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SYNTHESIS AND SOME PROPERTIES OF BIS(DIMETHYLALUMINIUM) SULPHIDE

M. BOLESŁAWSKI, S. PASYNKIEWICZ, A. KUNICKI and J. SMOŁA
Institute of Organic Chemistry and Technology, Technical University (Politechnika), Warsaw (Poland)

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Summary

Bis(dimethylaluminium) sulphide, $(Me_2Al)_2S$, was prepared by a reaction of trimethylaluminium with liquid hydrogen sulphide. The compound is sparingly soluble in aromatic and aliphatic hydrocarbons and soluble in pyridine, benzonitrile and dioxane. The formation of a bis(dimethylaluminium) sulphide/benzonitrile complex has been studied and its relative acid strength compared with those of trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride.

Introduction

Commercial use of organoaluminium compounds for synthesis of other organometallics and active systems catalyzing poly-, oligo- and co-polymerization has given unflagging impetus to studying this branch of chemistry. These considerations have prompted numerous investigators to get an insight into the properties and reactivities of organoaluminium compounds and modified derivatives thereof. Within the group of organoaluminium compounds of the >Al—S—Al< type, bis(diethylaluminium) sulphide, its preparation, certain properties and reactions with ketones, esters etc. [1] have been described. The sulphide was prepared by a reaction or triethylaluminium with hydrogen sulphide.

However, bis(dimethylaluminium) sulphide, its synthesis and properties, has not been reported.

Results and discussion

Bis(dimethylaluminium) sulphide was prepared by making trimethylaluminium react with liquid hydrogen sulphide. The reaction proceeds according to the scheme:

$$2(CH_3)_3Al + H_2S \xrightarrow[-78^\circ]{\text{n-hepane}} (Me_2Al)_2S + 2CH_4$$

The procedure was as follows: liquid hydrogen sulphide was added dropwise at a rate of 1 ml/h to a 10% trimethylaluminium solution in n-heptane at −78° with stirring. After all hydrogen sulphide had been added, the reaction mixture was allowed to warm up to room temperature and then the reaction was continued for 3 h with vigorous stirring. After the reaction had been completed, the solvent and trace amounts of trimethylaluminium were distilled off at 25°/15 mm to leave behind a white solid residue. (Found: Al, 36.68; active CH_3, 41.85. $C_4H_{12}Al_2S$ calcd.: Al, 36.94; active CH_3, 41.09%). The reaction proceeded with a good yield.

Bis(dimethylaluminium) sulphide reacts with atmospheric oxygen and moisture. Like bis(diethylaluminium) sulphide [1], bis(dimethylaluminium) sulphide disproportionates at temperatures higher than 100° to yield trimethylaluminium and polymeric products:

$$(Me_2Al)_2S \xrightarrow{\Delta} (CH_3)_3Al + [-Al(CH_3)-S-]_n$$

Above 300°, the polymeric residue decomposes.

The sulphide is poorly soluble in nonpolar aromatics and aliphatics and soluble in dioxane, pyridine and benzonitrile.

With benzonitrile, the sulphide forms a complex, as evidence by IR spectra. On formation of the complex, the C≡N band frequency rises from the $\nu(C{\equiv}N)$ 2230 cm^{-1} for free benzonitrile to $\nu(C{\equiv}N_{complex})$ 2278 cm^{-1} for the complexed benzonitrile.

At the sulphide/benzonitrile mole ratio 1/1 and 1/2, there appears, in addition to the strong $\nu(C{\equiv}N_{complex})$ 2278 cm^{-1} band, a band $\nu(C{\equiv}N)$ 2230 cm^{-1}. This indicates that, at the specified reactant mole ratios, free benzonitrile does exist alongside the complexed benzonitrile.

With the shift of the C≡N band in the complex adopted as a measure of the acid strength of an organoaluminium compound, it is possible to assess the relative acid strength of bis(diethylaluminium) sulphide. The acid strengths of the organoaluminium compounds previously investigated [2] may be arranged in the following increasing order:

$$\begin{array}{lccccccc} & Me_3Al & < & Me_2AlCl & < & MeAlCl_2 & < & AlCl_3 \\ \Delta\nu(C{\equiv}N) & +37 & & +52 & & +58 & & +59\ cm^{-1} \end{array}$$

The value $\Delta\nu(C{\equiv}N)$ 48 cm^{-1} for $(Me_2Al)_2S$ places the acid strength of the sulphide between those of trimethylaluminium and dimethylaluminium chloride.

TABLE 1

VARIATION IN THE NMR SPECTRA BAND AREA RATIO FOR THE REACTION BETWEEN $(Me_2Al)_2S$ AND PYRIDINE WITH THE REACTION TIME.

Internal standard: toluene (C_6H_5).

Reaction time (h)	Band position (Hz)		Band area ratio
	A	B	A/B
0.5	435	442	1/0.52
20	435	442	1/0.65
40	435	442	1/0.75

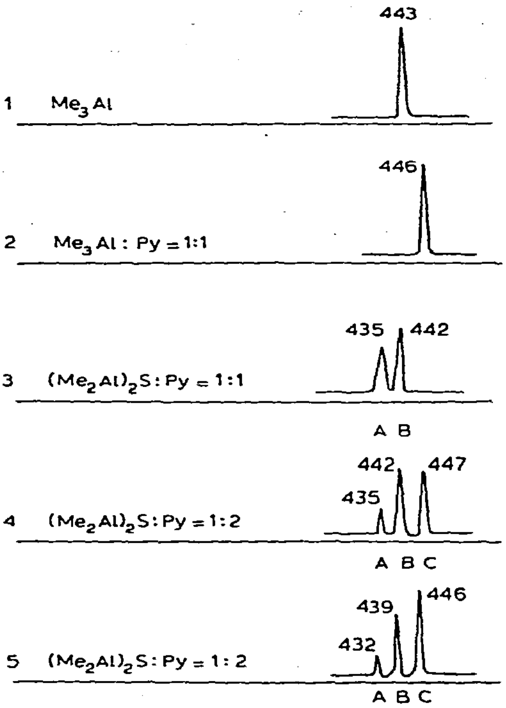

Fig. 1. The NMR spectra of the reaction between $(Me_2Al)_2S$ and pyridine in the toluene solution. Internal standard: toluene (C_6H_5). Spectrum No. 5 was recorded 24 h after the reactants had been mixed together.

Reaction mixtures of bis(dimethylaluminium) sulphide and pyridine at reactant mole ratios of 1/1 and 1/2 were studied in terms of NMR spectra. At the ratio 1/1 (Spectrum No. 3), two signals appeared (A and B), shifted to the right by 435 Hz(A) and 442 Hz(B) relative to the position of proton absorption in the toluene aromatic ring. The A/B band area ratio is 1/0.85. At the reactant mole ratio 1/2 (Spectrum No.4), a third band (C) appeared. The A/B/C band area ratio is 1/3.6/2.4. The spectra were recorded immediately after the reactants had been mixed together. In the spectrum of the 1/2 mixture recorded 24 h later the A/B/C band area ratio was changed to 1/3/4 (Spectrum No.5).

Signal intensities were found to vary also in the NMR spectra of a 1/0.9 sulphide/pyridine mixture recorded in ½, 20 and 40 h reckoned from the moment of mixing of the components. Data are listed in Table 1.

Presumably, the sulphide/pyridine mixture contains $(Me_2Al)_2S\cdot Py$ and $(Me_2Al)_2S\cdot 2Py$ complexes but the present data (Fig.1, Table 1) are too inconclusive to define unambiguously products of the reaction.

Work on establishing the nature of the sulphide/pyridine reaction products is in progress.

References

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