion pairs indicated above for $NaAlEt_4$ in DME is seen also for moderately dilute solutions of this salt in THF at favorable temperatures. Although a similar effect was noted[4b–d] for solutions of $LiAlMe_4$ in THF, quantitative differences are observed in the temperature and concentration dependence of these two salts. The decline in pattern definition (increase in line widths within the patterns) with increasing salt concentration in THF occurs more rapidly for $NaAlEt_4$ than for $LiAlMe_4$. This result is not unreasonable in view of the greater affinity[12] of the lithium cation for ethereal solvents, a consideration that would occasion a smaller equilibrium constant for the solvent separation process involving $NaAlEt_4$. The failure of $NaAlMe_4$ to exhibit a distinctly resolved ^{1}H–^{27}Al coupling under any conditions in THF has been interpreted[4c] as evidence that K_{eq} for this salt is smaller than for $LiAlMe_4$. K_{eq} for $NaAlMe_4$ is apparently smaller than for $NaAlEt_4$ as well. Since the cation is common to the two salts this difference can be rationalized in terms of the enhanced ability of the smaller anion to compete with solvent molecules for coordination sites on the sodium cation.

Secondly, as illustrated in Fig. 2, the temperature at which the spectrum of $NaAlEt_4$ in THF exhibits optimum pattern definition is somewhat above room temperature, whereas the corresponding temperature[4c] for $LiAlMe_4$ in THF is below 0°. It is known that solvent separation is favored at lowered temperatures[12]. The increase in pattern definition as one approaches the optimum temperature from above arises because the net spin-lattice relaxation time (T_1) for the aluminum nucleus increases as the proportion of the more symmetric, solvent-separated anions present in the equilibrium increases[4c]. The increase in the line width (determined from the

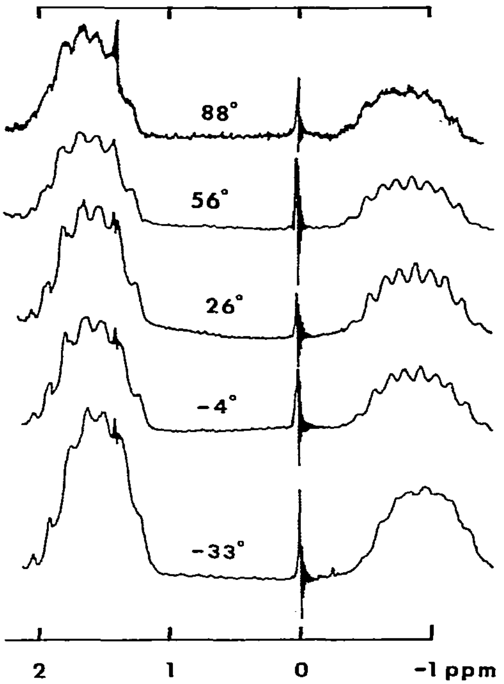

Fig. 2. 100-MHz NMR spectrum of a 0.69 *M* solution of $NaAlEt_4$ in THF at different temperatures. The singlet at $\delta = 0$ is TMS, and the darkened feature at ~1.4 ppm is an artifact.

diminution in pattern definition) as one continues to lower the temperature has been explained by Gore and Gutowsky[4c] as arising from a competition between the thermodynamics of the contact/solvent separated pair equilibrium and the kinetics of molecular reorientation. These authors derived an expression of the Arrhenius form for T_1 by assuming that molecular reorientation of the two exchanging (aluminate) species is solely responsible for T_1[13], and obtained a reasonable fit[4c] for the temperature dependence observed in solutions of $NaAlMe_4$ in THF. For a less substantial value of ΔG^0 (*i.e.*, a smaller K_{eq}, as noted above for $NaAlEt_4$) the decay of the first term with decreasing temperature will be enhanced. This would manifest itself in an elevation of the temperature at which optimum pattern definition is observed, as the K_{eq} for the dissociation into solvent-separated ion pairs decreases. Precisely this behavior is noted above for $NaAlEt_4$ in THF as compared to $LiAlMe_4$ in the same solvent; as the corresponding species are substantially similar in both equilibria, the same line of reasoning about T_1 provides an elegant rationalization of the relative temperature dependences of $NaAlEt_4$ and $LiAlMe_4$. Early in the development of this treatment, however, Moniz and Gutowsky[13] mentioned that study of the temperature dependence of T_1 is problematical because of difficulties in resolving various possible contributions to the relaxation processes of the quadrupolar nucleus, so that it is quite possible that this conceptualization represents an oversimplification of the processes actually occurring in the present and preceding studies.

The NMR spectrum of $NaAlEt_4$ in DMSO, in which free ions would be expected to exist, is essentially identical with Fig. 1a. Since the relative proportion of free $AlEt_4^-$ ions in the solvation equilibrium is unknown, but potentially quite substantial, it is not certain that PMR spectroscopy will be sufficiently sensitive to mark the distinction between solvent separated ion pairs and free ions.

The PMR spectrum of $NaAlEt_4$ in Et_2O is observed as poorly defined multiplets having approximately the same total width as the patterns in which coupling between ^1H and ^{27}Al is in evidence. The failure of the $AlEt_4^-$ lines to narrow in Et_2O, however, indicates that although solvent separated species are present to a large extent in this solvent, the equilibrium is not dominated by these species to the same extent as in DME and THF.

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