Proton NMR Investigation of Oligomer Equilibria in Diisobutylaluminum Hydride

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It is generally accepted that diisobutylaluminum hydride occurs, in neat liquid as well as in solution, as a trimer $(R_2AlH)_3$. In high resolution ^1H NMR spectrum, the hydride signal is accompanied by a satellite, which seems to arise from another oligomer. Studies of mixtures with an inert solvent confirm the occurence of an equilibrium between $(R_2AlH)_3$ and the second oligomer, with substantially higher molecular weight. The areas of the hydride peaks are carefully evaluated. However, the accuracy is not good enough to determine the exact number of monomer units in the new species; assuming that the main compound contains three monomers, the second species can contain 5 or 6 units. A monomeric or dimeric species is probably also present in low concentration.

The occurence of association phenomena has been of central interest already at the beginning of the studies of organometallic compounds of aluminum.[1,2] The self-association of electron-deficient compounds, such as boron hydrides, aluminum alkyls etc., has played an important role in the discussions of different types of chemical bonds as early as the 1930's.

The first studies of aluminum alkyl hydrides, R_2AlH, also deal with the self-association. The methyl compound ($R=CH_3$) has been shown to be a mixture of a dimer and a trimer in the gas phase and a trimer in dilute solution.[3] As part of the extensive work undertaken by the Ziegler group,[4] Hoffmann and Schomburg present careful cryoscopic measurements[5,6] whose results show that all R_2AlH compounds are trimers in solution. This is also claimed for the case of $R=i-Bu$, even though the bulky isobutyl groups prevent the association in $(i-Bu)_3Al$. Furthermore, the authors dismiss the possibility of an equilibrium between different oligomers. A cyclic structure with alternating aluminum and hydrogen atoms in a six-membered ring is proposed, without any other support than the molecular weight determination. The bridging function of the hydrogen atoms in hydrides has later been confirmed by electron diffraction studies.[7] In these studies, limited to dimethylaluminum hydride, only the monomer and dimer are found in gas phase – the trimer is probably not volatile enough. The early paper by Hoffmann,[8] propagating the applicability of NMR, contains 40 and 60 MHz proton spectra of $(C_2H_5)_2AlH$. Eisch and Rhee[9] have used NMR to study the complex between $i-Bu_3Al$ and $i-Bu_2AlH$, which earlier was noted in the work of the Ziegler group. Otherwise, literature on alkylaluminum hydrides during the last decades mainly reflects a continuing interest in the synthetic potential of hydroalumination reactions.

Literature on trialkylaluminum compounds contains much more data of physico-chemical interest, e.g. the X-ray structure of trimethylaluminum,[10] studies of internal alkyl group exchange[11-13] and external exchange processes,[14,15] investigations of monomer—dimer equilibria,[16] measurements of aluminum—carbon coupling constants[17] and studies of dynamic behaviour of triethylaluminum.[18]

In this paper, we report a proton NMR investigation of the oligomer equilibria in diisobutylaluminum hydride. By investigating solutions in a suitable inert solvent we show that, besides the dominant trimer, there also exists another $(i-Bu)_2AlH$ oligomer in equilibrium with the main species.

EXPERIMENTAL

$i-Bu_2AlH$ from different manufacturers (Merck—Schuchardt, Ethyl Co, Alfa Products) have been used either without further purification or distilled in vacuo. The solvent, perdeuterocyclohexane C_6D_{12}, has been purchased from Merck, dried over molecular sieves and distilled in vacuo. The mixtures have been prepared under inert atmosphere and sealed under vacuum in NMR tubes. The samples prepared in this way seem to be stable over a period of years.

Most of the ^1H NMR experiments have been performed at 2.35 Tesla (100 MHz ^1H resonance frequency) using Varian XL100 spectrometer with an external proton lock and the CW mode — some of the FT experiments performed on this instrument turned out to be unsuitable for quantitative evaluation. The peak areas have been measured carefully by manual planimetration of the main part of the peaks together with analytical estimates (based on the Lorentzian lineshapes) of the contributions of the broad wings of the peaks and the mutual contributions to the observed intensities, combined with an iterative procedure for determining the position of the baseline. The major part of the integrated intensity is thus obtained in an unbiased fashion while the remainder, difficult to measure directly, is estimated with a reasonable accuracy. The procedure is also well suited for work with the data in analog form, as obtained in a CW experiment. To facilitate the measurements of peak areas, the spectral width and amplitude have been set to provide the peak area of the main hydride peak at about $30-60$ cm^2. For spectra with relatively broad and overlapping lines, it is of critical importance to check the phase carefully by comparing the baseline on both sides of the peaks of interest. Sensitivity to the phase setting is unexpectedly high – a misseting by a few degrees results in considerable distortion of the peak, which is however not easy to detect upon inspection. Fortunately, a misset receiver phase in the present CW experiments also gives a distinct slope in the baseline, at a large distance (more than 1 ppm) from the hydride peaks. This sloping baseline is also very sensitive to the receiver phase setting. This phenomenon arises probably as a result of the far-reaching dispersion mode wings of the intense methyl peak. Thus, the horizontal baseline in the area of interest is a good test of the correct phasing and a prerequisite for accepting a spectrum for quantitative evaluation.

^{13}C NMR measurements have been carried on a JEOL GX 400 spectrometer operating at 9.4 Tesla (100 MHz ^{13}C resonance frequency).

RESULTS

A 60 MHz proton NMR spectrum of the neat compound (Fig. 1) shows the signals from methyl and methylene groups with fairly narrow lines, and a complicated multiplet from the methine group due to the coupling with six methyl and two methylene protons. Further, there is a broader line from the hydride proton.

At 100 MHz, one observes in addition a small peak close to the hydride line and with a similar line width. The relative intensity of this small peak, about 20 % of the main hydride line, is the same regardless of the sample manufacturer and remains unchanged after distillation. These facts indicate that the small peak is not due to an impurity. The hydride
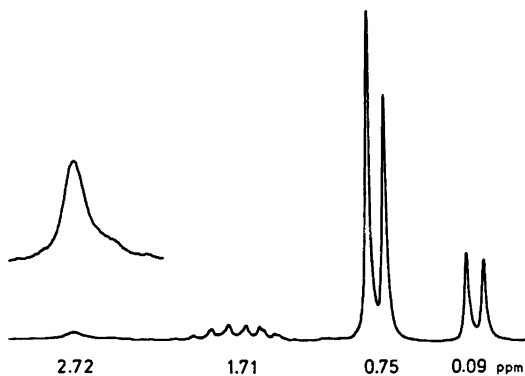
Fig. 1. ^{1}H NMR spectrum of neat i−Bu$_2$AlH at 60 MHz, 30 °C. The inset corresponds to an amplitude 16 times higher. The peaks are (from the left) AlH, CH (1), CH$_3$ (2), CH$_2$ (3). $J_{1,2}$=6.8 Hz, $J_{1,3}$=6.0 Hz.

peak and its satellite, denoted below as "large" and "small" peak, are sufficiently well separated to make the relative intensity changes upon dilution clearly observable upon visual inspection. Fig. 2 shows the two peaks in the mixture with different degrees of dilution: 90−70−50−30 % of i−Bu$_2$AlH. These curves have been recorded under identical instrumental conditions. the height of the main peak decreases successively to about 26 %, while the smaller signal in the last sample decreases to only 10−12 % of the intensity of the first sample. The separation between the peaks and the line width appear, on the other hand, unchanged. The effect becomes even more obvious if the dilution is compensated by a change in the receiver gain and/or sample dimension. Fig. 3 shows the signals from 100 % and 10 % i−Bu$_2$AlH, respectively. It can be seen that the small peak practically disappears in the 10 % solution; at the same time, another peak occurs on the low field side of the main peak.

It is important to stress that clear qualitative conclusions can be drawn at this stage without quantitative evaluation of the peak areas but merely using the results in Figs. 2 and 3:

(*a*) the small peak arises from an oligomeric form of i−Bu$_2$AlH, which remains in equilibrium with the main species.
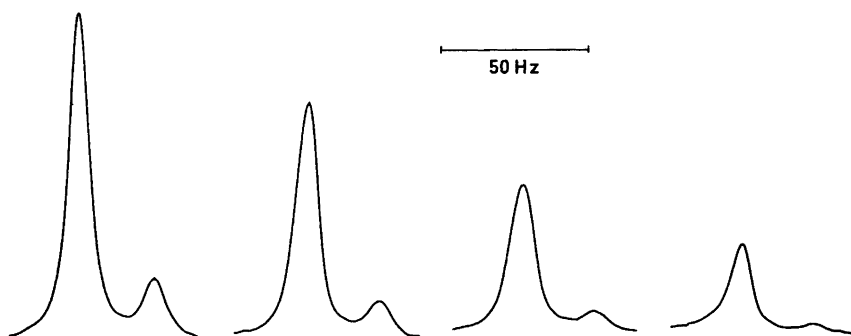

Fig. 2. i−Bu$_2$AlH dissolved in perdeuterocyclohexane. From the left: 90−70−50−30 vol %. ^{1}H at 100 MHz, hydride signal region, unchanged instrumental settings.
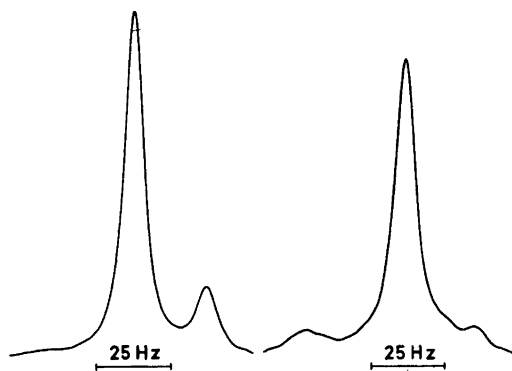
Fig. 3. Comparison of ^{1}H spectra of the hydride region of 100 % (left, 5mm sample) and 10 % (right, 10mm sample) i$-$Bu$_2$AlH. Instrumental setting adjusted for comparable intensity of the main peak.

(*b*) this oligomeric form has higher molecular weight than the main species, since it disappears upon dilution. If the main species is a trimer (i$-$Bu$_2$AlH)$_3$, in agreement with the prevalent notion, then the new species must consist of four or more monomer units.

(*c*) still another component, with a lower number of monomer units than that of the main species, seems to exist in a dilute solution.

The conclusion under (*a*) above is firmly supported by the high-field ^{13}C spectra for one of the samples: the methylene carbon resonance has a "satellite" with the same relative intensity as seen in the proton spectrum. In the proton-coupled ^{13}C spectrum, the main CH$_2$ line and the satellite display identical splitting, with ^{1}J(^{13}C^{1}H)=115 Hz. Also the methyl resonance has a satellite and the methine signal has a distinct shoulder.

The results of quantitative evaluations of the areas the small and large peak areas are listed in Table 1 as a function of the nominal monomer diisobutylaluminum hydride

Table 1. The nominal monomer concentrations, peak areas and I_S/I_L ratios for different solutions and different measurements for diisobutylaluminum hydride in cyclohexane.
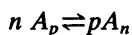
C, mol/l	Peak area, cm^2		I_S/I_L
	Large	Small	
5.612	57.44	12.18	0.212
5.612	35.80	7.41	0.207
5.051	55.64	11.24	0.202
5.051	54.41	10.81	0.198
4.490	47.21	9.16	0.194
3.928	43.58	6.98	0.160
3.367	36.82	5.19	0.141
2.806	31.18	3.96	0.127
2.806	39.27	5.10	0.130
1.683	33.43	3.04	0.091
1.683	32.47	3.05	0.094
1.122	56.98	4.05	0.071
0.561	52.03	2.29	0.044
0.561	60.98	2.20	0.036

concentration. We can see that the ratio increases monotonously with increasing concentration of i−Bu$_2$AlH.

It seems reasonable to first test whether the results can be interpreted in terms of two oligomers in equilibrium with each other according to

$$n \, (\text{i}-\text{Bu}_2\text{AlH})_p \rightleftharpoons p \, (\text{i}-\text{Bu}_2\text{AlH})_n \tag{1}$$

or, briefly

$$n \, A_p \rightleftharpoons p A_n$$

This is done by testing the validity of

$$A_n^p = K_{n,p} A_p^n \tag{2}$$

We assume, in agreement with the generally accepted view, that the large peak corresponds to a trimer, $p=3$. The following relation is obtained between the ratio A_n/A_3 and the total concentration of the trimer, A_3

$$\frac{A_n}{A_3} = \left(K_{n,3}\right)^{\frac{1}{3}} A_3^{\frac{n-3}{3}} \tag{3}$$

The ratio A_n/A_3 can be computed from the measured ratio I_S/I_L, taking into consideration the number of monomer units in each species. The concentration A_3 is calculated from the nominal monomer concentration C using

$$C_k = C \cdot I_L / \Sigma I \tag{4}$$

where C_k ($=3A_3$) is the molar concentration (in monomer units) of the free trimer and the sum in the denominator accounts for the fact that hydride proton intensity is distributed among several peaks. The relation to be tested can thus be written

$$\frac{I_S}{I_L} = \frac{n}{3} \cdot \left(\frac{1}{3}\right)^{\frac{n-3}{3}} \cdot \left(K_{n,3}\right)^{\frac{1}{3}} \cdot C_k^{\frac{n-3}{3}} \tag{5}$$

According to eqn. (5), one would expect a linear relation between I_S/I_L and C_k for $n=6$ (the small peak hexamer). It can be seen in Fig. 4 that such a linear relation in possible, considering the limited accuracy of the measurements. However, there seems to exist a systematic deviation both in form of a curvature and the difficulty in extrapolating the curve to the origin. If we wish to test the alternative $n=5$ (the small peak pentamer), the relation to be tested becomes

$$\frac{I_S}{I_L} = \kappa \, C_k^{\frac{2}{3}}$$
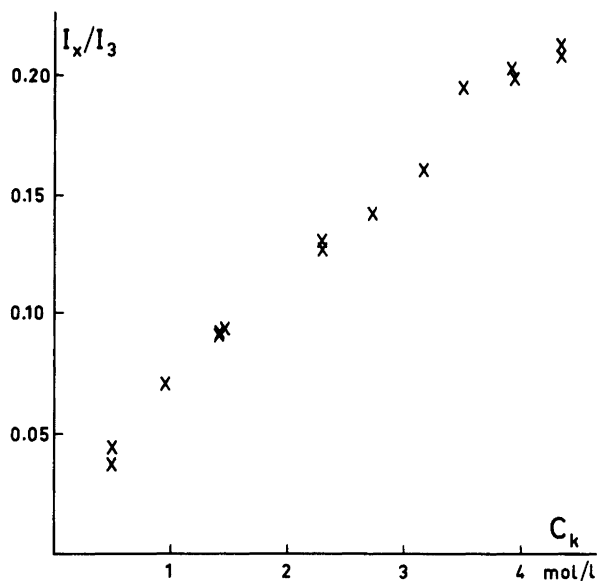
$$K_{5,3} = \frac{3^5}{5^3} \kappa^3 \tag{6}$$

Fig. 4. Test of the proportionality of I_S/I_L versus C_k.

according to which the ratio I_S/I_L is proportional to $C_k^{\frac{2}{3}}$ with the proportionality coefficient κ. It can be seen in Fig. 5 that this assumption very well agrees with the data. The coefficient κ is 0.077 ± 0.002, which corresponds to the equilibrium constant
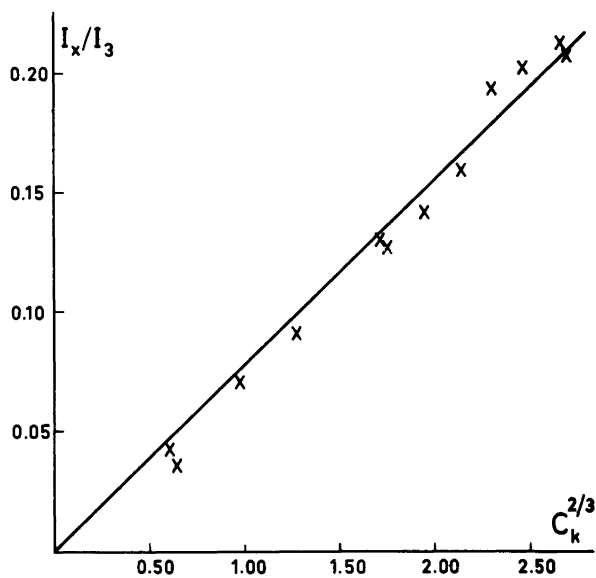
$$K_{5,3} = (9.0 \pm 0.8) \cdot 10^{-4} l^2 mol^{-2}$$

Fig. 5. Test of the proportionality of I_S/I_L versus $C_k^{\frac{2}{3}}$. The solid line is the result of a least-squares fit of a straight line through origin.

From the sum of squares of the deviations between the measured I_S/I_L values and the calculated ones, one obtains a standard deviation $\sigma(I_S/I_L)=\pm0.008$ or 6 % of the average value. This is insignificantly larger than the uncertainty estimated *a priori* by re-measuring all the I_S/I_L ratios. Nevertheless, we do not find that the pentamer-alternative definitely has been proved by these experiments. Experiments of this kind are subject to several systematic error sources, which can lead to a bias in the functional relationships. We consider the alternative $n=6$ as possible, but the standard deviation in the I_S/I_L ratio corresponding to this hypothesis is almost twice as large as for the case of $n=5$: $\sigma=\pm0.014$ or 10 %. On the other hand, the alternatives $n=4$ and $n=7$ are out of the question. We have also tested the possibility that the main species has a lower degree of association than 3, *e.g.* $p=2$, but this assumption is also in clear disagreement with the results.

In Fig. 3, one more minor peak (about 35 Hz downfield from the large peak) can be observed, whose intensity is dependent on the dilution. In the neat compound its area is hardly measurable; it can be estimated at about 2 % of the large peak. Upon dilution to 10 %, the peak becomes distinct, though poorly shaped. Its area is estimated at 8.2 % of the large peak. Using eqn. (5), one finds this peak consistent with $n=1$, *i.e.* a monomer.

REFERENCES

1. Laubengayer, A.W. and Gilliam, W.F. *J. Am. Chem. Soc. 63* (1941) 477.
2. Pitzer, K.S. and Gutowsky, H.S. *J. Am. Chem. Soc. 68* (1946) 2204.
3. Wartik, T. and Schlesinger, H.I. *J. Am. Chem. Soc. 75* (1953) 835.
4. Ziegler, K., Gellert, H.G., Lehmkuhl, H., Pfohl, W. and Zosel, K. *Justus Liebigs Ann. Chem. 629* (1960) 1.
5. Hoffmann, E.G. *Justus Liebigs Ann. Chem. 629* (1960) 104.
6. Hoffmann, E.G. and Schomburg, G. *Z. Elektrochem. 61* (1957) 1101.
7. Anderson, G.A., Almenningen, A., Forgaard, F.R. and Haaland, A. *Chem. Commun.* (1971) 480; *Acta Chem. Scand. 26* (1972) 2315.
8. Hoffmann, E.G. *Z. Anal. Chem. 170* (1959) 177.
9. Eisch, J.J. and Rhee, S.G. *J. Organomet. Chem. 42* (1972) C73.
10. Lewis, P.H. and Rundle, R.E. *J. Chem. Phys. 21* (1953) 986.
11. Muller, N. and Pritchard, D.E. *J. Am. Chem. Soc. 82* (1960) 248.
12. Ramey, K.C., O'Brien, J.F., Hasegawa, I. and Borchert, A.E. *J. Phys. Chem. 69* (1965) 3418.
13. Yamamoto, O., Hayamizu, K. and Yanagisawa, M. *J. Organomet. Chem. 73* (1974) 17.
14. Hoffmann, E.G. *Trans. Faraday Soc. 58* (1962) 642.
15. Stanford, T.B. and Henold, K.L. *Inorg. Chem. 14* (1975) 2426.
16. Smith, M.B. *J. Organomet. Chem. 22* (1970) 273; *J. Phys. Chem. 71* (1967) 364.
17. Yamamoto, O. *J. Chem. Phys. 63* (1975) 2988.
18. Vestin, U., Kowalewski, J. and Henriksson, U. *Org. Magn. Reson. 16* (1981) 119.

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