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THE REACTION OF TRIMETHYLALUMINIUM WITH LEAD SULPHIDE

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Summary

The reaction of trimethylaluminium with lead sulphide gives tetramethyllead, lead and bis(dimethylaluminium) sulphide. Under the experimental conditions the maximum degree of conversion of the methyl groups was 22.5% (0.5 h, 135°). The products were analysed by NMR spectroscopy.

Results and discussion

In our previous article results of the investigation of the reaction of trimethylaluminium with lead monoxide were shown [1]. It was established that in this reaction tetramethyllead and bis(dimethylalumoxane) are formed.

The purpose of this work was to investigate the reaction of trimethylaluminium with lead sulphide. It has been established that trimethylaluminium reacts with lead sulphide giving tetramethyllead, lead and bis(dimethylaluminium) sulphide (eqn. 1).

$$4(CH_3)_3Al + 2PbS \rightarrow (CH_3)_4Pb + Pb + 2[(CH_3)_2Al]_2S \qquad (1)$$

The yield of tetramethyllead increases with rise of temperature (40—140°). The largest increases of yield were noted between 70 and 100° (Fig. 1).

The influence of reaction time on the yield of tetramethyllead is shown in Fig. 2. In the reactions proceeding at 135° the highest yield* (X = 25.2%) was obtained after 2.5 h. By prolonging the reaction time the yield of tetramethyllead decreased, probably due to its thermal decomposition.

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* The reaction yield was calculated as the conversion (X) of the trimethylaluminium methyl groups into tetramethyllead and also as conversion (Z) of lead sulphide. $X(\%) = 4/3\,(m_{TML} \cdot M_{TMA})/(m_{TMA} \cdot M_{TML}) \times 100$; $Z(\%) = (m_{TML} \cdot M_{PbS})/(m_{PbS} \cdot M_{TML}) \times 100$, where the m quantities denote the weights of the resulting tetramethyllead (TML) and the reactants used, trimethylaluminium (TMA) and lead sulphide (PbS); the M values are the molecular weights of the respective compounds.

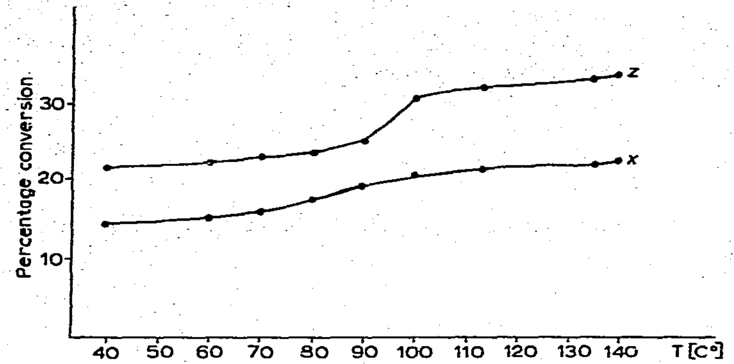


Fig. 1. The yield of Me_4Pb as a function of temperature in the reaction of Me_3Al with PbS. Reaction time: 2 h, molar ratio $Me_3Al/PbS = 2/1$; initial concentration of Me_3Al in xylene ca. 50% weight. For X and Z see footnote p. 000.

The influence of the molar ratio of the reactants on the yield of tetramethyllead was determined. The highest yield ($X = 22.4\%$) in the investigated range was obtained for the molar ratio of trimethylaluminium to lead sulphide 1/1, the highest value of $Z = 41.1\%$ for the molar ratio 4/1 (Fig. 3).

The utilization of methyl groups X 33% (Fig. 1, 2, 3), as was confirmed also in the reaction of trimethylaluminium with lead monoxide, shows that only one methyl group from trimethylaluminium takes part in the formation of tetramethyllead.

Besides tetramethyllead, bis(dimethylaluminium) sulphide $(CH_3)_2AlSAl(CH_3)_2$ (I) is formed. Due to the low solubility of this compound in the reaction medium it was separated as a complex with ethyl ether. The NMR spectrum (Fig. 4) and the analysis results indicate that it is a complex of bis(di-

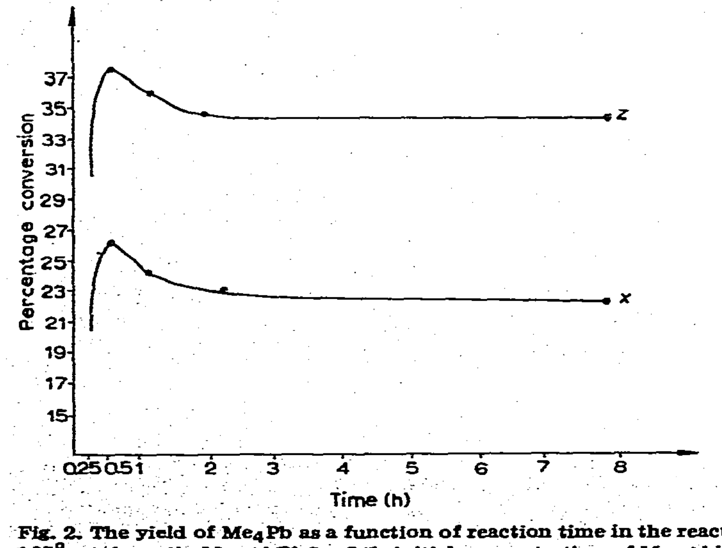


Fig. 2. The yield of Me_4Pb as a function of reaction time in the reaction of Me_3Al with PbS. Temperature, 135°; molar ratio $Me_3Al/PbS = 2/1$; initial concentration of Me_3Al in xylene ca. 50% weight. For X and Z see footnote p. 000.

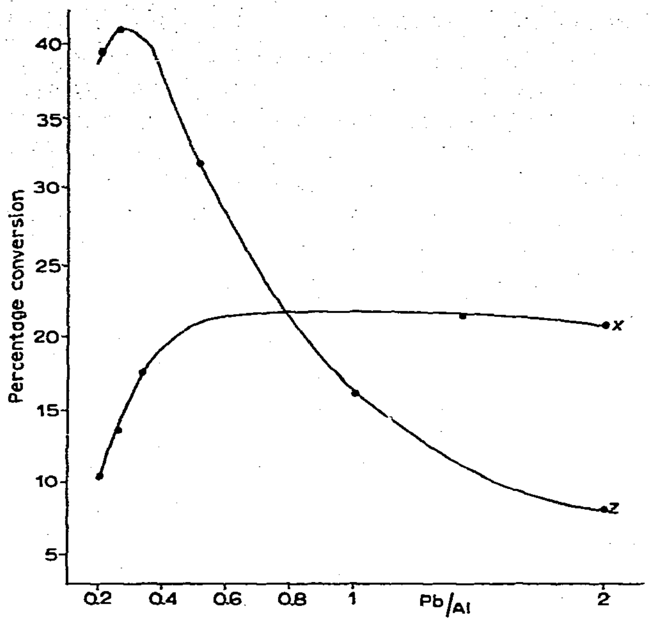


Fig. 3. The yield of Me_4Pb as a function of the molar ratios Me_3Al/PbS. Temperature: 135°; reaction time 2 h; initial concentration of Me_3Al in xylene ca. 50% weight. For X and Z see footnote p. 000.

methylaluminium) sulphide with ethyl ether with the molar ratio 1/1: $[(CH_3)_2Al]_2S\cdot(C_2H_5)_2O$ (II). (Anal. found: Al, 24.49; CH_3, 27.38; $(C_2H_5)_2O$, 31.5. calcd. for II: Al, 24.54; CH_3, 27.27; $(C_2H_5)_2O$, 33%.) The amount of sulphur was not determined.

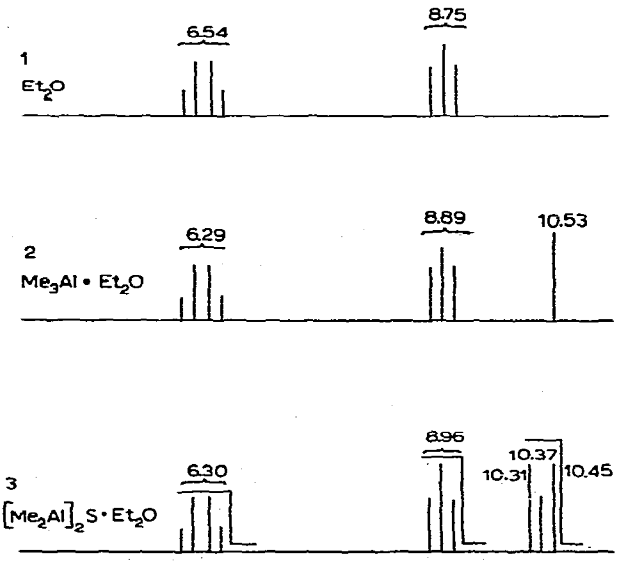
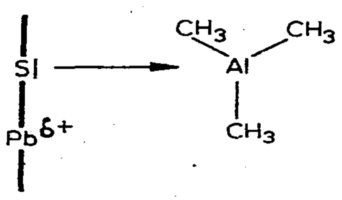


Fig. 4. The comparison of the chemical shift in the NMR spectra.

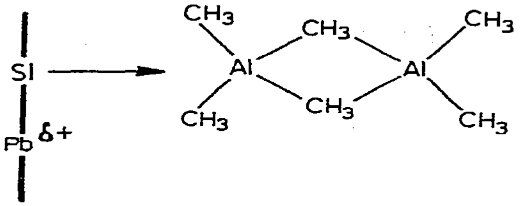
The molar ratio of bis(dimethylaluminium) sulphide to ethyl ether in this complex is confirmed by the NMR spectrum (Fig. 4). Calculations show that for the 1/1 complex the respective proton ratio should be 12/10, which is the case. The NMR spectrum of complex II, in the field attributed to the resonances of protons of the methyl groups bonded with aluminium, show three peaks with the area ratio 1/0.6/1. The resonance band of the signals differs from the resonance band of the protons in the trimethylaluminium—ethyl ether complex methyl groups (Fig. 4). The presence of three peaks is probably the result of partial association. The molecular weight of complex II in benzene was 318, which gives the degree of association $n = 1.44$.

Bis(dimethylaluminium) sulphide was previously obtained in the reaction of trimethylaluminium with hydrogen sulphide [2]. This compound is a white, amorphous powder which reacts with oxygen and water. It is insoluble in non-polar aromatic and aliphatic solvents. With pyridine and benzonitrile it forms donor-acceptor complexes. Accepting the frequency difference $\Delta\nu(C\equiv N)$ in the IR spectrum between free and organoaluminium-complexed benzonitrile as a measure of acidity, it was determined that trimethylaluminium is a weaker Lewis acid than bis(dimethylaluminium) sulphide. We assume that in the reaction conditions, dimethyllead may form a complex with bis(dimethylaluminium) sulphide. Studies are in progress on the formation of donor-acceptor complexes of R_2Pb compounds with organoaluminium compounds.

The results of reaction of $MeAlCl_2$ with $PbCl_2$ [3] and Me_3Al with PbO [1] indicate that complexes of organoaluminium compounds with lead salts can be formed. We assume that the first stage of the reaction of Me_3Al with PbS is the formation of IIIa or IIIb.

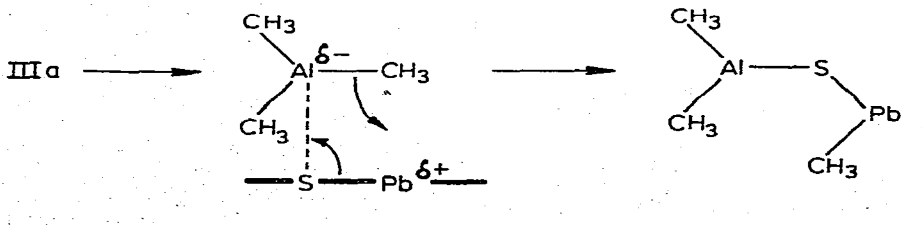


(IIIa)

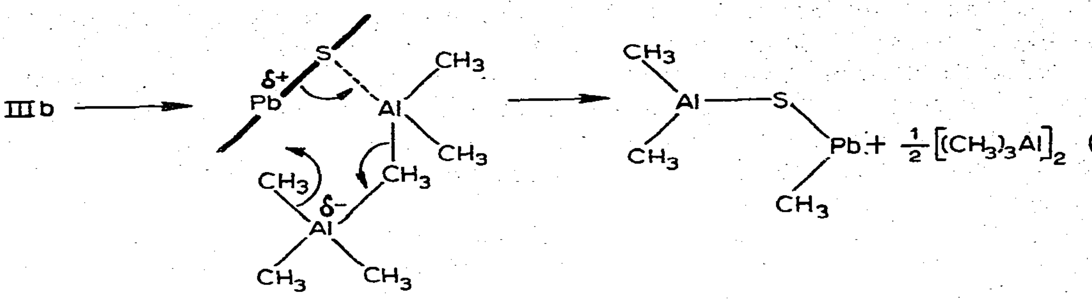


(IIIb)

Due to the charge distribution in the complexes formed an intramolecular alkylation reaction proceeds. At the same time the reacting lead sulphide molecule is released from the crystal lattice. The reaction can proceed in a four- or six-centre system according to eqns. 2 and 3.



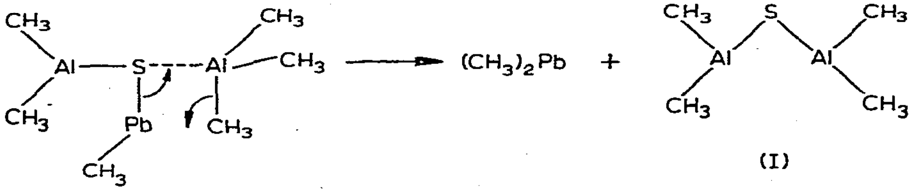
(IV) (V) (2)



(VI) (V)

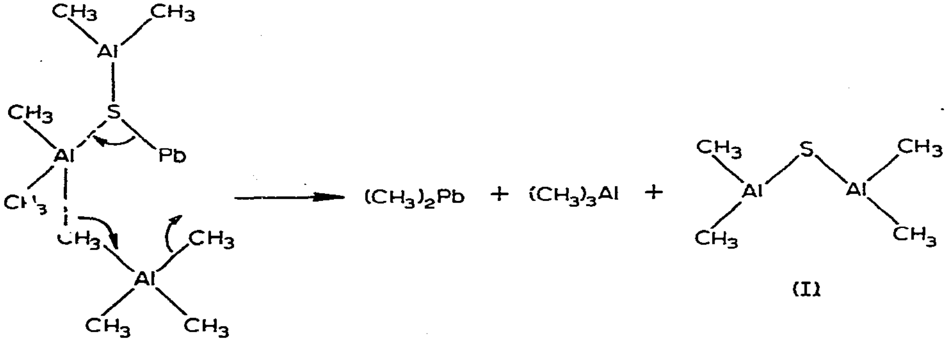
(3)

The intermediate compound V can then react with the subsequent molecule of trimethylaluminium (eqns. 4 and 5).



(VII) (I)

(4)



(VIII) (I)

(5)

As a result of reactions 4 or 5 bis(dimethylaluminium) sulphide and dimethyllead are formed. Dimethyllead undergoes disproportionation and stabilizes as previously described.

Experimental

Trimethylaluminium was prepared by a conventional method and used as a product of 99% purity.

Analytically pure lead sulphide (POCh-Gliwice, Poland) was ground, dried for 12 h at 150°, and then stored over a capillary sorbent. The solvents toluene, benzene, xylene and ethyl ether were distilled from sodium in a pure nitrogen atmosphere.

A weighed amount of lead sulphide was placed in a nitrogen flushed three-necked 15 ml flask equipped with a stirrer and cold trap. The flask was thermostatted to the required temperature. To the reactor thus prepared, a solution of trimethylaluminium in xylene was then injected into the reaction vessel. After the reaction was complete, the flask and its contents were cooled and the mixture was hydrolyzed with dilute (1/9) hydrochloric acid. Tetramethyllead was determined in the organic layer.

Results of the investigation of the influence of temperature, reaction time and molar ratio of the reactants on the yield of tetramethyllead are shown in Figs. 1, 2 and 3.

In the determination of the products in the reaction of trimethylaluminium with lead sulphide the following procedure was employed. To a reactor flushed out with dry nitrogen, 33.5 g (0.14 mole) lead sulphide, 25 ml benzene, and finally 20.0 g (0.28 mole) trimethylaluminium were added. The reactor was thermostatted at 70°, and its contents were vigorously stirred. After two hours the mixture was cooled to room temperature and 60 ml of ethyl ether was added. After the reaction had been completed the residual solution was distilled at 200°/ 0.02 mm Hg. In the distillate the presence of benzene, tetramethyllead, ethyl ether was ascertained. The residue after distillation [bis(dimethylaluminium) sulphide etherate[was analysed and its NMR spectrum recorded (Fig. 4).

NMR spectra were recorded on a JEOL JNM-60-H spectrometer.

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