Equilibration of Lithium Alkoxyaluminates derived from n-Butyl, s-Butyl, and t-Butyl Alcohols studied by ^{27}Al Nuclear Magnetic Resonance

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$LiAlD_4$ in tetrahydrofuran was titrated with solutions of n-butyl, s-butyl, and t-butyl alcohols in tetrahydrofuran. The reactions were followed by ^{27}Al and ^{13}C n.m.r. In all three cases, $LiAlD_4$ was present in large amounts when 1 mol equiv. of alcohol had been added. The establishment of equilibria was verified by back titrations. Computer fittings to experimental ^{27}Al n.m.r. data of a proposed model for disproportionation of alkoxyaluminates, leading to re-formation of $LiAlD_4$, were performed. Strong support is presented for this model in the case of t-butyl alcohol. Experimentally derived $LiAlD_4$ concentrations can be explained in the same way in the case of n- and s-butyl alcohols. In all three cases, disproportionation of the monoalkoxyaluminates to a high degree and in the dialkoxyaluminates to a much lower degree was indicated.

Alkoxyaluminates formed by reaction between $LiAlH_4$ and alcohols [equation (1)] are important species since they serve as

$$LiAlH_4 + nROH \longrightarrow LiAlH_{4-n}(OR)_n + nH_2 \quad (1)$$

useful selective reducing agents. Many approaches to the design of chiral complex metal hydrides for asymmetric reduction of prochiral carbonyl compounds involve the reaction of $LiAlH_4$ with chiral alcohols or amino alcohols.[1] It has been suggested[2,3] that in ethereal solutions the initially formed alkoxyaluminates are unstable and take part in disproportionation equilibria according to equations (2)—(4). An understanding of

$$2LiAlH_3OR \overset{K_1}{\rightleftharpoons} LiAlH_4 + LiAlH_2(OR)_2 \quad (2)$$

$$2LiAlH_2(OR)_2 \overset{K_2}{\rightleftharpoons} LiAlH_3OR + LiAlH(OR)_3 \quad (3)$$

$$2LiAlH(OR)_3 \overset{K_3}{\rightleftharpoons} LiAlH_2(OR)_2 + LiAl(OR)_4 \quad (4)$$

the factors controlling asymmetric induction requires a knowledge of the identity of the active reducing species.

Some attempts to study lithium alkoxyaluminates by n.m.r. have been reported.[4,5] We have previously studied the reaction between $LiAlH_4$ and some chiral amino alcohols in tetrahydrofuran (THF) by ^{27}Al n.m.r.[6] The concentration of $LiAlH_4$ was followed as a function of amount of added alcohol, and the disproportionation scheme [reactions (2)—(4)] was fitted to the experimental data. In that work, support was obtained for the disproportionation of monoalkoxyaluminates [reaction (2)] formed with (−)-quinine and (−)-*N*-methylephedrine. However, in these systems, the ^{27}Al n.m.r. signals from the reaction products are very broad, and quantification can be made accurately only for the narrow signal from $LiAlH_4$. More information about the relative concentrations of the alkoxyaluminates is needed before any estimation can be made of the importance of reactions (3) and (4). The work by Horne[5] indicated that, in the $LiAlH_4$–t-butyl alcohol system, the ^{27}Al n.m.r. signals from the alkoxyaluminates are narrow enough to be studied quantitatively. We have therefore titrated $LiAlD_4$ with this alcohol, in the same way as with the amino alcohols, and followed the change in concentration of all the reactants by ^{27}Al n.m.r. The aim was to determine if disproportionation according to reactions (2)—(4) takes place and, if so, to obtain a more precise estimation of the equilibrium constants. According to Horne's interpretation,[5] reaction (2) is ruled out and $LiAlH_3OR$ does not exist in detectable amounts in solution.

Calculated values of concentrations for the different species in equations (2)—(4) were then fitted to experimentally derived concentrations by a least-squares minimization method, and the equilibrium constants were estimated. It has been suggested[2] that disproportionation only takes place when a secondary alcohol is used. Therefore we have also studied the reaction of $LiAlD_4$ with n- and s-butyl alcohol, to test for possible differences in the degree of disproportionation amongst the three alcohols. The validity of the proposed model in the three cases is discussed.

Results

^{27}Al *N.m.r. Measurements.*—In accord with our previous work[6] we have titrated a solution of $LiAlD_4$ in THF with solutions of n-butyl (**1**), s-butyl (**2**), and t-butyl (**3**) alcohols. Each addition corresponded to 0.1 or 0.2 mol equiv. of alcohol. As repeated experiments have shown, there is no apparent difference between $LiAlH_4$ and $LiAlD_4$ in the reaction with alcohols, and the two hydrides have been used interchangeably in this study. The ^{27}Al n.m.r. spectrum was recorded after each addition. The aluminium signals appeared as partly unresolved patterns. The relatively narrow peak from $LiAlD_4$ (δ 98 p.p.m.; $\Delta\nu_{1/2}$ 110 Hz) could be clearly distinguished in all cases. In the case of (**1**) and (**2**) there was only one more detectable broad band, whereas in the case of (**3**) two such bands were observed. When 1.0 equiv. of (**1**), (**2**), or (**3**) had been added, $LiAlD_4$ was present in solution in considerable amount (Figure 1).

$CH_3CH_2CH_2CH_2OH$ (**1**)
$CH_3CH_2CHOHCH_3$ (**2**)
$(CH_3)_3COH$ (**3**)

This could result from equilibration of the initially formed alkoxyaluminates, re-forming $LiAlD_4$ as in reaction (2), or it could result from the irreversible reaction of one molecule of $LiAlD_4$ with more than one molecule of alcohol. To distinguish between these two possibilities, mixtures of $LiAlD_4$ and 2.0 equiv. of (**1**), (**2**), and (**3**) were 'back titrated,' *i.e.* $LiAlD_4$ was added in portions so that the molar ratio of ROH to $LiAlD_4$ was lowered from 2.0 to 0.5 : 1. In all cases, ^{27}Al spectra identical

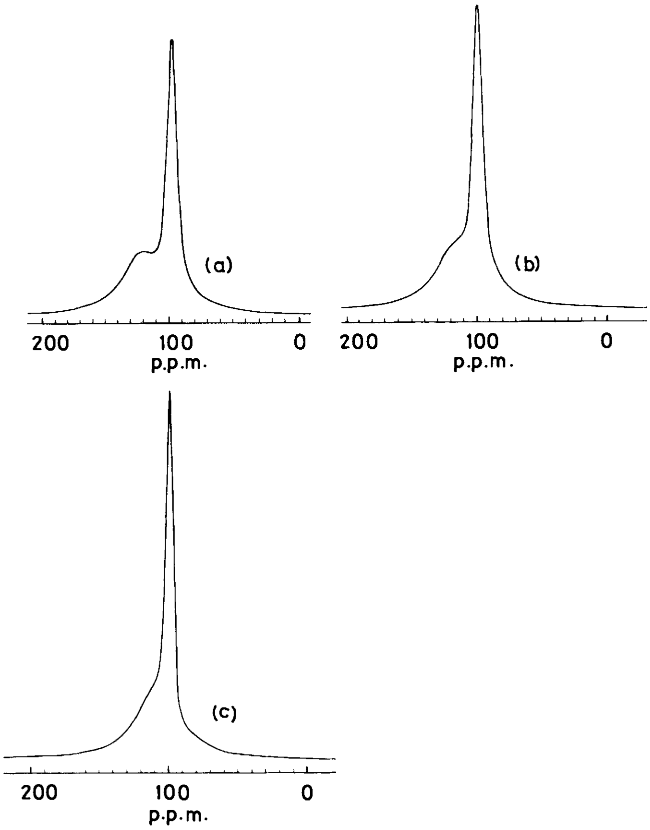

Figure 1. ^{27}Al Spectra from THF solutions: (a) n-butyl alcohol–$LiAlD_4$, molar ratio 1:1; (b) s-butyl alcohol–$LiAlD_4$, molar ratio 1:1; (c) t-butyl alcohol–$LiAlD_4$, molar ratio 1:1

with those observed in the forward titrations were obtained for any given ROH:$LiAlD_4$ molar ratio. The time required to reach equilibrium was determined in each case by observing the spectra for up to 12 h in separate experiments. The concentration of $LiAlD_4$ during a titration is independent of the order of addition of reactants. We therefore conclude that equilibration involving $LiAlD_4$ takes place in THF solution in all three cases. In the cases of (**1**) and (**2**) the titrations were complicated by the formation of precipitates [when 3.0 equiv. of (**1**) and 2.2 equiv. of (**2**) had been added]. Thus, some of the polyalkoxy compounds formed in the reactions are insoluble in THF even in dilute solutions. Therefore the titrations could not be followed beyond these points. Further evidence for equilibration is that the precipitates immediately dissolved upon addition of $LiAlD_4$ in THF, whereas addition of pure THF caused no dissolution.

Measurements show that when $LiAlD_4$ reacts with (**1**) and (**2**), hydrogen gas (HD) corresponding to the quantitative reaction of all four deuterides is immediately evolved. In the case of (**3**) only three deuterides react at room temperature, the third one very slowly. This means that with (**1**) and (**2**) equilibria involving the tetra-alkoxyaluminates must be taken into account, whereas with (**3**) the formation of such a compound, as in reaction (4), need not to be considered at room temperature. To test whether the proposed model for disproportionation could explain the experimentally derived data, ^{27}Al spectra from titrations of $LiAlD_4$ with (**1**), (**2**), and (**3**) were quantified.

Calculations.—The spectra were analysed in the following way. To some spectra baseline flattening algorithms were applied, in order to reduce baseline artefacts. Owing to a technical accident, the original data stored on disc memory were destroyed, and the plotted spectra had to be redigitized. This was done with a digitization tablet having the necessary resolution and precision to rescue the lost information.

Baseline flattening of the spectra was performed, in the case of t-butyl alcohol by least-squares fitting of a third-degree polynomial to the flanks of the obtained spectra, and then subtracting this from the data. For the program for this, the NAG library[7] routines E02ADF and E02AEF were employed for the fitting and evaluation of the polynomial, respectively. A sum of one, two, or three bandshape-modelling functions was then fitted to each digitized spectrum. The fitting was performed with the least-squares minimization routine STEPIT and the main program CURVFIT from the STEPT package by J. P. Chandler.[8]

In order to choose appropriate model functions, the lineshape of the ^{27}Al signal from $LiAlD_4$ was studied in some detail. Since the ^{27}Al spin is coupled to four ^2H nuclei with spin one, it is split into a nonet. This multiplet was synthesized using the UEAITR program, modified to produce plots of the calculated spectrum with Lorentzian lineshapes.[9] In this way a set of spectra was prepared with different line broadening, chosen large enough to conceal the multiplet structure, thus simulating the experimental situation. These spectra were then digitized and analysed by fitting a single Lorentzian line to them. It was found that the area was significantly overestimated (by about 25% in the case corresponding to the experimental situation). This deviation in lineshape for the main peak of the model function from the observed line had an even greater effect on the area estimation of small unresolved lines appearing on the wings of the $LiAlD_4$ signal. Thus the function to model the narrowest of the observed signals was constructed from a set of nine appropriately broadened Lorentzians with the theoretical intensity ratios 1:4:10:16:20:16:10:4:1 and a fixed spacing corresponding to $J_{\mathrm{Al,H}}/6.514 = 26.9$ Hz, not allowing for isotope effects on the coupling constant. In this way the error of the area determination was reduced to a few percent in the synthesized cases, and the fit to the shape of the experimental lines was significantly improved. The other signals in the spectrum were broad enough to have a Lorentzian profile.

Furthermore, each Lorentzian was constructed to contain also the dispersion mode by vectorially adding the absorption mode and the dispersion mode functions.[8] This enabled the reconstruction of the theoretical spectra from some of the experimental spectra, which were inadvertently recorded with slight misadjusted phase correction, owing to baseline distortion of the n.m.r. instrument. A frequency-independent phase offset was found to be sufficient. In test cases it was found that even a grossly misset phase could be handled by including the phase among the varied parameters in the fitting, and the peak parameters, such as area, could be accurately estimated. This facility was important again in modelling of small peaks on the wings of large neighbours. The function used for a band was thus as given in equation (5). The parameters varied by the

$$I = \frac{2A[\Delta\nu_{1/2}\cos\varphi + 2(\nu - \nu_0)\sin\varphi]}{\pi^2\Delta\nu_{1/2} + 4\pi(\nu - \nu_0)^2} + B_1(\nu - \nu_{\mathrm{cent}}) + B_0 \quad (5)$$

least-squares program were area (A), half-height width ($\Delta\nu_{1/2}$), chemical shift (ν_0), base-line slope (B_1), and base-line offset (B_0). The area was used in place of intensity (derived from the formulae in ref. 10) and base-line slope calculated from the centre of the spectrum to reduce correlation between the parameters as much as possible. The phase offset (φ), common for all the Lorentzians, was mostly kept constant at fixed values, chosen from inspection of the superimposed graphs of experimental and calculated spectra.

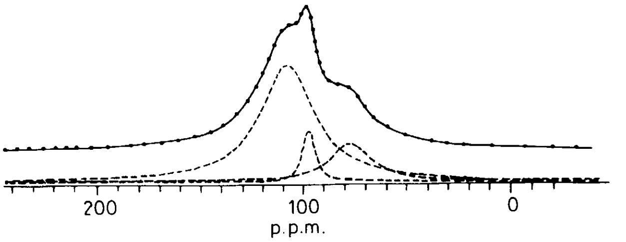

Figure 2. Computer resolution of the partly unresolved ^{27}Al signals in a digitized spectrum. The sample is a solution of t-butyl alcohol and $LiAlD_4$ (molar ratio 1.8:1) in THF. The dots represent the experimental and the solid line the calculated spectrum

The narrow line in the unresolved spectra, modelled as a multiplet, was well defined by the fitting procedure in all cases, and its area could thus be separated from the rest of the signal area. The residual signal(s) were modelled by one or two Lorentzians and the residual area was thus estimated (Figure 2). The model for the equilibria was constructed in the following way. The system corresponding to the chemical equilibria (2)—(4) and to the relations for the total concentrations of aluminium and alcohol, respectively, is presented as equations (6)—(14). Concentrations are expressed in relative units corrected for dilution; $m = i + 2$ is the number of species in the

$$K_i = \frac{c_i c_{i+2}}{(c_{i+1})^2} \quad (i = 1, 2, \text{ or } 3) \qquad (6)\text{—}(8)$$

$$1 = \sum_{k=1}^{i+2} c_k \quad (i = 1, 2, \text{ or } 3) \qquad (9)\text{—}(11)$$

$$E = \sum_{k=2}^{i+2} (k-1)c_k \quad (i = 1, 2, \text{ or } 3) \qquad (12)\text{—}(14)$$

model, c_1 is the concentration of $LiAlD_4$, and c_2, c_3, c_4, and c_5 are the concentrations of mono-, di-, tri-, and tetra-alkoxy compounds, respectively; E is the number of equivalents of alcohol in the solution, with regard to equation (1), determined by the experimental conditions; K_i are the equilibrium constants. It is convenient to discuss three different models composed from these equations. Model 1 corresponds to a case where only one equilibrium is necessary to explain the data ($i = 1$); thus the system of equations is made up from (6), (9), and (12). Model 2 considers two equilibria ($i = 2$) and is composed of the equations (6), (7), (10), and (13); model 3 ($i = 3$) is composed of the equations (6), (7), (8), (11), and (14).

The relevant model was fitted to the titration data in the following way. For chosen values of the equilibrium constant(s), the system of equations was solved for the unknown concentrations ($\bar{C}$) (column vector) of the different species, for each point on the titration curve. A new vector $\bar{P}$ is formed, the elements of which are linear combinations of these concentrations, by scalar left multiplying $\bar{C}$ with a rectangular matrix A. The matrix A has the elements a_{ij} and dimensions $n \times m$, where n is the number of resolved lines in the spectrum (after the curve fit) and m is the number of species. The vector $\bar{C}$ has the elements c_i and dimension m. Then $\bar{P} = A\bar{C}$. The vector $\bar{P}$ thus has a dimension equal to the number of resolvable bands in the n.m.r. spectra, and the matrix A is defined by the expression (15).

$$a_{ij} = \begin{cases} 1, \text{ if peak } i \text{ is assigned to species } j \\ 0, \text{ otherwise} \end{cases} \qquad (15)$$

The matrix A represents the assignment of the peaks, and an element of $\bar{P}$ may be a sum of more than one calculated concentration, if different unresolved species give rise to the corresponding n.m.r. band area. The experimental data from the area determination by curve fitting were standardized in a way corresponding to that for the calculated data, *i.e.* relative area and correction for dilution. The values of the elements of $\bar{P}$ were then compared with the experimental values in a least-squares sense. The sum of squares of the deviations thus formed represents a measure of the fit of the model to all experimental information simultaneously, subject to the current interpretation of the n.m.r. spectrum. A given interpretation was easy to change by a simple input to a program, which generated the A matrix, and the fit to data of several different assignments could thus be tested. By varying the equilibrium constants until convergence was reached and optimal values of the equilibrium constants were found, the concentrations of all the contemplated species in the solution could be displayed. In the Figures the symbols represent the experimental n.m.r. line areas. The solid lines represent the functions $\bar{P}$ fitted to data for the assignments chosen, and the dotted lines represent the concentrations of the single species.

Discussion

A major complication in the quantitative analyses of ^{27}Al n.m.r. data is that the total integral may not account for all aluminium present in solution. Asymmetry around the ^{27}Al nucleus causes rapid relaxation *via* the quadrupolar mechanism resulting in severe line broadening.[11] It is thus possible that some species have a relaxation time short enough to prevent observation by ^{27}Al n.m.r. In measurements of large spectral widths, acoustic ringings from the probe result in severe baseline distortions. Because of this, broad signals can be difficult to distinguish from the baseline, especially in dilute solutions. Thus, quantitative measurements are accurate only with fairly narrow signals. In our $LiAlH_4$–amino alcohol study[6] the total integral of aluminium decreased considerably during a titration. The peaks visible from the reaction products were very broad. Thus, computer fittings could be made only with $LiAlH_4$ concentration. The accuracy of K_1 was estimated to within about ±50%, but the fits were less sensitive to variations in K_2 and K_3. When $LiAlD_4$ reacted with (**2**) and (**3**) the total integral was 5—10% short of the theoretical value; the higher value is obtained towards the end of the titration. This could be the result if the peaks from some alkoxyaluminates are sufficiently broadened from asymmetry or chemical exchange. Since the amount of aluminium 'missing' is hard to estimate with any degree of accuracy, it is difficult to assign this value to a discrete species in the quantification. In this case, the amount is small enough to be explained by experimental uncertainties associated with the handling of these extremely reactive compounds and with errors in the integration procedure. If we adopt the hypothesis that all species taking part in the equilibria are visible in the spectra, relative areas instead of absolute areas should be used in the computer fittings. The results of this treatment with data for (**1**), (**2**), and (**3**) are shown in Figure 3.

In the case of (**3**), the broad high-frequency peak was assigned to the mono- and di-substituted species and the more narrow low-frequency peak to the trisubstituted compound (Figure 2). This assignment seems reasonable in view of their order of appearance in spectra during a titration. On the basis of the curve in Figure 3(c), allowing for the variations due to experimental uncertainties, a qualitative description of n.m.r. data in terms of reactions (2)—(4) seems feasible. ^{13}C Spectra from the reaction of $LiAlH_4$ with (**3**) show the signal from the methyl carbon atoms split into two peaks separated by about 0.7 p.p.m.[5] At ROH:$LiAlH_4$ molar ratios less than 2.0:1, the low-frequency peak predominates . [The ^{13}C n.m.r. spectrum from the reaction of $LiAlD_4$ with (**3**) is identical with the spectra reported in Horne's work.[5]] This peak could be assigned to

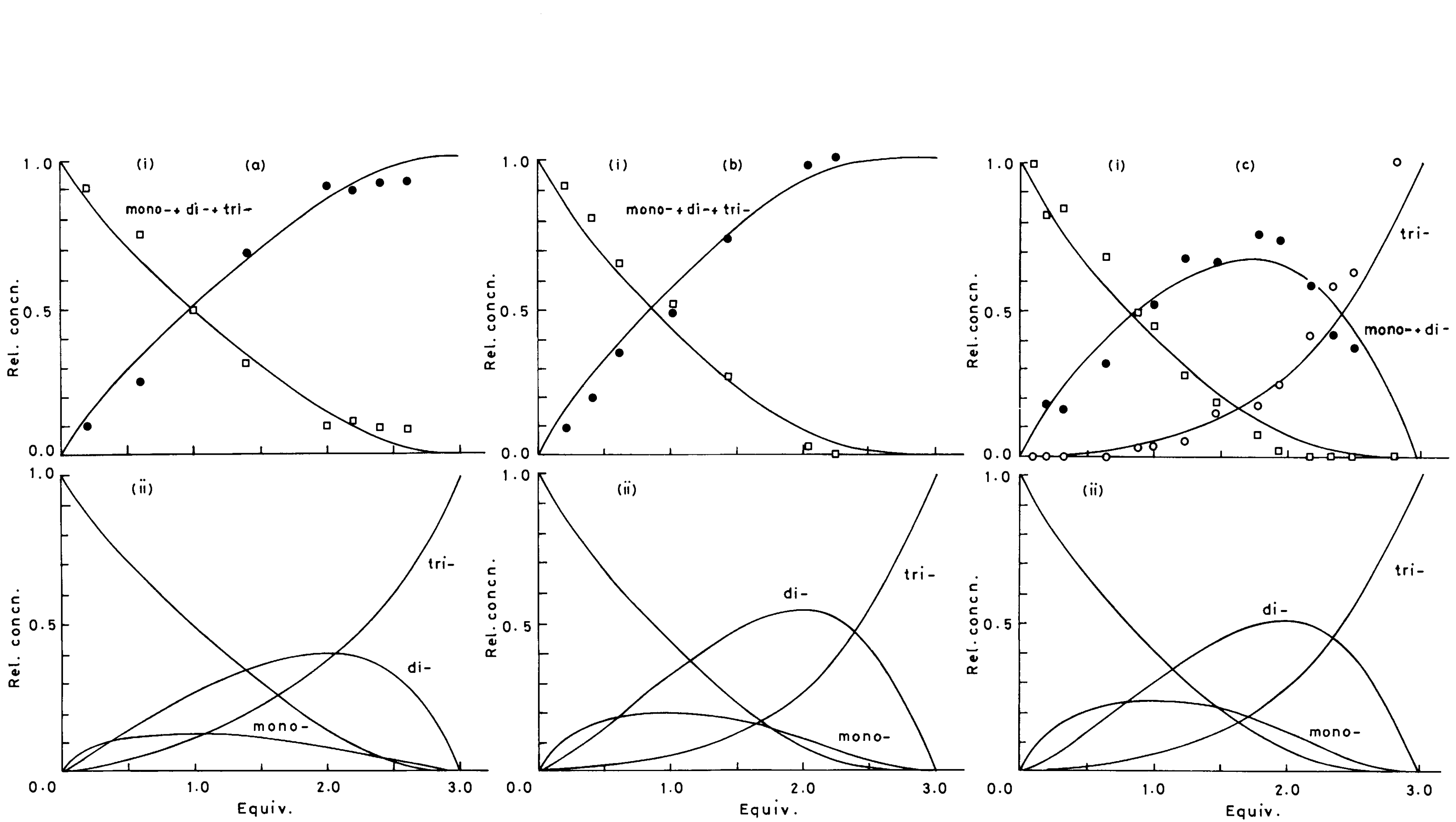

Figure 3. Results of titrations of $LiAlD_4$ with (a) n-butyl alcohol and (b) s-butyl alcohol: (i) □ measured AlD_4^- concentrations, ○ concentrations of species giving rise to the broad components in the ^{27}Al spectra; solid curves represent the best fits to experimental data; (ii) composition of the solutions calculated from the equilibrium constants obtained from the best fits to experimental data. (c) With t-butyl alcohol: (i) □ measured concentrations, ○ and ● concentrations of species giving rise to the broad components in the ^{27}Al spectra; assignments are discussed in the text; solid curves represent the best fits to experimental data; (ii) compositions of the solutions calculated from the equilibrium constants obtained from the best fits to experimental data

the mono- and di-alkoxy compounds appearing as a coalesced singlet as a result of fast exchange on the ^{13}C n.m.r. timescale. If this exchange is represented by reaction (2), it involves also $LiAlD(H)_4$. Since no line broadening or chemical-shift change is apparent for $LiAlD_4$ this exchange must be slow on the ^{27}Al timescale. In view of the large ^{27}Al chemical-shift differences and coupling constants, this interpretation is feasible provided that the ^{13}C chemical-shift difference of the mono- and di-alkoxyaluminates is small (less than about 0.16 p.p.m.).

At 2.0 equiv. the high-frequency peak starts to increase and at 2.5 equiv. the two peaks are about equal in intensity. At 3.0 equiv. the high-field peak dominates the spectrum. ^{27}Al N.m.r. of this sample shows one Lorentzian-shaped singlet (δ 78 p.p.m.; $\Delta v_{1/2}$ 560 Hz). Comparison with Figure 3(c) shows that with the foregoing peak assignments adopted ^{13}C data agree with ^{27}Al data, indicating that disproportionation of alkoxyaluminates derived from **(3)** takes place in THF. Values of K_1 and K_2 estimated from the best fit were 2.0 and 0.15, respectively. These values are slightly too high, since the total integrals of the ^{27}Al spectra were somewhat too low (see before).

In the case of **(2)**, the broad peak was assigned to all four alkoxyaluminates in reactions (2)—(4) [Figure 3(b)]. The curves are less informative because the fitting was done with only two areas. The explanation of $LiAlD_4$ concentrations in terms of the proposed model is still valid, however. The best fit estimated K_1 as 3.5 and K_2 as 0.1 for this system. These values are slightly too high in this case also. The higher value of K_1 for **(2)** compared with that of **(3)** could be explained on steric grounds. The value for K_2 is more uncertain than the value for K_1. Contrary to the case with the amino alcohols, however, reaction (3) had to be included for a good fit, *i.e.* K_2 can be determined. The fit was not improved by the inclusion of reaction (4). ^{13}C Data for the reaction with **(2)** show the signal from the methylene carbon split into two peaks, the low-frequency peak dominating at low ROH:$LiAlD_4$ molar ratios. Thus, the same interpretation as in the case of **(3)** must be adopted, involving a coalesced ^{13}C signal from the mono- and di-alkoxyaluminates. Further correlations are difficult to make since the dotted curves in Figure 3(b) are very uncertain.

The titration of $LiAlD_4$ with **(1)** presents a more complicated case. The total integral in this case was about 25—30% short of the theoretical, which is more than can be explained by experimental errors. In Figure 3(a) the broad peak was assigned to all four alkoxyaluminates in reactions (2)—(4). The values of 8.0 for K_1 and 0.2 for K_2 are grossly overestimated in this case. It is possible that aggregation of alkoxyaluminates could cause line broadenings as a result of exchange between a monomer and a dimer. According to Ashby,[12] t-butoxyaluminates are monomeric in THF in the concentration range studied here (0.2—0.1M). Methoxyaluminates have been shown to be highly associated. Although no such data are available for n-butoxyaluminates it is possible that these species also form aggregates in THF solution.

Conclusion

In this study we have shown that equilibration of alkoxyaluminates, derived from n-, s-, and t-butyl alcohols and $LiAlD_4$, takes place in THF solution. The amounts of $LiAlD_4$ present at any given ROH:$LiAlD_4$ molar ratio are quite similar in the three cases.

Computer fittings to ^{27}Al n.m.r. data strongly indicate that disproportionation of t-butoxyaluminates takes place, according to reactions (2)—(4). In the case of n- and s-butyl alcohols, $LiAlD_4$ concentrations during a titration can be explained by this model. The estimated values of K_1 show a rough correlation of the degree of disproportionation with steric bulk of the alcohol. In all three cases, disproportionation of both mono- and di-alkoxyaluminates had to be considered in order to explain the experimental data, although the degree of disproportionation is much higher for the former than for the latter. The stability of the trialkoxyaluminates [reaction (4)] cannot be estimated from the present data.

Experimental

N.m.r. Measurements.—The ^{27}Al spectra were recorded at 23.5 MHz with a Bruker CXP-100 spectrometer. The maximal spectral width (125 kHz) and bandwidth (1 MHz) of the instrument were used. The pulse-repetition rate was 50 ms. Chemical shifts were related to $[Al(H_2O)_6]^{3+}$ (external standard). ^{13}C Spectra were recorded at 50.3 MHz with a Bruker WP-200 instrument; 5% C_6D_6 was added as internal lock.

Computer Calculations.—All final calculations were performed with a VAX 11/780 computer. Preliminary calculations were carried out with the attached array processor FPS-164. The program developed for the fittings contained routines from the STEPT package,[8] modified to optimize the fit of $\bar{P}$ to experimental data, and the routines C05PCF from the NAG library[7] for the solution of the system of nonlinear equations and F01DAF for the scalar matrix multiplication. To produce the plots, a program was developed utilizing the NAG routines C05PCF to solve the system of equations at twenty equidistant points, and then using E01BAF and E02BBF to fit and evaluate a cubic spline to the solutions at these points. The plotting routines were choosen from Tektronix PLOT 10 4010C01 Interactive Graphics Library routines, level 5.1.

Materials.—THF (Merck p.a.) was distilled from $LiAlH_4$ and stored over 4 Å molecular sieves.

Stock solutions of hydride reagent were prepared by refluxing $LiAlD_4$ (Fluka; >99 atom % D) in THF, centrifuging the slurries, and transferring the clear solutions to storage bottles equipped with Teflon stopcocks and rubber septums. Prior to use, the solutions were analysed by iodometric titration[13] and by measuring the amount of HD gas evolved upon hydrolysis in an acidic water–THF (50:50) mixture at ±0 °C. The results of the two methods always agreed within ±2%. Stock solutions of 0.1—0.2M concentration were prepared.

n-Butyl alcohol, b.p. 117—118 °C, was pre-dried ($CaSO_4$), then filtered, refluxed, and fractionally distilled from small amounts of sodium metal under dry nitrogen. It was stored over 4 Å molecular sieves.

s-Butyl alcohol, b.p. 99—100 °C, was pre-dried ($CaSO_4$), filtered, then refluxed with and fractionally distilled from CaH_2. It was stored over ground 4 Å molecular sieves.

t-Butyl alcohol, m.p. 25 °C, b.p. 82—83 °C, was pre-dried ($CaSO_4$), filtered, refluxed with CaH_2, and fractionally distilled under dry nitrogen. It was stored (as a solid) over 4 Å molecular sieves.

Alcohols were added as 50 or 25% solutions in THF to $LiAlD_4$. The titrations were performed by injecting the reactants into 10 mm n.m.r. tubes equipped with Teflon-coated rubber septums. A needle connected to the N_2 gas flush system provided the necessary gas outlet. Efficient mixing was ensured by the use of a whirlmixer.

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