

REACTION OF TRIMETHYLALUMINIUM WITH LEAD MONOXIDE

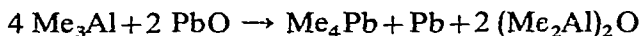
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SUMMARY

At elevated temperatures, trimethylaluminium reacts with yellow lead oxide to yield tetramethyllead and bis(dimethylaluminium) oxide. The reaction proceeds according to the equation:



Under the experimental conditions, only one of the trimethylaluminium methyl groups produces a Pb–C bond (tetramethyllead). The observed maximum conversions of methyl groups were 25.9% (8 h; 135°) and 28.1% (140 h; 80°).

In addition to tetramethyllead, the reaction of trimethylaluminium with yellow lead oxide affords some dimethylmethoxyaluminium. Lewis bases, if present in the reaction mixture, inhibit the synthesis of tetramethyllead.

The reaction products have been studied by NMR and IR spectral methods and by quantitative analysis.

INTRODUCTION

The vital importance of tetramethyllead and tetraethyllead as antiknock agents has given rise to a considerable literature concerned with this subject^{1–3}. This is, however, mostly patent literature, rather than papers elucidating the mechanisms of the reactions involved.

Earlier we explored the possibility of synthesizing tetraethyllead and tetramethyllead from organoaluminium compounds and lead salts^{4,5}, while more recently we have been interested in elucidating the mechanisms of the reactions of plumbous compounds with organoaluminium compounds^{6–10}.

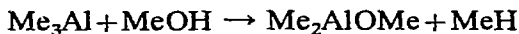
The purpose of this work was to study the reaction of lead monoxide with trimethylaluminium, to identify its products and to explain its course.

EXPERIMENTAL

1. *Reactants*

Trimethylaluminium was prepared by a method reported elsewhere¹¹ and used as a product of 99% purity.

Dimethylmethoxyaluminium was prepared by the reaction:



and purified by distillation at 87–88°/10 mmHg (Found: Al, 30.52. Me_2AlOMe calcd.: Al, 30.68%).

Pure-grade yellow lead oxide ("Budochemia", Gorzów, Poland) was ground, dried for 12 h at a temperature of 150°, and then stored over a type 4A molecular sieve.

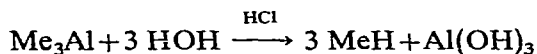
Solvents, namely benzene, xylene and cyclohexane, were distilled from sodium in a nitrogen atmosphere.

Lewis bases, namely dimethylformamide (Loba Chemie, Austria) and benzonitrile ("POCh" Reagent Works, Poland), were dried over a type 4A molecular sieve and distilled in a nitrogen atmosphere just before the use.

Technical grade nitrogen gas was purified in a conventional manner.

2. Analysis

Organoaluminium compounds were analyzed by decomposition with water according to the equation:



and subsequently determining active Me–Al methyl groups (volumetrically by measuring the methane evolved) and aluminium (by titrating with sodium versenate at pH 4.5–5.0) with the aid of the procedure described by Dahlig and Pasynkiewicz¹².

Tetramethyllead was determined iodometrically by the Newman procedure¹³.

For determining tetramethyllead in presence of organoaluminium compounds, a sample was hydrolyzed with a diluted (1/9) hydrochloric acid, the hydrolyzate was repeatedly extracted with small volumes of xylene and tetramethyllead was determined after the method described by Newman¹³.

In order to effect the analysis of lead in the presence of aluminium, a sample was dissolved in nitric acid and the lead determined gravimetrically as lead sulphate (PbSO_4). After the lead had been separated, aluminium was determined titrimetrically with sodium versenate as mentioned before.

3. Study of the effect of reaction parameters on the yield of tetramethyllead in the reaction of trimethylaluminium with yellow lead oxide

A weighed amount of lead monoxide was placed in a three-necked 15 ml flask equipped with stirrer and cold trap. The flask was flushed out with nitrogen and thermostated to the required temperature. To the reactor thus prepared, a solution of trimethylaluminium in xylene was injected through a serum cap, the reaction time being estimated from the moment of addition of the organoaluminium compound.

When reactions with organic donors were undertaken, both trimethylaluminium and the donor were placed in a well-cooled reactor flask, reaction time now being estimated from the moment the flask was introduced into the thermostat.

After the reaction had been completed, the flask and its contents were cooled and the mixture was hydrolyzed with 10 ml of a diluted (1/9) hydrochloric acid. Tetramethyllead was determined in the organic layer.

The reaction yield was calculated as the conversion (X) of the trimethylaluminium methyl groups into tetramethyllead, and also as the amount of reaction (Y) of lead monoxide.

$$X(\%) = \frac{4}{3} \frac{m_{\text{TML}} \cdot M_{\text{TMA}}}{m_{\text{TMA}} \cdot M_{\text{TML}}} \times 100$$

$$Y(\%) = 2 \frac{m_{\text{TML}} \cdot M_{\text{PbO}}}{m_{\text{PbO}} \cdot M_{\text{TML}}} \times 100$$

where the m quantities denote the weights of the resulting tetramethyllead (TML) and the reactants used, trimethylaluminium (TMA) and lead oxide (PbO); the M values are the molecular weights of the respective compounds.

Results of the study of various reaction parameters are summarized in Tables 1 and 2 and presented graphically in Figs. 1 and 2.

4. Determination of the maximum conversion of methyl groups

To a flask flushed out with dry nitrogen, 187 g of lead oxide, 70 ml of benzene (61.3 g), and 40.2 g of trimethylaluminium were added. The flask was thermostated

TABLE 1

THE EFFECT OF TEMPERATURE ON THE YIELD OF TETRAMETHYLLEAD IN THE REACTION OF PbO WITH TRIMETHYLALUMINIUM^a

Temperature (°C)	Conversion of methyl groups X (%)	Amount of reaction of PbO Y (%)
50	1.47	2.20
80	1.32	2.00
100	1.42	2.12
120	5.90	9.20
135	14.35	22.30

^a Reactant mole ratio $\text{Me}_3\text{Al}/\text{PbO} = 1/1$; reaction time, 4 h; concentration of Me_3Al in xylene, ca. 40%.

TABLE 2

INFLUENCE OF REACTION TIME ON THE YIELD OF TETRAMETHYLLEAD IN THE REACTION OF PbO WITH TRIMETHYLALUMINIUM^a

Reaction time (h)	Conversion of methyl groups X (%)	Amount of reaction of PbO Y (%)
1	2.34	3.50
2	4.42	6.60
4	14.35	22.30
6	21.90	33.00
8	25.90	38.80

^a Reactant mole ratio $\text{Me}_3\text{Al}/\text{PbO} = 1/1$; temperature, 135°; concentration of Me_3Al in xylene, ca. 40%.

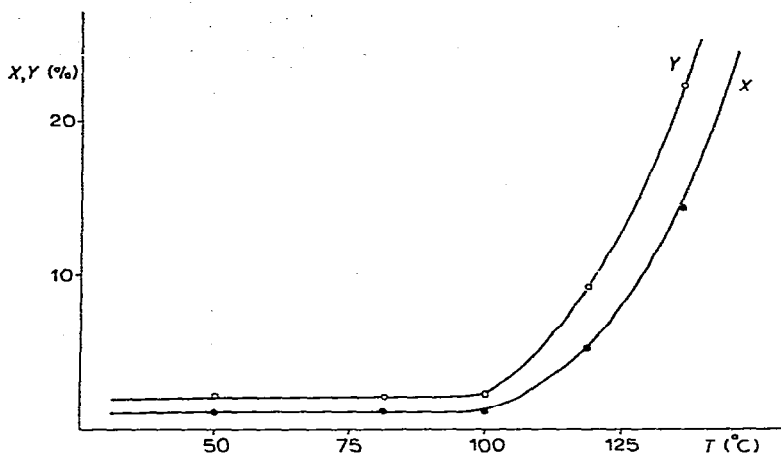


Fig. 1. The yield of TML as a function of temperature.

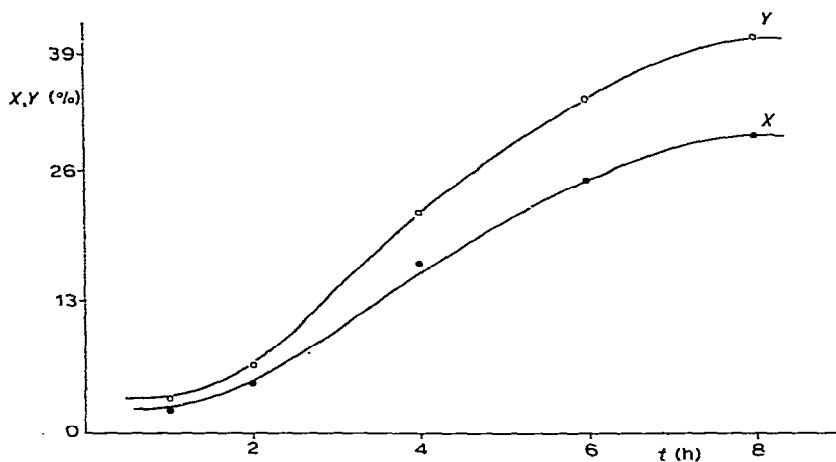


Fig. 2. The yield of TML as a function of reaction time.

at a temperature of 80° and the cold trap was filled with Dry-Ice. The mixture was vigorously stirred and the reaction was continued for 140 h. Samples of the reaction mixture were withdrawn at regular intervals for analysis for hydrolyzable methyl groups, aluminium and tetramethyllead, the samples totalling 11.42 g of the reaction solution. Data are listed in Table 3.

After 140 h, the flask and its contents were weighed and the sediment formed was isolated from the solution.

The sediment was repeatedly extracted with benzene and dried *in vacuo*. It was found to contain 5.1% (9.5 g) of aluminium.

After the yellow liquid mixture obtained from the reaction was analyzed and its NMR spectrum recorded, it was concentrated *in vacuo* to yield 28.1 g of TML ($X = 28.1\%$) and 110.5 g of a viscous by-product. The by-product could not be distilled even at reduced pressures of 0.3 mmHg and temperatures up to 70°. From the ex-

TABLE 3

THE INFLUENCE OF REACTION TIME ON THE MOLE RATIO OF HYDROLYZABLE $\text{CH}_3\text{-Al}$ METHYL GROUPS TO ALUMINIUM AND ON THE CONVERSION OF METHYL GROUPS IN THE $\text{Me}_3\text{Al/PbO}$ REACTION^a

Reaction time (h)	Hydrolyzable Me-to-Al (moles/mole)	Conversion of methyl groups X (%)
0	2.94	
15	2.74	6.25
23	2.52	8.35
35.5	2.43	11.85
59	2.54	18.00
84	2.23	22.76
108	2.12	25.30
140	2.06	28.10

^a Reactants: Me_3Al , 40.2 g; PbO , 187 g; C_6H_6 , 61.3 g; reaction temperature, 80°.

TABLE 4

THE MATERIAL BALANCE OF METHYL GROUPS AND ALUMINIUM AND THE MOLE RATIO OF HYDROLYZABLE ($\text{CH}_3\text{-Al}$) METHYL GROUPS TO ALUMINIUM IN THE $\text{Me}_3\text{-Al/PbO}$ REACTION

CH_3	Al
<i>Before reaction:</i>	
Me in Me_3Al 23.65 g	Al in Me_3Al 14.37 g
<i>After reaction:</i>	
Me in Me_4Pb 7.05 g	Al in reaction sediment 9.51
Hydrolyzable Me in soln. 3.83	
Me combined as OCH_3^a 0.93	Al in reaction soln. 3.35
Total Me in samples 1.34	Total Al in samples 1.18
SUB-TOTAL 13.15 g	TOTAL 14.04 g
Me in sediment 10.50	
TOTAL 23.65 g	
<i>Mole ratio of hydrolyzable methyl groups to aluminium</i>	
<i>In reaction solution:</i>	<i>In sediment:</i>
$-\text{CH}_3$ 3.83 g = 0.255 mole	$-\text{CH}_3$ 10.50 g = 0.700 mole
Al 3.35 g = 0.124 mole	Al 9.50 g = 0.351 mole
$\text{CH}_3/\text{Al} = 2.06$	$\text{CH}_3/\text{Al} = 1.99$

^a Estimated from the greater than stoichiometric amount of oxygen added as $\text{Pb}_{1.000}\text{O}_{1.074}^{12}$.

perimental data a material balance of methyl groups and aluminium was computed (Table 4). (Found: Al, 30.92%.)

An analogous reaction, which was continued for 37 h at a temperature of

80°, afforded 14.5 g of tetramethyllead ($X = 15.5\%$) and 9.5 g of a by-product. When heated to 200° at 0.3 mmHg, the by-product yielded 4.2 g of dimethylmethoxyaluminium and 5.1 g of a glassy product. (Found: Al, 35.85%.)

5. Partial hydrolysis of trimethylaluminium with water

The hydrolysis was undertaken using the techniques and equipment described elsewhere¹⁴. The reactants included 90 ml of n-heptane, 19.3 g of trimethylaluminium and 1.7 g of distilled water. The water was added in the form of water vapour borne by nitrogen as a carrier gas. Nitrogen was passed for ca. 15 h and the reactor temperature was maintained at temperatures within the range -25 to -30° . After the completion of the reaction the solution was filtered, the solvent evaporated and the contents of the flask finally heated to a temperature of 85° at 0.6 mmHg pressure to yield 3.7 g of a yellow viscous liquid. (Found: Al, 30.80%.)

The synthesis was repeated a number of times with slightly modified conditions. The product of the reaction was analyzed for aluminium and its NMR spectrum was recorded. When heated at a temperature of 200° and a pressure of 0.6 mmHg, the product gave small amounts of dimethylmethoxyaluminium and a glassy residue. (Found: Al, 36.40%.)

6. Spectral studies

IR spectra were run on benzene solutions and recorded with the aid of a Zeiss UR-10 spectrophotometer equipped with potassium chloride optics. NMR spectra were run on 3–10% solutions and recorded by the use of a JNM-60-H spectrometer (JEOL, Tokyo). Samples for spectral studies were withdrawn and prepared in an atmosphere of purified nitrogen.

7. Measurements of adsorption of trimethylaluminium by lead monoxide

A standard solution of trimethylaluminium in benzene, containing Me_3Al 3.5, C_6H_{12} 4.3 and C_6H_6 92.2 wt. % was used for the measurements. NMR methods were used to measure the relative intensity of the peak associated with the trimethylaluminium methyl group protons relative to that of the cyclohexane protons. To the standard solution, lead oxide was added in a known amount at a temperature of 15°. The reactants were mixed for 5 min and the supernatant liquid was then sampled for spectral studies. The variation of the relative intensity of the peak due to the methyl protons in relation to the amount of lead oxide added is recorded in Table 6 and in Fig. 5. The spectra exhibit no peaks associated with tetramethyllead. The lead oxide sediment remaining after completion of the reaction was isolated from the liquid, washed repeatedly with benzene, and dried *in vacuo* (50°, 0.5 mmHg). The aluminium content of the sediment had an average value of 0.70–0.90%. No aluminium was detected in the original oxide used for the reaction.

RESULTS AND DISCUSSION

Trimethylaluminium reacts with lead monoxide in a non-polar solvent (benzene, xylene) to yield tetramethyllead. The reaction is not exothermic. During the course of the synthesis the reaction mixture darkens, first turns yellow and finally black on account of the metallic lead generated.

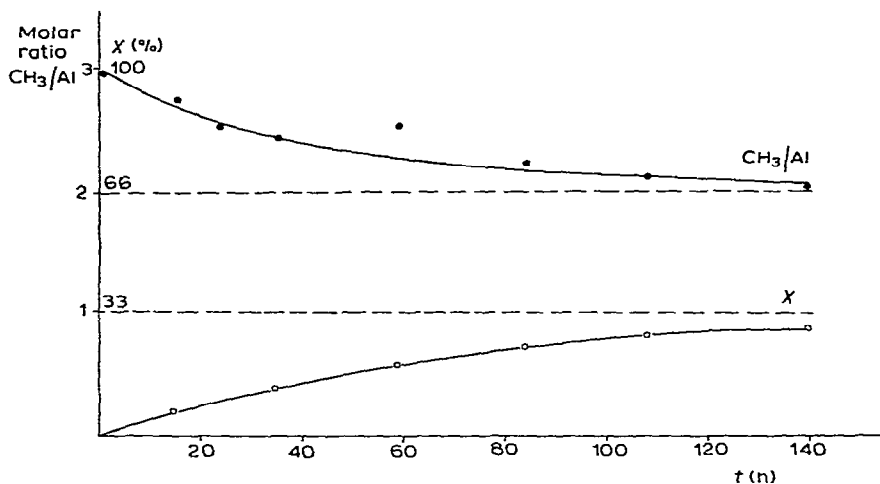
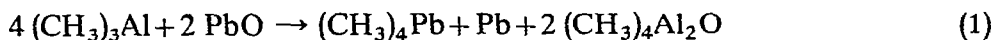


Fig. 3. The mole ratio of hydrolyzable methyl groups to aluminium, CH_3/Al , and conversion of methyl groups as a function of reaction time.

The yield of tetramethyllead from the reaction, relative to the temperature and the reaction time, is presented in Tables 1 and 2 and Figs. 1 and 2.

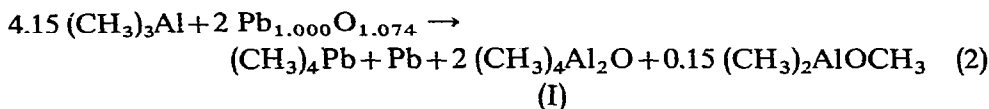
Over the temperature range 50–100°, the reaction is independent of the temperature and proceeds with low yields ($X^* = 1.4\%$). As the temperature is increased above 100°, the conversion (X) of the methyl groups and the amount of reaction (Y) of lead oxide rapidly increase. Increasing the length of time of the reaction increases the yield of tetramethyllead. The shape of the curve relating X and time, t , (Fig. 2) and the maximum conversion of the methyl groups, $X = 25.9\%$ (135°, 8 h), indicate that under the experimental conditions employed, complete removal of one methyl group from trimethylaluminium is not achieved as the final degree of conversion is less than $X = 33.3\%$. This is confirmed by the data listed in Table 3 and presented graphically in Fig. 3. Figure 3 presents the variation in the molar ratio of hydrolysable methyl groups to aluminium in the reaction solution and an increase in the extent of removal of methyl groups when the reaction was carried out for 140 h at 80°. The molar ratio of hydrolyzable methyl groups to aluminium in the reaction mixture falls from the initial value of 3/1 at the start of the reaction to a final value of 2/1 as the reaction proceeds. This indicates that only one methyl group in trimethylaluminium reacts with lead monoxide to form a non-hydrolyzable $\text{Pb}-\text{CH}_3$ bond (in tetramethyllead). This is further supported by the fact that the extent of conversion of methyl groups, X , increases from 0% at the start of the reaction and tends towards 33%. Thus of the three methyl groups in trimethylaluminium, only one reacts to yield tetramethyllead:



* X , or the conversion of methyl groups, is the ratio of the methyl groups in the resulting tetramethyllead to the initial amount of methyl groups present in the system through the addition of the organoaluminium compound.

Y , or the extent of reaction of lead monoxide, is the ratio of the amount of lead in the resulting tetramethyllead to the initial amount of lead present in the system through the addition of lead oxide.

Clark and Rowan¹⁵ found that yellow lead oxide contains more than the stoichiometric amount of oxygen, *i.e.* 1.074 mole to 1 mole of lead. The excess oxygen reacts with trimethylaluminium to yield dimethylmethoxyaluminium. Therefore, reaction (1) may be rewritten as follows:



This suggested scheme for reaction (2) is compatible with the proportion of methyl groups and aluminium found in the system as given in Table 4 for the reaction carried out at 80° for 140 h.

In addition to tetramethyllead and metallic lead, reaction (2) also affords bis(dimethylaluminium)oxide (I) and dimethylmethoxyaluminium. The two last-mentioned compounds were isolated from the reaction solution as a mixture. Attempts to isolate pure (I) from this mixture failed, but dimethyldimethoxyaluminium could be isolated.

According to the literature, bis(dialkylaluminium) oxides $(\text{R}_2\text{Al})_2\text{O}$ (where $\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$) can be prepared by partial hydrolysis of trialkylaluminium:



The resulting bis(dialkylaluminium) oxides are nearly or completely non-volatile and highly reactive towards water and oxygen^{14,16,17}. Neither the synthesis nor the properties of bis(dimethylaluminium) oxide have been reported in the literature to date.

In this work the partial hydrolysis of trimethylaluminium has been investigated, synthesis of the compound being achieved by the method of Sakharovskaya¹⁴.

The physical properties and the IR and NMR spectral data of the products of the partial hydrolysis of trimethylaluminium and of the reaction of lead monoxide with trimethylaluminium confirm that the products obtained in these reactions are similar (Fig. 4).

The IR spectra of the products of these reactions exhibited a strong band due to an Al—O—Al stretching vibration at 650–655 cm^{-1} . Sakharovskaya *et al.*¹⁶ performed model calculations for the normal Al—O—Al stretching vibrations and found that symmetric valence vibrations should occur at 636 cm^{-1} . The experimental value found by these authors was 650 cm^{-1} .

The mixture of bis(dimethylaluminium) oxide and dimethylmethoxyaluminium, $(\text{Me}_2\text{Al})_2\text{O}/\text{Me}_2\text{AlOMe}$, afforded by reaction (2) above exhibits three NMR peaks attributable to resonances of the methyl group protons at τ 6.75, 10.27 and 10.48 ppm (Fig. 4). The τ 6.75 and the 10.48 bands are attributable to the respective resonances of the $-\text{OCH}_3$ protons and the CH_3 protons in dimethylmethoxyaluminium. The areas of these peaks are in the ratio of 1/2. The τ 10.27 band corresponding to resonance of the protons in the CH_3 group attached to the aluminium atom must be attributed to a methyl group in bis(dimethylaluminium) oxide because it differs from the resonance band of the protons in the trimethylaluminium methyl group (τ 10.20 ppm).

When heated to 200° at 0.3 mmHg, the products of the reaction of trimethylaluminium with lead oxide start to foam and on continuing the heating dimethyl-

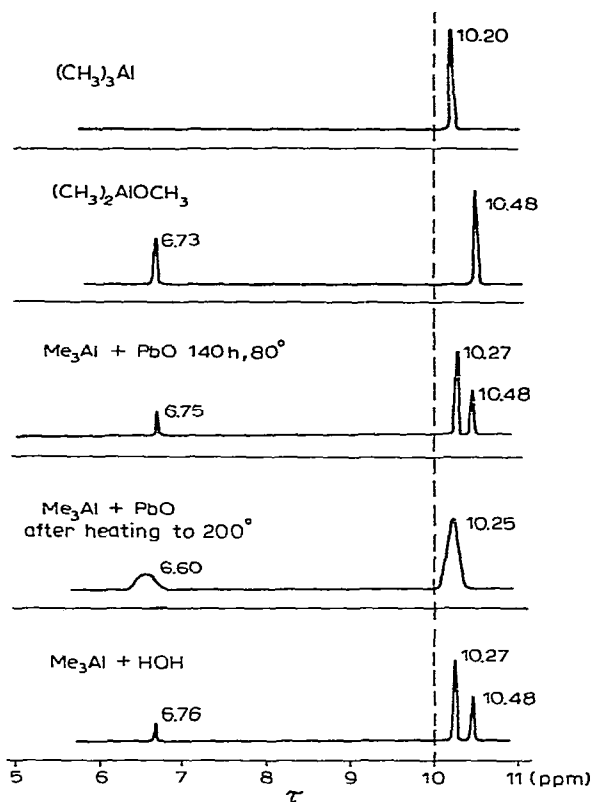
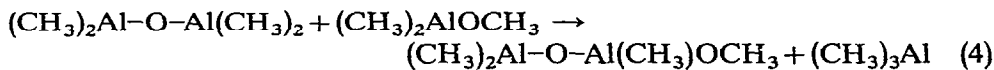


Fig. 4. NMR chemical shifts of the Al-CH₃ and Al-O-CH₃ groups.

methoxyaluminium was distilled off. The aluminium contents in the respective residual glasses increased from initial values of 30.80 and 30.92% to 35.85 and 36.40% after heating. The NMR spectrum exhibited a considerable broadening of the line and a shift of the methoxy group from τ 6.75 to 6.60 ppm (Fig. 4). The presence of an -OCH₃ group in the NMR spectrum together with an accompanying shift, despite the isolation of dimethylmethoxyaluminium, suggests that heating must result in the following reaction:



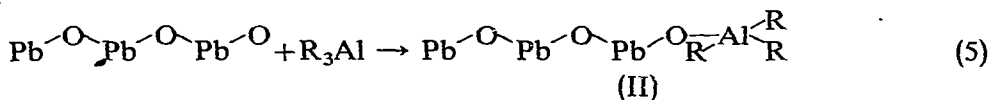
The final aluminium content of the resulting glasses (35.85 and 36.40%) are slightly lower than that required for trimethylmethoxyaluminium (36.98%). The observed broadening of the resonance line may be attributed to the poor solubility of the compound in aromatic hydrocarbons and to its high tendency to associate or polymerise.

Lead oxide has a lamellar structure and forms infinite lamellae. Each lamella consists of tetracoordinate lead and oxygen atoms arranged in a characteristic zigzag pattern. The lamellae are held together by weak interaction forces of the Van der Waals type. The minimum Pb-O distance is 2.00 Å^{18,19}.

The oxygen atoms at the surface of the PbO crystal lattice possess higher partial negative charges than the atoms in the bulk of the crystal. Within the crystal,

one tetracoordinate oxygen atom utilizes its 2s and 2p electrons to produce four bonds to the lead atom, while at the surface some portion of the charge remains uncombined.

The first stage of the reaction of trimethylaluminium with lead monoxide is likely to involve chemisorption of trimethylaluminium onto the oxide surface with the formation of a coordination bond between the aluminium and the basic oxygen atom:



This first stage in the reaction is confirmed by results of the study of the effect of Lewis bases on the yield of tetramethyllead in the reaction of trimethylaluminium with lead monoxide (Table 5). Lewis bases inhibit this reaction presumably through the formation of a strong donor-acceptor complex, *e.g.* $\text{Me}_3\text{Al} \cdot \text{C}_6\text{H}_5\text{CN}$, thus inhibiting reaction (7) and preventing the formation of complex (II).

Quantitative NMR spectral studies on the adsorption of trimethylaluminium on lead oxide surfaces (Table 6, Fig. 5) support the above suggestions regarding the first stage of the reaction. The variation in the intensity of the methyl group protons in the NMR spectrum indicates the existence of a simple quantitative relationship between the observed decrease in concentration of trimethylaluminium in the reaction solution and the amount of lead oxide used during the reaction (number of active centres for chemisorption).

The fact that lead monoxide treated with a dilute solution of trimethylaluminium for 5 min at 15°, *i.e.* under conditions which prevent the synthesis of tetramethyllead, contained 0.8% of aluminium is also in keeping with the above scheme for the first stage in the reaction. Repeated washing with benzene and drying *in vacuo* (0.5 mmHg, 50°, 20 h) failed to remove the organoaluminium compound from the lead oxide surface. A similar observation has been made by Tyrlik²⁰ who found that AlCl_3 , sublimed onto PbO , completely inhibited the formation of lead benzoate. The sublimed chloride could not be removed by repeated washing with ethyl ether, which is known to dissolve AlCl_3 readily through the formation of the complex $\text{Et}_2\text{O} \cdot \text{AlCl}_3$.

TABLE 5

THE EFFECT OF LEWIS BASES ON THE YIELD OF TETRAMETHYLLEAD IN THE REACTION OF LEAD MONOXIDE WITH TRIMETHYLALUMINIUM^a

Lewis base	Reactant mole ratio $\text{Me}_3\text{Al}/\text{PbO}/\text{D}^b$	Conversion of methyl groups <i>X</i> (%)	Amount of PbO reaction <i>Y</i> (%)
	1/1/0	13.60	9.90
$\text{C}_6\text{H}_5\text{CN}$	1/1/1	2.02	1.50
$\text{HCON}(\text{CH}_3)_2$	1/1/0.5	3.71	2.78
$\text{HCON}(\text{CH}_3)_2$	1/1/1	2.18	1.64

^a Reaction time, 4 h; temperature, 135°; concentration of Me_3Al in xylene, ca. 20%. ^b D stands for a Lewis base.

TABLE 6

VARIATION OF THE INTENSITY OF THE METHYL GROUP PROTONS IN THE NMR SPECTRUM WITH THE MOLE RATIO OF LEAD MONOXIDE TO TRIMETHYLALUMINIUM

Run No.	PbO/Me ₃ Al (mole ratio)	Relative integration ^a for the methyl group	
		<i>I</i> _{rel.}	(<i>I</i> _{rel.}) _{av.}
1	0/1	0.807	0.762
		0.734	
		0.750	
2	3/1	0.756	0.712
		0.739	
		0.679	
		0.715	
3	6/1	0.715	0.658
		0.687	
		0.603	
		0.674	
4	12/1	0.666	0.535
		0.563	
		0.516	
		0.527	

^a Relative integration: $I_{rel.} = (I_{Me_3Al} / I_{C_6H_{12}})$.

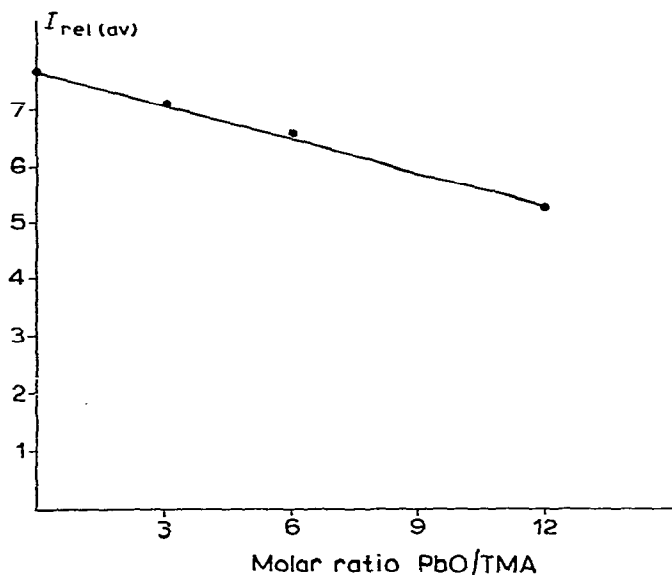
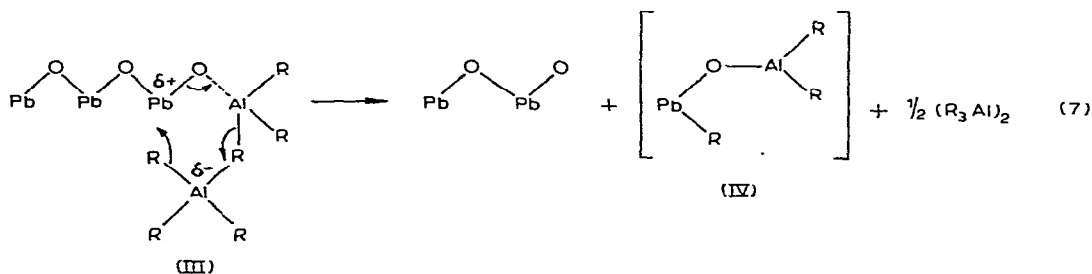
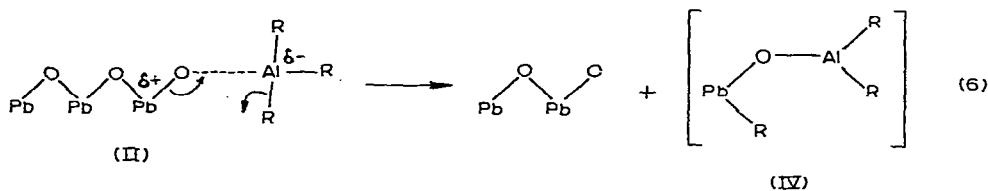


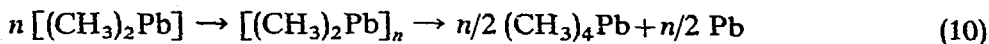
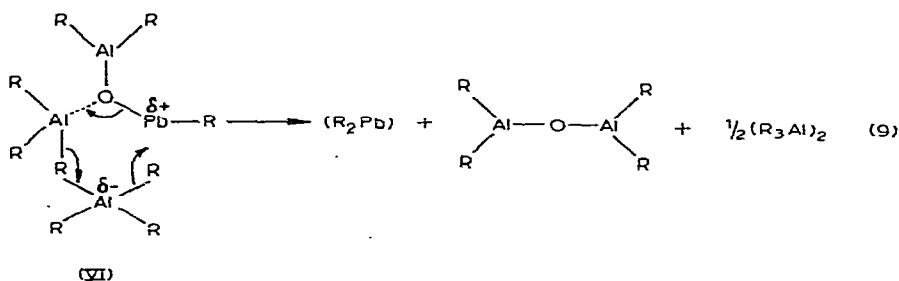
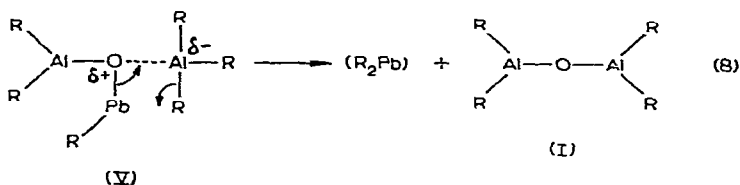
Fig. 5. Decrease in the Me₃Al methyl group intensity in the NMR spectrum as the result of adsorption of Me₃Al on the PbO surface.

Through displacement of the oxygen electrons toward the aluminium atom in the resulting complex (II) a partial positive charge is created on the lead atom, thus allowing the rearrangement of the alkyl anion from the aluminium to the lead atom in the four- or six-centre system.



During the reaction, the reacting lead oxide molecule is presumably extracted from the crystal lattice. This exposes a further PbO molecule which allows the first stage of reaction (7) to proceed. The resulting intermediate (IV) reacts with a second molecule of trimethylaluminium in the four- or six-centre system with electron transfer, to yield dimethyllead and bis(dimethylaluminium) oxide.

The resulting dimethyllead formed in reaction (8) or (9) disproportionates (reaction 10) to yield tetramethyllead and metallic lead.



The elimination of metallic lead predicted by this equation results in the black colour of the final reaction mixture.

REFERENCES

- 1 L. C. Willemsens, *Organolead Chemistry*, New York, 1964.
 - 2 T. H. Pearson and S. M. Blitzer, *U.S. Pat.* 2,859,255-2,859,232; 2,955,124; 2,985,675; 2,989,558; 3,007,955.
 - 3 R. W. Leeper, L. Summers and H. Gilman, *Chem. Rev.*, 54 (1954) 101.
 - 4 W. Dahlig, S. Pasynkiewicz and K. Ważyński, *Przem. Chem.*, 39 (1960) 436.
 - 5 S. Pasynkiewicz, S. Malinowski and J. Bitter, *Przem. Chem.*, 44 (1965) 500.
 - 6 S. Pasynkiewicz and M. Bolesławski, *Intern. Conf. on Organometal. Chem.*, Munich, 1967, p. 302.
 - 7 M. Bolesławski, Thesis, Technical University (Politechnika), Warsaw, 1969.
 - 8 M. Bolesławski and S. Pasynkiewicz, *Vth Intern. Conf. on Organometal. Chem.*, Moscow, 1971, 179 1467.
 - 9 M. Bolesławski, S. Pasynkiewicz and K. Jaworski, *J. Organometal. Chem.*, 30 (1971) 199.
 - 10 M. Bolesławski, S. Pasynkiewicz and H. Pszonka, *J. Organometal. Chem.*, 28 (1971) C31.
 - 11 S. Pasynkiewicz and M. Bolesławski, *J. Organometal. Chem.*, 25 (1970) 29.
 - 12 W. Dahlig and S. Pasynkiewicz, *Przem. Chem.*, 39 (1960) 300.
 - 13 L. Newman, T. F. Philip and A. R. Jensen, *Anal. Chem.*, 19 (1947) 451.
 - 14 G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, E. I. Larikov and A. F. Zhigach, *Zh. Obshch. Khim.*, 34 (1964) 3435.
 - 15 G. L. Clark and R. Rowan, *J. Amer. Chem. Soc.*, 63 (1941) 1305.
 - 16 G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, J. Kissin, S. Mierzykowski, E. Krystalny, *Zh. Obshch. Khim.*, 39 (1969) 788.
 - 17 A. Storr, K. Jones and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 90 (1968) 3173.
 - 18 J. Leciejewicz, *Acta Crystallogr.*, 14 (1961) 66.
 - 19 B. Dickens, *J. Inorg. Nucl. Chem.*, 27 (1965) 1495.
 - 20 S. Tyrlík, Thesis, Polish Academy of Sciences, Warsaw, 1964.
- J. Organometal. Chem.*, 43 (1972)