STUDY OF THE STRUCTURE OF LITHIUM AND SODIUM HYDRIDOALKOXOALUMINATES BY INFRARED SPECTROSCOPY

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Infrared spectra of $MAlH_{4-n}(OR)_n$, where M = Na, Li; R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, were measured. The stretching vibration of the bridge Al—H—Al bond was attributed to the broad band at 1464 cm^{-1}, based on the isotopic shift of the heavy isotopomer and on the comparison of the spectra of solid $LiAlH_2(OCH_3)_2$ and its solution.

The bridge Al—H—Al bond represents one of the possible ways of oligomeration of hydridoalkoxoaluminates; a convincing evidence of the position of the band corresponding to the stretching vibration of the Al—H—Al bonding, however, has not yet been found. Wallbridge[1] assumes Al—H—Al bridging in complexes of triphenylphosphine with $Al(BH_4)_3$, based on the peaky spectrum in the region of 1700 to 400 cm^{-1}. Davidson and Wartik[2] also suggest, without proof, the bridge structure in the adduct of N,N,N',N'-tetramethylmethylenediamine with aluminium hydride. In the spectrum of $LiAlH_4$, Hilal[3] ascribed — also without proof — the band at 1642 cm^{-1} to the Al—H—Al stretching vibration, even though he himself reports the region of $1800-1500$ cm^{-1} as the range of the stretching vibrations of terminal Al—H bonds — the band at 1642 cm^{-1} in the spectrum of $LiAlH_4$ has also been attributed to the latter vibrations by many authors[4-7]. Regarding the discrepancies we decided to attempt to identify the band of the stretching Al—H—Al vibrations by employing the analysis of the infrared spectra of simple hydridoalkoxoaluminates.

EXPERIMENTAL

All operations were performed in the atmosphere of pure nitrogen in whole-glass apparatus or in a dry box. Infrared spectra were measured on a spectrometer Beckman IR 20 A as 15% mulls in Florube or a solutions in diethyl ether or tetrahydrofuran in cells 0·01 cm. The content of the hydride hydrogen was determined volumetrically after hydrolysis of the sample. $LiAlH_4$ or $NaAlH_4$ used was recrystallized from diethyl ether prior to use, and was kept under nitrogen in sealed ampoules. Purity was min 99%. $LiAlD_4$ was dissolved in diethyl ether, filtered over granulated aluminium powder and used directly for reaction as 7·3% solution. The alcohols were absolutized by boiling with CaH_2 and redistilled before use.

Attempt at the preparation of lithium trihydridomethoxoaluminate (I). 30 ml of ether was condensed to 0·9704 g (0·0255 mol) of $LiAlH_4$ in a vacuum line. After dissolving, the solution was cooled down to $-20°C$ and 1·034 ml (0·0255 mol) of methanol was added with stirring. The precipitate was filtered off and dried at 50°C and 10^{-2} Torr. 1·63 g of solid substance was obtained. For *I* calculated: 39·69% Al, 4·45% $H^{(-)}$, found: 28·48% Al, 2·40% $H^{(-)}$. According to the results of analysis, the substance corresponds to $LiAlH_2(OCH_3)_2$ (*II*).

Lithium dihydridodimethoxoaluminate (II) was prepared by the same procedure from 0·8636 g (0·0227 mol) of $LiAlH_4$ and 1·839 ml (0·0454 mol) of methanol; 2·23 g (100%) of *II* was obtained. For *II* calculated: 27·53% Al, 2·06% $H^{(-)}$; found: 25·89% Al, 1·91% $H^{(-)}$.

Lithium hydridotrimethoxoaluminate (III) was prepared by the same procedure from 0·6831 g (0·018 mol) of $LiAlH_4$ and 2·181 ml (0·054 mol) of methanol; 1·85 g (80%) of *III* was obtained. For *III* calculated: 27·01% Al, 0·79% $H^{(-)}$; found: 21·02% Al, 0·51% $H^{(-)}$.

Natrium dihydridodimethoxoaluminate (IV). 40 ml of tetrahydrofuran was distilled to 0·8680 g (0·0161 mol) of $NaAlH_4$ in a vacuum line. The solution was cooled down to $-20°C$ and 1·462 ml (0·0322 mol) of methanol was added dropwise with stirring. The solution was evaporated and the residue dried at 50°C and 10^{-2} Torr. For *IV* calculated: 23·65% Al, 1·76% $H^{(-)}$; found: 19·86% Al, 1·17% $H^{(-)}$.

Lithium dideuteriodimethoxoaluminate (V) was prepared by the same procedure as *I* from 0·5148 g (0·123 mol) of $LiAlD_4$ and 0·992 ml (0·0245 mol) of methanol; 1·25 g (100%) of *V* was obtained.

RESULTS AND DISCUSSION

In solution, *I* undergoes disproportionation with the formation of insoluble *II* and $LiAlH_4$ according to equation (A)
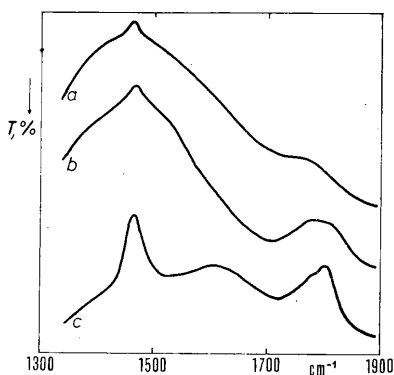

FIG. 1

Infrared Spectra of $LiAlH_{4-n}(OCH_3)_n$ in Florube
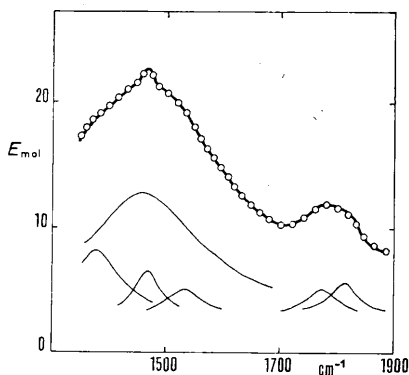
　a n = 1 (*I*); *b n* = 2 (*II*); *c n* = 3 (*III*).

FIG. 2

Separated Bands of the Infrared Spectrum of $LiAlH_2(OCH_3)_2$　(*II*)

　○ Experimental points; ——— separated bands; ▬▬ sum curve.

$$2 \, LiAlH_3OCH_3 \;\rightarrow\; LiAlH_4 \,+\, LiAlH_2(OCH_3)_2 \,. \qquad\qquad (A)$$

This is evidenced by the identity of the infrared spectra of the insoluble products (Fig. 1), and the results of analyses. *II* is precipitated quantitatively and $LiAlH_4$ remains in the solution. So the identity of the spectra of solutions of *I* and of $LiAlH_4$, pointed out by Hilal[3], is explained.

We found, in contrast to Hilal, *II* to be completely insoluble in ether. Haubenstock[8] suggests that *II* disproportionates to $LiAlH_4$ and $LiAl(OCH_3)_4$ (*VI*). From our results it follows that this disproportionation does not occur, since in that case $LiAlH_4$ would remain in the solution. Also, *VI* is partly soluble in ether. The disproportionation product cannot be Li_3AlH_6 either, as follows from the results of X-ray diffraction. In the spectrum of *II* (Fig. 1*b*), in the range of the Al—H stretching vibrations we found an intense, broad band with a sharp maximum at $1465 \; cm^{-1}$ and a band at $1770 \; cm^{-1}$. The spectrum was subjected to band separation by employing a computer[9] (Table I, Fig. 2). The separated bands at 1377 and $1473 \; cm^{-1}$ can be attributed to bending vibrations of the methyl group. The bands at 1464 and $1772 \; cm^{-1}$ belong to the Al—H stretching vibrations, as follows from the wavenumber values for the isotopomer *V* $(1080$ and $1312 \; cm^{-1})$ (Fig. 3). The low-intensity band at $1550 \; cm^{-1}$ can be considered as a manifestation of the deviation of the real band shape from the ideal Lorentz curve form used for calculation. The broad band at $1464 \; cm^{-1}$ was attributed to the Al—H—Al stretching vibration; its considerable half band width $(127 \; cm^{-1})$ complies with the assumption of a multiple broadening of the band on the formation of the bridge bond[10]. A considerable lowering of the wavenumber of the Al—H—Al stretching vibration at $1464 \; cm^{-1}$ as compared with that of the stretching vibration of the terminal Al—H bond at $1772 \; cm^{-1}$ results from the decrease of the value of the force constant of the bridge Al—H—Al bond in comparison

TABLE I

Parameters of the Separated Bands of the Infrared Spectrum of $LiAlH_2(OCH_3)_2$ (*II*)

ν, cm^{-1}	$\Delta\nu_{1/2}$, $cm^{-1\,a}$	$E_{mol}{}^b$	B^c
1 377	60	5·3	1 007
1 464	127	11·2	4 435
1 473	27	4·0	339
1 550	23	2·5	178
1 772	34	2·3	246
1 816	36	2·9	334

[a] Half band width; [b] molar absorptivity, $1 \; mol^{-1} \; cm^{-1}$; [c] molar integrated intensity, $1 . mol^{-1} . cm^{-2}$.

with the terminal Al—H bond, and is in accordance with the data found for dibora-ne[11], aluminium halides[12], alkali metal borohydrides[13], and alkoxy substituted aluminium hydrides[14]. Due to the low value of the force constant, the bridge Al—H—Al bond is very weak and is disposed to breakdown in solutions of strong Lewis bases in favour of the forming coordination bond donor–aluminium. In the spectrum of *II* in tetrahydrofuran (Fig. 4*b*) a new band appears in the range of stretching vibration of the terminal Al—H bond, at $1\,690\,\mathrm{cm}^{-1}$, instead of the band of the Al—H—Al vibration. The appearance of the band cannot be explained by a shift from $1\,464\,\mathrm{cm}^{-1}$ on account of solvation, because the wavenumber value should decrease on increasing the coordination number of aluminium[7,15–17]. The original nature of the spectrum is reestablished on the evaporation of the solution to dryness (Fig. 4*c*). In the spectrum of *II*, the band of the AlH_2 bending vibrations was not observed in the usual range of $750\,\mathrm{cm}^{-1}$, since this group is blocked by the formation of the Al—H—Al bridge.

In the structure of *III* the bridge Al—H—Al bond cannot occur, because the corresponding band in the spectrum is lacking (Fig. 1*a*). It can be stated that *III* is a chemically uniform compound, as disproportionation would manifest itself by the presence of the band at $1\,464\,\mathrm{cm}^{-1}$ which is characteristic of *II*. In the case of the ethoxy deri-
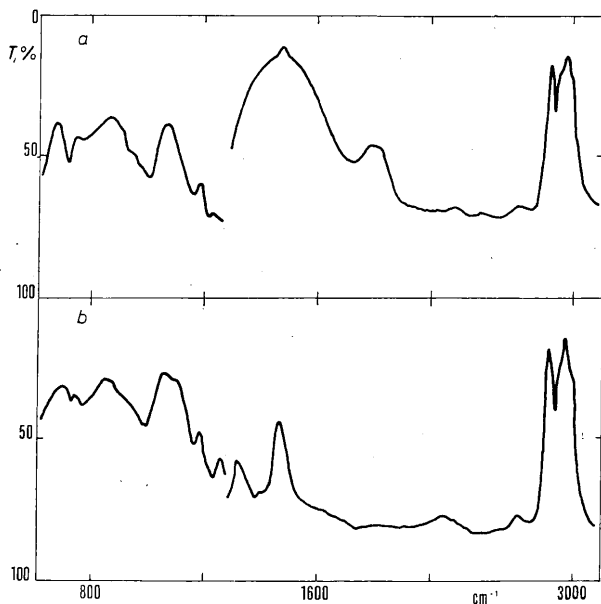

FIG. 3

Infrared Spectra of $LiAlH_2(OCH_3)_2$ (*II*) and $LiAlD_2(OCH_3)_2$ (*V*) in Florube
  a $LiAlH_2(OCH_3)_2$; *b* $LiAlD_2(OCH_3)_2$.

vatives $LiAlH_{4-n}(OC_2H_5)_n$ (VII) disproportionation occurs and VII with $n = 4$ precipitates from the solutions. The presence of the bridge Al—H—Al bonding was proved only for the evaporated filtrate of VII, $n = 1$, since a broad, intense band appears in the spectrum at 1500 cm^{-1}, half band width about 150 cm^{-1} (Fig. 5). In the case of $LiAlH_{4-n}(O\text{-}i\text{-}C_3H_7)_n$ $(VIII)$, complete disproportionation proceeds to $LiAlH_4$ and $VIII$, $n = 4$. Only in the case of tert-butoxy derivatives we have found, in contrast to Brown[18-20], that in ether solutions disproportionation equilibrium establishes and the least soluble $LiAlH(O\text{-}t\text{-}C_4H_9)_3$, displaying the terminal Al—H stretching at 1760 cm^{-1}, precipitates.
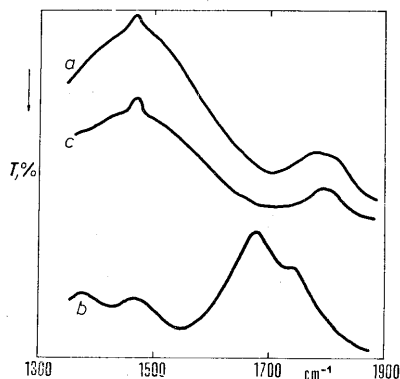

FIG. 4

Infrared Spectra of $LiAlH_2(OCH_3)_2$
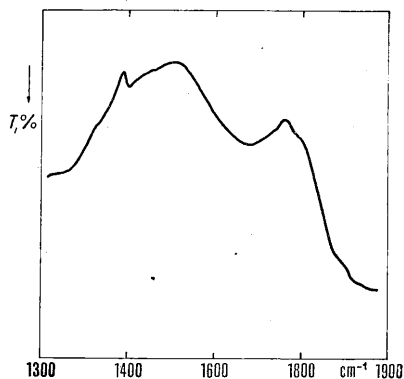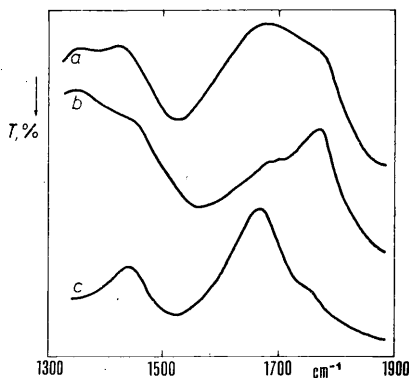   *a* florube mull; *b* solution in tetrahydrofuran; *c* Florube mull of the evaporation residue of the solution.

FIG. 5

Infrared Spectrum of the Evaporation Residue of the Filtrate of $LiAlH_3OC_2H_5$ in Florube

FIG. 6

Infrared Spectra of $NaAlH_{4-n}(OCH_3)_n$ in Florube
   a $n = 1$; *b* $n = 2$ (IV); *c* $n = 3$.

In the series of sodium hydridoalkoxoaluminates we found oligomeration to proceed through Al—H—Al bridges only in the case of *IV*, as indicated by the broad band of Al—H—Al stretching at 1350 cm^{-1} (Fig. 6). In this series the situation is complicated by the fact that, because of the solubility of $NaAlH_4$, tetrahydrofuran must be used as the solvent. In this solvent all the products are well soluble, hence, in contrast to the lithium derivatives, the possible equilibrium disproportionations cannot be followed.

The shift of the Al—H—Al stretching vibration at 1350 cm^{-1} in the case of *IV* as compared with the lithium analog *II* $\left(1464 \text{ cm}^{-1}\right)$ agrees with the observations of Ashby[21], who found the AlH vibration band at 1400 cm^{-1} in Li_3AlH_6 and at 1300 cm^{-1} in Na_3AlH_6.

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