

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Polymerization of Some Derivatives of Trimethylaluminum

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Certain classes of aluminum compounds are of considerable interest in structural chemistry because their members are polymerized to dimers, trimers or tetramers. Although these polymerizations are probably to be attributed to the tendency of the trivalent aluminum atom to achieve a coordination number of four or higher, the particular factors which govern the degree and strength of the association are not understood.

To illustrate the puzzling nature of the problem, attention may be called to aluminum chloride³ and trimethylaluminum.⁴ Both of these compounds are associated to dimers in the vapor state; both react with coordinating agents such as amines and ethers to form coordination derivatives of the monomers; and the energy of association is of the same order of magnitude (20.2 kcal. for trimethylaluminum⁵ as compared with 29.0 kcal. for aluminum chloride).³ This evidence is concordant with the hypothesis that the mode of polymerization of these two related substances is similar, yet the results of electron diffraction investigations indicate that aluminum chloride associates through the formation of chlorine bridges (A),⁶ whereas trimethylaluminum apparently possesses a bridge-free, ethane-like structure (B).^{6,7}

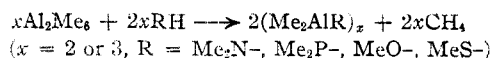
The phenomenon becomes even more puzzling when it is considered that numerous trimers and tetramers of aluminum compounds are known, es-

pecially among the aluminum alcoholates.⁸ No correlation between the composition of a given derivative and the degree of its polymerization has been brought forth.

In the present investigation an attempt was made to throw some light on the problem by studying the effect of structure, in some relatively simple derivatives of trimethylaluminum, upon the degree and strength of the polymerization.

Results and Discussion

The derivatives studied were $\text{Me}_2\text{AlNMe}_2$, $\text{Me}_2\text{AlPMe}_2$, Me_2AlOMe , Me_2AlSMe , Me_2AlCl and Me_2AlBr (empirical formulas). The first four were prepared by the action of trimethylaluminum upon the calculated quantity of dimethylamine, dimethylphosphine, methyl alcohol and methyl mercaptan, respectively. The reactions are indicated by the equation



The halogen derivatives (Me_2AlCl and Me_2AlBr) were prepared by the reactions of aluminum with methyl chloride and bromide.⁹

These derivatives are liquids or solids at room temperature and volatile at elevated temperatures. The substances $\text{Me}_2\text{AlNMe}_2$, Me_2AlSMe , Me_2AlCl and Me_2AlBr were found to be dimeric as vapors and are not measurably dissociated at 150° and 30 mm. pressure (Al_2Me_6 is over 50% dissociated under these conditions); the substances $\text{Me}_2\text{AlPMe}_2$ and Me_2AlOMe were found to be trimeric under similar conditions. (Descriptive data are summarized in Table I.)

Since none of the compounds under investigation is measurably dissociated in the vapor state under the experimental conditions used in this investigation, an indirect method was used to compare their stabilities, relative to dissociation into monomers. For this purpose, the reactions of the polymers with coordinating agents such as trimethylamine and dimethyl ether were studied. Thus it was found that dimeric dimethylaluminum chloride (Me_2AlCl)₂ reacts with trimethylamine and with dimethyl ether to form the stable

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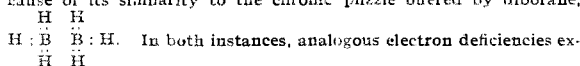
(3) Smits and Meijering, *Z. physik. Chem.*, **B41**, 98 (1938).

(4) Laubengayer and Gilliam, *THIS JOURNAL*, **63**, 477 (1941).

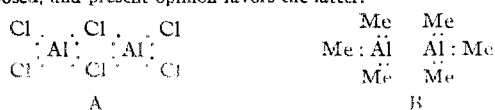
(5) Palmer and Elliot, *ibid.*, **60**, 1852 (1938).

(6) Davidson, Hugill, Skinner and Sutton, *Trans. Faraday Soc.*, **26**, 1212 (1940); Brockway and Davidson, *THIS JOURNAL*, **63**, 3287 (1941).

(7) The case of trimethylaluminum is particularly interesting because of its similarity to the chronic puzzle offered by diborane,



In both instances, analogous electron deficiencies exist. For diborane, both bridged and ethane-like structures have been proposed, and present opinion favors the latter.



(8) (a) Robinson and Peak, *J. Phys. Chem.*, **39**, 1125 (1935); (b) Ulich and Nespital, *Z. physik. Chem.*, **A165**, 294 (1933).

(9) Von Grosse and Mavity, *J. Org. Chem.*, **5**, 406 (1940).

TABLE I

Compound	A ($\times 10^{-3}$), (of eqn., $\log_{10} p$, mm. = $-A/T + B$)	B	ΔH (vap.) kcal.	B. p., °C. ^a (extrapolated)	Trouton's ^a constant	M. p., °C.
(Me ₂ AlNMe ₂) ₂ (solid)	2.773	8.944	13.22			154-156
(Me ₂ AlSMe) ₂ (liq.)	3.070	9.005	14.1	228	28	103
(Me ₂ AlCl) ₂	2.150	8.362	9.84	119.4	25.0	-45 -21.0
(Me ₂ AlBr) ₂	2.280	8.259	10.44	150	24.6	
(Me ₂ AlOMe) ₃	2.92	9.24	13.9			
Me ₃ N:AlMe ₃ (solid)	2.732	9.146	12.5			105
(liq.)	2.38	8.19	10.9	177	24.4	
Me ₂ O:AlMe ₃	2.148	7.832	9.85	159	22.9	-29.9
Me ₃ P:AlMe ₃ (liq.)	2.566	8.520	11.8	189	25.6	62.5
Me ₂ S:AlMe ₃ (liq.) [*]	2.462	8.740	11.3	141	27.2	
Me ₂ NH:AlMe ₃	2.62	8.60	12.0	186	26.1	51
Me ₂ PH:AlMe ₃	2.429	8.388	11.10	169	25.2	
Me ₃ N:AlMe ₂ Cl (solid)	3.14	9.31	14.4			124
Me ₂ O:AlMe ₂ Cl	2.332	7.571	10.70	224	22.8	

^a Due to the large extrapolation involved, these values must be considered as approximate.

addition compounds, Me₃N:AlMe₂Cl and Me₂O:AlMe₂Cl, neither of which is dissociated in the vapor state. Evidently the bond or bonds joining two Me₂AlCl molecules to each other is weaker than the bond between this molecule and either trimethylamine or dimethyl ether.

The mercaptyl derivative (Me₂AlSMe)₂ reacts in a similar fashion with trimethylamine but does not react with dimethyl ether and thus appears to be more stable than the chloro derivative. (In general, trimethylamine is a stronger coordinating agent than is dimethyl ether.) The substance (Me₂AlNMe₂)₂ reacts with neither trimethylamine nor dimethyl ether and thus appears to be the most stable of the three dimers. Neither of the trimers, (Me₂AlPMe₂)₃ or (Me₂AlOMe)₃, reacts with trimethylamine; they appear to have a high degree of stability.

Before proceeding with the argument, it must be pointed out that there is a possible flaw in the reasoning which has led to the preceding conclusions. The order of reactivity of the polymers toward coordinating agents may be regarded as a qualitative measure of the sum of two terms: the free energy of dissociation of the polymers into the monomeric forms and the free energy of the reaction of the monomer with the coordinating agent. Only if changes in the latter quantity are small compared to changes in the former do the observed reactions have the significance ascribed to them.¹⁰

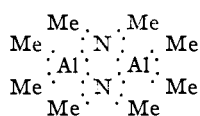
(10) Certainly this second factor is not absolutely negligible; although Al₂Me₆ dissociates more readily than does (Me₂AlCl)₂, the reaction (Me₂AlCl)₂ + 2Me₂O:AlMe₃ \rightleftharpoons Al₂Me₆ + 2Me₂O:AlMe₂Cl proceeds quantitatively to the right. If the greater stability of Me₂O:AlMe₂Cl as against Me₂O:AlMe₃ is attributed to an inductive effect of the polar Al-Cl bond, it would be expected that the order of decreasing acceptor power of the monomers toward coordinating agents would be Me₂AlCl, Me₂AlNMe₂, and Me₂AlSMe (based on the Pauling electronegativity table).

To coordinate the observations recorded, a second line of investigation was undertaken, *i. e.*, a study of the relative stabilities of the one to one addition compounds of trimethylaluminum with the coordinating agents, trimethylamine, trimethylphosphine, dimethyl ether and dimethyl sulfide. (Descriptive data are summarized in Table I.) These addition compounds are solids or liquids, volatile at elevated temperatures. The vapor of dimethyl sulfide-trimethylaluminum,¹¹ Me₂S:AlMe₃, is partially dissociated at 120° and 40 mm. pressure; the other substances are not measurably dissociated at 150° and the same pressure. Hence the relative stabilities were determined by displacement reactions. Thus the reaction Me₃N + Me₃P:AlMe₃ \rightarrow Me₃P + Me₃N:AlMe₃ proceeds quantitatively, demonstrating that, toward trimethylaluminum, trimethylamine is a stronger coordinating agent than is trimethylphosphine. From such experiments it was concluded that the coordinating power of these reagents toward trimethylaluminum decreases in the order: trimethylamine, trimethylphosphine, dimethyl ether and dimethyl sulfide. The substance methyl chloride does not react with tri-

(11) There is no generally accepted method of naming addition compounds such as Me₂S:AlMe₃. It has been suggested [THIS JOURNAL, **63**, 889 (1941)] that such substances be referred to as the "compound of trimethylaluminum with dimethyl sulfide," but this nomenclature becomes exceedingly cumbersome when, as in the present paper, numerous references to such substances must be made. It is believed that the adoption of a hybrid name, with the components separated by a hyphen, is to be preferred. Thus, according to this system, Me₂S:AlMe₃ is called dimethyl sulfide-trimethylaluminum. In naming the components, it is suggested that the donor molecule (*i. e.*, the "base") be given first, followed by the acceptor molecule (the "acid"), and in writing the formula of the compound, the same sequence be observed. The use of the symbol: to indicate the formation of an electron-pair bond is recommended. The symbol \cdot is then to be restricted to double compounds (or compounds of higher order) of unknown structure.

methylaluminum and is placed last on the list.¹²

It is thus seen that the coördinating powers of the methyl derivatives of the elements nitrogen, sulfur and chlorine decrease in the same order as do the stabilities of the polymeric substances, $(\text{Me}_2\text{AlNMe}_2)_2$, $(\text{Me}_2\text{AlSMe})_2$ and $(\text{Me}_2\text{AlCl})_2$ containing these elements. Such a relationship would be expected if the dimeric compounds are of the bridged type, since the polymerization then depends on the coördinating power of the bridging atom. These observations are then concordant with the electron diffraction data which indicate bridged structures for the substances $(\text{Me}_2\text{AlCl})_2$ and $(\text{Me}_2\text{AlBr})_2$,⁶ and considered in conjunction with this latter evidence, they afford strong support for the hypothesis that the other dimeric compounds also have bridged structures. The structure of the nitrogen compound, for example, is taken to be¹³



It cannot be said, of course, that the chemical evidence excludes an ethane-like structure for the polymers since in terms of that hypothesis there is no known basis for predicting trends in their stability.

There is no direct evidence for the structure of the trimers, $(\text{Me}_2\text{AlPMe}_2)_3$ and $(\text{Me}_2\text{AlOMe})_3$. It is not unreasonable to assume, however, that they are six-membered ring bridged compounds. Such an assumption is consistent with the observation that they do not react with trimethylamine. No reason can be advanced for the fact that these two substances differ from those which are dimeric; indeed it is not apparent why any bridged compound should be dimeric as against trimeric, or conversely.

Attention is called to the high stability of these ring systems containing coördinate links. In terms of a simple bond energy picture, the stability of $(\text{Me}_2\text{AlNMe}_2)_2$ is that due to the formation of two nitrogen-aluminum coördinate links

(12) Dimethylphosphine-trimethylaluminum is appreciably dissociated in the vapor state at 150° and 30 mm. pressure showing that dimethylphosphine is a weaker coördinating agent than is trimethylphosphine. This fact provides an example of what may be a fairly general increase in coördinating power as methyl is substituted for hydrogen, cf. $\text{H}_3\text{N}:\text{BMe}_3$ and $\text{Me}_2\text{N}:\text{BMe}_3$ [Stock, *Ber.*, **54**, 531 (1921); Schlesinger, Flodin and Burg, *THIS JOURNAL*, **61**, 1078 (1939)].

(13) Stereochemical consequences of this structure must, of course, be based upon tetrahedral coördination around both nitrogen and aluminum atoms.

minus the strain energy of the four-membered ring, yet this substance does not react with trimethylamine to form two nitrogen to aluminum coördinate links with no strain. Methyl chloride has practically no coördinating properties, yet dimethylaluminum chloride is strongly dimerized. It may well be that resonance with ionic structures plays an important role in the surprisingly high stability of these compounds; an increased entropy of formation due to symmetry factors is also significant.

None of the experiments described in this report sheds any light upon the puzzling and still unsolved problem of the mode of polymerization of trimethylaluminum itself, except in the negative sense that they emphasize the distinction between trimethylaluminum and the bridged compounds to which normal electron-pair bond structures may be assigned. One experimental study of the polymerizing tendencies of monomeric trimethylaluminum was made and is perhaps worthy of mention. By analogy with aluminum borohydride, $\text{Al}(\text{BH}_4)_3$,¹⁴ it might be expected that the compound $\text{Al}(\text{BMe}_4)_3$ would exist. Favorable conditions for its formation would be a high concentration of trimethylboron and a low concentration of Al_2Me_6 . The molecular weight of trimethylaluminum in dilute solution in trimethylboron (at -20°) was determined tensimetrically, and corresponded to the formula Al_2Me_6 ; whereas if the compound $\text{Al}(\text{BMe}_4)_3$ had formed, an apparent molecular weight corresponding to a monomeric formula would have been observed.

Experimental Part

Apparatus and Methods.—The vacuum apparatus and technical methods used in this investigation are similar to those described by Stock¹⁵ and by Schlesinger and co-workers.¹⁶ Particular attention is called to the device described by Burg and Schlesinger¹⁷ for the determination of vapor tensions or quantities of vapor¹⁸ at elevated temperatures. (For convenience this device will be referred to as the "high temperature bulb.") It has the advantage that it may be repeatedly opened to the rest of the vacuum apparatus for the introduction of reagents or the removal of volatile reaction products.

(14) Schlesinger, Sanderson and Burg, *THIS JOURNAL*, **62**, 3421 (1940).

(15) Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; *Ber.*, **54A**, 142 (1921).

(16) Schlesinger and Walker, *THIS JOURNAL*, **57**, 622 (1935); Burg, *ibid.*, **56**, 499 (1934).

(17) Burg and Schlesinger, *ibid.*, **59**, 785 (1937).

(18) In this paper, quantities of a material are given in "cc.," designating the volume of a gas or vapor (calculated to standard conditions) or the normal gas equivalent of a non-volatile substance.

The handling of trimethylaluminum in the vacuum apparatus offered considerable difficulties. When even a thoroughly baked-out section of the vacuum apparatus was exposed to the vapors of trimethylaluminum, non-condensable gases were formed, and for some time thereafter it was difficult to reduce the pressure below 10^{-4} mm. No further difficulty was experienced if trimethylaluminum were handled continuously in that section of the apparatus—the glass appeared to become “saturated” with the substance. However, after the introduction and handling of other materials, such as trimethylamine, the apparatus had to be “resaturated” with trimethylaluminum. Dimethylaluminum chloride and dimethylaluminum bromide exhibited the same phenomenon. Such substances were best distilled from one part of the apparatus to another by condensing them in U-tubes, on far side of which a high vacuum was maintained.

Since these substances attack stopcock grease,¹⁹ their molecular weights were determined in the following manner. A sample of known volume (measured in the device mentioned above) was distilled into small, weighed U-tubes, connected to the line by means of picein cement. After the sample had been collected, the U-tubes were sealed at constrictions on both limbs of the U, removed from the line, and weighed.

Materials.—Trimethylaluminum was prepared by the reduction of dimethylmercury with aluminum; the observed vapor tensions and melting point agreed well with recent literature values.^{4,14}

Dimethylamine was the anhydrous Eastman Kodak Co. product. A tensimetrically homogeneous sample ($p = 562$ mm. at 0°) was used. Trimethylamine and monomethylamine were isolated from their hydrochlorides and used after careful fractionation in the vacuum apparatus.

Dimethylphosphine was prepared by the interaction of phosphonium iodide and methyl iodide in the presence of zinc oxide.²⁰ A tensimetrically homogeneous sample ($p = 30$ mm. at -47°) was used. The trimethylphosphine was prepared by the interaction of phosphorus trichloride and dimethylzinc.^{21,22} The sample used melted from -85.3 to -84.3° and exerted a vapor tension of 159 mm. at 0° .²³

Methyl mercaptan and dimethyl sulfide were Eastman Kodak Co. products. They were fractionated in the vacuum apparatus and tensimetrically homogeneous samples ($p = 601$ mm. at 0° ²⁴ and $p = 167$ at 0° ²⁴, respectively) were isolated and used.

Preparation of $\text{Me}_2\text{HN}:\text{AlMe}_3$ and $(\text{Me}_2\text{AlNMe}_2)_2$.—A 4.14 cc. sample of Al_2Me_6 (in the high temperature bulb) absorbed 8.3 cc. of dimethylamine to form the solid addition compound, dimethylamine-trimethylaluminum, m. p.

(19) Even Apiezon grease, which is unaffected by diborane, is attacked by these substances.

(20) Hofmann, *Ber.*, **4**, 605 (1871); Davidson and Brown, *THIS JOURNAL*, forthcoming publication.

(21) Cahours and Hofmann, *Ann.*, **104**, 29 (1857).

(22) WARNING: this exothermic reaction starts at about -20° and proceeds with extreme and uncontrollable vigor; great caution must be observed if large quantities of materials are used in a preparation.

(23) Rosenbaum and Sandberg, *THIS JOURNAL*, **62**, 1622 (1940).

(24) Berthoud and Brum [*J. Chim. Phys.*, **21**, 151 (1924)] give 595 mm. and 172 mm., respectively, as experimental values for these substances, but in their summarizing tables list the values 570 mm. and 175 mm.

51° . The vapor tensions of the compound are given in Table II.

TABLE II²⁵

VAPOR TENSIONS OF DIMETHYLAMINE-TRIMETHYLALUMINUM

Temp., °C.	42	54	68	89
p , mm., obsd.	1.7	3.7	7.8	22.1
p , mm., calcd.		3.7	7.6	22.1

At temperatures above 90° , the pressure increased rapidly with time, indicating that the reaction $2\text{Me}_2\text{HN}:\text{AlMe}_3 \rightarrow (\text{Me}_2\text{AlNMe}_2)_2 + 2\text{CH}_4$ was occurring. The temperature was maintained at 120° for one-half hour. From the reaction mixture, 8.3 cc. of methane (identified by its vapor tension [$p = 12$ mm. at -193°]) was obtained. The vapor tensions of the residual white solid, m. p. 154 – 156° , were determined (Table III). The discrepancy be-

TABLE III²⁵VAPOR TENSIONS OF $(\text{Me}_2\text{AlNMe}_2)_2$

Temp., °C.	49.0	73.0	79.5	95.0	100
p , mm., obsd.	1.4	8.3	11.9	25.2	32
p , mm., calcd.	4.4	8.5	11.9	25.7	32

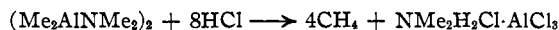
tween the calculated vapor tension and the repeatedly observed value at 49° indicates a deviation from linearity of the $(\log p, 1/T)$ plot. The substance is sufficiently volatile at room temperature to permit the sublimation of small quantities through the vacuum apparatus in a reasonable time.

Two facts testify to the homogeneity of the preparation. At 100° , less than 5% of the sample was present in the solid phase but the observed pressure fits on the extrapolated vapor tension curve within 1%. Moreover, after half the sample had been sublimed away, the observed vapor tensions agreed with those observed for the total sample.

The standard volume of the sample, as a vapor, from 110 to 150° was 4.00 ± 0.04 cc. (pressures ca. 35 mm.). A volume of 4.15 cc. was expected for a dimer. Since a small amount of substance was probably carried away with the methane, the observed volume demonstrates the dimeric formula; the constancy of the volume indicates that there is no dissociation.

Reactions of $\text{Me}_2\text{NAlMe}_2$.—A mixture of the compound with trimethylamine exerted the pressures to be anticipated if no reaction occurs, an observation the significance of which already has been discussed. When it is treated with water, methane is evolved slowly (compare with the vigorous hydrolysis of trimethylaluminum or dimethylaluminum chloride). A 1.35 ± 0.1 -cc. sample hydrolyzed to give 5.2 ± 0.2 cc. of methane (calculated for complete hydrolysis, 5.4 ± 0.4 cc.).

With hydrogen chloride, the substance reacts according to the over-all equation



A 2.7-cc. sample of $(\text{Me}_2\text{AlNMe}_2)_2$ required 21.5 cc. of hydrogen chloride (calcd., 21.6) and 10.7 cc. of methane was liberated (calcd., 10.8). The product of empirical formula $\text{NMe}_2\text{H}_2\text{Cl} \cdot \text{AlCl}_3$ is a solid, melting at 104° . At 150° it has no observable vapor tension, whereas at this

(25) The constants of the vapor tension equation and derived data are listed in Table I.

temperature aluminum trichloride has a vapor tension of 87 mm.³ This fact makes it probable that an actual compound rather than merely a mixture of dimethylammonium chloride and aluminum trichloride was present; the structure of such a compound is presumably $[\text{NMe}_2\text{H}_2^+][\text{AlCl}_4^-]$.

At room temperature, the substance $(\text{Me}_2\text{AlNMe}_2)_2$ seems to be stable to dry air.

Preparation of $(\text{Me}_2\text{AlSMe})_2$.—A 5.5-cc. sample of Al_2Me_6 reacted with 11.0 cc. of methyl mercaptan to give 10.9 cc. of methane. The white solid residue melted at 103° and was completely volatilized at 160°, at which temperature its pressure corresponded to a volume of 5.6 cc., thus demonstrating the dimeric formula. This result was checked on several other preparations. The vapor tensions of the compound are given in Table IV. The data

TABLE IV²⁵VAPOR TENSIONS OF $(\text{Me}_2\text{AlSMe})_2$

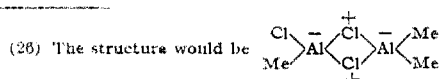
Temp., °C.	93	107.8	118.9	129.3	140.8	149.2
<i>p</i> , mm., obsd.	3.4	8.2	14.5	23.8	37.8	51.7
<i>p</i> , mm., calcd.	4.1	8.7	14.5	23.4	37.8	53.0

in the temperature range 120–140° are adequately expressed by the equation $\log p = -3070/T + 9.005$, but below and above this range, the vapor tensions are below those predicted by the equation. Since there was some decomposition at higher temperatures (as evidenced by the development of non-condensable gas), it did not seem justifiable to fit the data to a more complex equation. The calculated values of the boiling point (228°) and of the Trouton constant (28) are not very reliable. The true boiling point must be somewhat higher and the true Trouton constant (measured at the boiling point) somewhat lower. The substance is not sufficiently volatile to be conveniently moved about the vacuum apparatus.

Reactions of $(\text{Me}_2\text{AlSMe})_2$.— $(\text{Me}_2\text{AlSMe})_2$ does not absorb dimethyl ether, either at room temperature or at elevated temperatures.

At room temperature, trimethylamine is absorbed very slowly, but above 37° (the melting point of the product), absorption is rapid to give a substance of empirical formula $\text{Me}_3\text{N}:\text{AlMe}_2(\text{SMe})$. That the product does not vaporize as a 1:1 compound is indicated by the observation that the "vapor tension" of a sample of this substance (in a bulb of fixed volume) varies with the size of the sample. Possibly it vaporizes by dissociation into $(\text{Me}_2\text{AlSMe})_2$ and Me_3N , but a careful examination of this hypothesis was prevented by an irreversible decomposition above 150°. Trimethylamine and dimethyl sulfide were observed among the decomposition products.

Preparation of $(\text{Me}_2\text{AlCl})_2$.—Dimethylaluminum chloride was prepared by the action of aluminum on methyl chloride.⁹ The purification of the dimethylaluminum chloride from the accompanying monomethylaluminum dichloride, by simple distillation in the vacuum apparatus, proved to be unexpectedly difficult, in view of the fact that the two substances differ considerably in their vapor tensions. It is probable that an unstable substance of the formula $\text{Me}_2\text{Al}_2\text{Cl}_2$ ²⁶ of intermediate volatility is formed.



The purification was finally achieved by a careful fractionation through a column (packed with a wire spiral) operating essentially like that described by Burg.¹⁶

The composition of the substance was established by analysis and a molecular weight determination. A 9.1-cc. sample reacted with water to give 35.5 cc. of methane (calcd., 36.4); an 8.9-cc. sample gave 0.0804 g. of silver chloride (calcd., 0.0796). A 9.05-cc. sample weighed 0.0788 g., implying a molecular weight of 195, which corresponds exactly to that calculated for a dimer. No measurable dissociation was observed in the temperature range 92° to 155°.

Dimethylaluminum chloride is dimorphic, with one melting point close to -45° and the other at -21.0°. It frequently condenses at -80° as a viscous liquid. The vapor tensions of the compound are given in Table V.

TABLE V²⁵

VAPOR TENSIONS OF DIMETHYLALUMINUM CHLORIDE

Temp., °C.	25.2	35.0	45.2	56.1	66.0	74.1
<i>p</i> , mm., obsd.	14.2	24.5	41.4	69.0	105.2	144.2
<i>p</i> , mm., calcd.	14.2	24.5	42.3	70.2	105.2	140.9

Reactions of $(\text{Me}_2\text{AlCl})_2$.—A 9.1-cc. sample of $(\text{Me}_2\text{AlCl})_2$ absorbed 18.3 cc. of dimethyl ether to yield the addition compound, $\text{Me}_2\text{O}:\text{AlMe}_2\text{Cl}$. This substance is a liquid at room temperature; its vapor tensions are given in Table VI.

TABLE VI²⁵

VAPOR TENSIONS OF DIMETHYLETHER-DIMETHYLALUMINUM CHLORIDE

Temp., °C.	68.0	87.4	112.5	123.0	143.5	152.2	159.5
<i>p</i> , mm., obsd.	5.7	12.3	33.0	49.2	96.0	99.0	153
<i>p</i> , mm., calcd.	5.7	12.7	33.3	49.0	94.5	94.5	152

A 2.0-cc. sample of $(\text{Me}_2\text{AlCl})_2$ absorbed 4.0 cc. of trimethylamine to yield the solid addition compound, trimethylamine-dimethylaluminum chloride, m. p. 124°. The vapor tensions of the compound are given in Table VII. At 137°, the observed pressure (35 mm.) corresponded to a volume of 3.9 cc. showing that, as a vapor, the substance is monomeric and not dissociated.

TABLE VII²⁵

VAPOR TENSIONS OF TRIMETHYLAMINE-DIMETHYLALUMINUM CHLORIDE

Temp., °C.	75	84	90	102.6	112.5	124
<i>p</i> , mm., obsd.	1.8	3.6	4.4	9.0	14.3	23.8
<i>p</i> , mm., calcd.	1.9	3.2	4.4	10.5	14.3	24.6

Preparation of $(\text{Me}_2\text{AlBr})_2$.—Dimethylaluminum bromide was prepared by the action of aluminum on methyl bromide.⁹ It was purified by repeated distillation through a U-tube at 0°. The substance melted from -21.5 to -19.6°. Its vapor tensions are given in Table VIII.

TABLE VIII²⁵

VAPOR TENSIONS OF DIMETHYLALUMINUM BROMIDE

Temp., °C.	29.0	37.0	52.5	74.9	91.9	109.5
<i>p</i> , mm., obsd.	5.1	8.2	18.5	51.4	102.0	188
<i>p</i> , mm., calcd.	5.2	8.2	18.4	51.4	101.0	197

The total standard volume of the sample was 23.8 cc.; the volume corresponding to the pressure at 109.5° is 22.2

cc.; hence with only 7% of the material present as a liquid, the pressure was only 5% below the extrapolated value, indicating satisfactory, although not perfect, homogeneity. The 23.8-cc. sample weighed 0.2945 g., implying a molecular weight of 277 (calcd., 274). Hydrolysis yielded 92.7 cc. of methane (calcd., 95.2).

Preparation of $\text{Me}_2\text{HP}:\text{AlMe}_3$ and $(\text{Me}_2\text{AlPMe}_2)_3$.—An 8.4-cc. sample of Al_2Me_6 absorbed 16.8 cc. of dimethylphosphine to give the addition compound dimethylphosphine-trimethylaluminum. This substance is a liquid at room temperature. No methane was evolved at temperatures as high as 150°. The vapor tensions of the compound are given in Table IX. At higher temperature the

TABLE IX²⁵

VAPOR TENSIONS OF DIMETHYLPHOSPHINE-TRIMETHYLALUMINUM

Temp., °C.	21.0	68.1	88.0	100.1	115.5
<i>p</i> , mm., obsd.	2.7	18.0	45.5	73.7	139
<i>p</i> , mm., calcd.	1.4	18.0	45.5	73.7	139

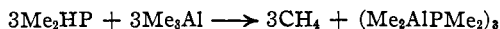
substance exhibits considerable dissociation as shown by the data in Table X. The calculated values were obtained assuming no dissociation for the completely volatilized sample (16.8 cc.).

TABLE X

DISSOCIATION OF DIMETHYLPHOSPHINE-TRIMETHYLALUMINUM

Temp., °C.	122.5	129.5	135.5	145
<i>p</i> , mm., obsd.	158.5	165.0	168.0	179
<i>p</i> , mm., calcd.	147.0	149.0	152.0	155

The preparation and study of the compound $(\text{Me}_2\text{AlPMe}_2)_3$ was complicated by several factors. First, the reaction between dimethylphosphine and trimethylaluminum according to the equation

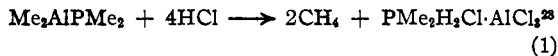


required rather high temperatures (215°). Second, the reaction is accompanied by the formation of a small quantity of non-volatile material. Since the compound $(\text{Me}_2\text{AlPMe}_2)_3$ is itself only slightly more volatile than mercury, considerable difficulty was encountered in purifying the sample, introducing it into the apparatus, and determining the quantity involved.

In practice, 4- to 8-cc. samples of dimethylphosphine-trimethylaluminum with approximately 1% of hydrogen chloride were heated in sealed tubes (5-cc. capacity) at 215° for several hours. The tube was then opened to a measuring bulb by means of a magnetic breaker, similar to that described by Burg and Schlesinger.²⁷ The methane produced was removed and measured, and the sample sublimed into the high temperature bulb at 130°, leaving behind some white solid which (estimated visually) appeared to be several per cent. of the amount which had sublimed. The reaction tube was then sealed off and the vapor tensions of the sample and the volume of the completely volatilized material were observed.

The analysis of the substance was carried out by means of the reactions represented by the equations

(27) Burg and Schlesinger, *THIS JOURNAL*, **62**, 3426 (1940).



The methane and dimethylphosphine were measured as gases; aluminum was determined as the 8-hydroxyquinolate. Comparison of analytical data thus obtained with the measured volume of the completely vaporized sample, demonstrated that the compound exists as a trimer.

Two typical experiments are described to illustrate the procedure and indicate the accuracy of the results.

Experiment I.—The reaction mixture consisted of 8.6 cc. of dimethylphosphine-trimethylaluminum and 0.1 cc. of hydrogen chloride; 8.4 cc. of methane was evolved. The product was sublimed into the high temperature bulb and the vapor tensions measured (Table XI). (To ensure that the correction for the partial pressure of mercury was the vapor tension of mercury at the temperature of measurement, the bulb was first heated 5° higher and then slowly cooled to the desired temperature.) The analysis was carried out as described previously. Hydrogen chloride brought about the evolution of 17.2 cc. of methane; treatment of the residue with triethylamine liberated 8.1 cc. of dimethylphosphine; the residue contained 0.362 millimole of aluminum, corresponding to 8.1 "cc." Thus the empirical formula was $\text{Me}_{17.2}\text{Al}_{8.1}(\text{PMe}_2)_{8.15}$ or 8.2 "cc." of monomeric $\text{Me}_{2.10}\text{Al}_{0.99}(\text{PMe}_2)_{0.996}$. The observed pressure of the completely vaporized sample corresponds to 2.8 cc. of gas, so that the degree of polymerization is calculated to be $8.2/2.8 = 2.9 \pm 0.2$, or within the experimental error, 3.

Experiment II.—A second series of measurements were made in the absence of mercury vapor using a "sickle" type Bourdon gage as a pressure indicator.²⁹ The reaction mixture consisted of 6.6 cc. of dimethylphosphine-trimethylaluminum and 0.06 cc. of hydrogen chloride; 6.4 cc. of methane was evolved. The sample was sublimed into the apparatus and its vapor tensions determined (Table XI). The standard volume of the vapor is calculated³⁰ to be 2.2 ± 0.2 cc.; the quantity of aluminum in the sublimed sample was determined as 0.287 millimole or 6.4 "cc.;" hence the calculated degree of polymerization is $6.4/2.2 = 2.9 \pm 0.3$, in substantial agreement with the previous result.

TABLE XI

VAPOR TENSIONS OF $(\text{Me}_2\text{AlPMe}_2)_3$						
Exp. I. Temp., °C.	25	155	185	194.5	208	217
<i>p</i> , mm., obsd.	0.0	5.3	18	25	30 ^a	30 ^a
Exp. II. Temp., °C.	25	156	184	197	210	218
<i>p</i> , mm., obsd.	0	5	17	24 ^a	24.5 ^a	24.5 ^a

^a Sample completely vaporized.

It appears fairly certain then that the $\text{Me}_2\text{AlPMe}_2$ is polymerized to a trimer. The weakest point in the argument is the failure to demonstrate the homogeneity of the

(28) By analogy with $\text{NMe}_2\text{H}_2\text{Cl}\cdot\text{AlCl}_3$ [$(\text{NMe}_2\text{H}_2^+)(\text{AlCl}_4^-)$]; it may actually have been a mixture of aluminum trichloride and dimethylphosphonium chloride.

(29) The system was very similar to that described by Laubengayer and Schirmer, *THIS JOURNAL*, **62**, 1578 (1940).

(30) Upon cooling the sample to room temperature, a residual pressure of 2 mm. was observed. Therefore, an intermediate value of 23.5 mm. was adopted for the pressure of the condensable substance in calculating its standard volume.

solid of empirical formula $\text{Me}_2\text{AlPMe}_2$ and a mean polymerization of three. The vapor tensions are over too small a temperature range and not sufficiently precise to permit the test depending on the linearity of the ($\log p$, $1/T$) plot. The melting point was over 220° and was not observed. The only arguments for homogeneity are the analogy with the other substances described in this paper and the qualitative observation that the sample sublimed and condensed in the manner of a homogeneous substance.

Reactions of $(\text{Me}_2\text{AlPMe}_2)_3$.— $(\text{Me}_2\text{AlPMe}_2)_3$ did not absorb trimethylamine. Its reaction with hydrogen chloride has been discussed in the description of the analysis.

Preparation of $(\text{Me}_2\text{AlOMe})_3$.—Dimethylaluminum methoxide has been prepared previously by the interaction of trimethylaluminum and aluminum methoxide;⁹ in the present instance it was prepared from the calculated quantities of trimethylaluminum and methyl alcohol.

A 6.5-cc. sample of Al_2Me_6 in the high temperature bulb was treated with 13.0 cc. of methyl alcohol. Methane was evolved at temperatures as low as -40° . At room temperature the product was a mixture of liquid and solid: it probably consisted of a mixture of trimethylaluminum and its mono-, di-, and trimethoxide derivatives. Raising the temperature of the mixture to 90° transformed it into a pure homogeneous substance which was identified as dimethylaluminum methoxide by its analysis, its melting point³¹ of 35° (sharp) and its vapor tensions (Table XII).

TABLE XII³²

VAPOR TENSIONS OF DIMETHYLALUMINUM METHOXIDE ³²					
Temp., °C.	76.0	81.0	87.0	93.0	107.0
p , mm., obsd.	7.4	9.7	13.6	18.0	36.0
p , mm., calcd.	7.4	9.7	13.6	17.9	36.0

One series of measurements of the degree of polymerization is presented in detail to indicate the (rather low) accuracy and reproducibility attained. A preparation from 7.5 cc. of Al_2Me_6 and 15.0 cc. of methyl alcohol was heated to 136° where the pressure, 46.4 mm., corresponded to a volume of 5.14 cc. (degree of polymerization = 2.92). It was cooled down and then revaporized at 139° , $p = 47.6$ mm., $V = 5.27$ cc., and the degree of polymerization is 2.85. The sample, distilled at room temperature into a

(31) Von Grosse and Mavity, ref. 9, report 33° .

(32) Dimethylaluminum methoxide requires unusually long periods of time to achieve its equilibrium vapor tension at any temperature. Usual quantities of an ordinary pure substance require less than a minute to come to thermal equilibrium in the high temperature bulb. When Me_2AlOMe is heated to 87° , the immediately observed vapor tension is usually 9–11 mm.; after the sample has stood for about fifteen minutes, the vapor tension has risen to its equilibrium value of 13.6 mm. When a sample is cooled from an elevated temperature, the immediately observed value may be 19 or 20 mm., and this slowly decreases to the equilibrium value.

A possible explanation of the long time required to achieve an equilibrium vapor tension is the following: the three valences of oxygen in coordination compounds of oxygen do not lie in a plane. In a (hypothetical) dimeric bridge compound of the methoxyl group, there would be *cis* and *trans* isomers, depending on whether the methyl groups were on the same or different sides of the plane of the bridging ring. Whatever the structure of the trimeric form, the same possibilities would, in all probability, be present. An equilibrium between the two (or more) forms, varying with temperature, and only slowly achieved, would account for the observed vapor tension phenomena

weighing U-tube (see Apparatus and Technique), weighed 0.0383 g. (calculated from the quantities of starting materials, 0.0390 g.).

The sample was then distilled directly into another high temperature bulb through a vacuum tube opener attached to the bulb. The tube opener was sealed off and the sample volatilized. The quantity of gas was 5.35 cc. (degree of polymerization = 2.80). Upon addition of water, 29.5 cc. of methane was evolved. A 5.14-cc. sample of $(\text{Me}_2\text{AlOMe})_3$ would give 30.8 cc.

These data suggest that the degree of polymerization is actually three, and that the observed values are somewhat lower because of a slow irreversible decomposition. The decrease in the degree of polymerization with time of heating was observed with all the samples studied. In several experiments, the values obtained approximated 2.8 (Table XIII) and showed no consistent variation with temperature and pressure. This last fact makes it unlikely that there is an equilibrium between, say, a tetramer and a dimer, giving rise to an apparent degree of polymerization of 2.8. It appears safe to conclude, therefore, that within experimental error the degree of polymerization is threefold.

TABLE XIII

MEASUREMENTS OF THE DEGREE OF POLYMERIZATION OF DIMETHYLALUMINUM METHOXIDE

Temp., °C.	123	116	136	106
p , mm., obsd.	22.3	40.5	46.4	10.6
V , cc., obsd. ^a	2.54	4.75	5.14	1.2
"cc." $\text{Me}_2\text{AlOMe}^b$	7.4	13.0	15.0	3.3
Polymerization	2.92	2.74	2.92	2.75

^a Standard volume of vapor. ^b Standard volume of monomer, calculated from quantity of starting material.

Reactions of $(\text{Me}_2\text{AlOMe})_3$.—Dimethylaluminum methoxide does not react with appreciable quantities of trimethylamine at room temperature. At elevated temperatures, relatively small quantities are taken up with the formation of a non-volatile white solid.

Trimethylamine-trimethylaluminum.—Trimethylamine-trimethylaluminum was prepared by the direct union of 9.5 cc. of Al_2Me_6 and 18.6 cc. of trimethylamine. It is a white solid which melts at 105° . The vapor tensions are given in Table XIV. The compound is not noticeably dissociated at temperatures up to 148° as shown by the

TABLE XIV³³

VAPOR TENSIONS OF TRIMETHYLAMINE-TRIMETHYLALUMINUM

Temp., °C.	47.0	60.3	79.9	102.0	110.8	120.3
p , mm., obsd.	4.3	9.3	27.8	71.0	98.2	138.2
p , mm., calcd.	4.3	9.5	22.4	71.0	98.2	138.2

observation that the above sample, completely vaporized at 148° , exerted a pressure (171 mm. in a 126-cc. bulb) corresponding to a standard volume of 18.4 cc. of gas.

Dimethylether-trimethylaluminum.—Dimethylether-trimethylaluminum was prepared by the direct combination of 8.25 cc. of Al_2Me_6 and 16.5 cc. of dimethyl ether. The product melts at -29.9° . The vapor tensions are given in Table XV. The low temperature points were checked several times and are definitely less than the calcu-

TABLE XV²⁵

Temp., °C.	25.5	37.5	47.3	60.2	75.5	89.2	96.8
<i>p</i> , mm., obsd.	3.2	7.3	13.3	25.3	48.5	83.3	108.1
<i>p</i> , mm., calcd.	4.2	8.0	13.3	24.3	47.5	82.0	107.7

lated values; the ($\log p, 1/T$) plot must actually have a slight curvature, and the boiling point may be somewhat higher than the extrapolated value recorded in Table I.

When completely volatilized at 120°, the same sample exerted a pressure of 141 mm., implying a standard volume of 16.4 cc., thus demonstrating that the substance is not dissociated. Studies on other samples demonstrated that the substance is not measurably dissociated at 40 mm. pressure and 150°. ³³

Trimethylphosphine-trimethylaluminum was prepared by the direct union of 5.30 cc. of Al_2Me_6 and 10.4 cc. of trimethylphosphine. It melted sharply at 62.5°. The sample was completely vaporized at 135° where the observed pressure (94 mm.) corresponded to a standard volume of 10.5 cc., indicating the absence of dissociation. The vapor tension data are given in Table XVI.

TABLE XVI²⁵

Temp., °C.	37.5	52	61.5	77.0	84.0	102.8
<i>p</i> , mm., obsd.	1.3	3.6	7.2	15.5	21.5	49.5
<i>p</i> , mm., calcd.				15.5	21.5	49.5

Dimethyl sulfide-trimethylaluminum.—Dimethyl sulfide-trimethylaluminum was prepared from 5.1 cc. of Al_2Me_6 and 10.1 cc. of dimethyl sulfide. The product melts at -20°. The vapor tensions are given in Table XVII.

TABLE XVII²⁵

Temp., °C.	24.0	47.5	58.9	65.6	72.3	82.5
<i>p</i> , mm., obsd.	2.7	11.3	20.8	28.6	40.9	64.1
<i>p</i> , mm., calcd.	2.8	11.5	20.6	28.6	39.4	63.4

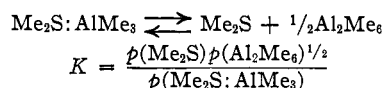
The data conform to the equation, $\log p = -2462/T + 8.740$. The substance is partially decomposed into its components (Table XVIII) so that the less volatile component will concentrate in the liquid phase in a sample of over-all composition one to one, and the "vapor tension" of such a sample will depend on the relative quantities of liquid and vapor present. However, below 120°, the degree of dissociation at the "saturation" pressure is small, so that the above equation may safely be used when the quantity of gas is not too great relative to the quantity of liquid.

(33) In order to determine whether the substance $Me_2O:AlMe_3$ takes on two more moles of ether to give a compound in which the coordination number of the aluminum is six, a pressure composition curve for mixtures of dimethyl ether and dimethyl ether-trimethylaluminum was determined at -80°. Between the composition $1Me_2O:AlMe_3 \cdot 1.7Me_2O$ and pure dimethyl ether, the pressure varied monotonically (and in fact almost linearly with mole fraction) between 16 mm. and 35 mm. (pure dimethyl ether); the system appeared to be all liquid. Below this composition, a solid phase was present, and the pressure was constant at 16 mm. This constant pressure must represent a saturated solution of the etherate in ether; no addition compound was formed.

TABLE XVIII

Temp., °C.	94.7	107.8	117.3	126.2
<i>p</i> , mm., obsd.	93.8	100.2	106.0	111.7
<i>p</i> , mm., calcd.	81.9	84.7	86.8	88.7
% Dissoc.	24.9	29.4	34.0	38.4
<i>K</i>	0.97	1.26	1.68	2.14

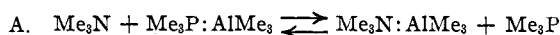
In Table XVIII, *K* is the equilibrium constant for the reaction³⁴



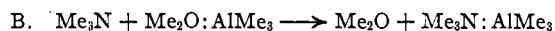
The calculations are slightly involved because it is necessary to consider the equilibrium, $Al_2Me_6 \rightleftharpoons 2AlMe_3$, but the equilibrium constant for this reaction is known.⁴

The values of $\log K$ when plotted against $1/T$ lie on a straight line, giving a value of ΔH of 8.5 ± 2 kcal. For the reaction $\frac{1}{2}Al_2Me_6 \rightarrow AlMe_3$, $\Delta H = 10.5$ kcal.; therefore, for the reaction $Me_2S + AlMe_3 \rightarrow Me_2S:AlMe_3$, $-\Delta H = 19 \pm 2$ kcal.

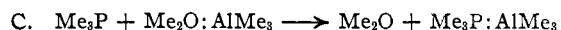
Relative Stabilities of Addition Compounds.—The relative stabilities of the addition compounds of trimethylaluminum were established by the following displacement reactions



A 3.4-cc. sample of trimethylphosphine-trimethylaluminum was treated with 3.4 cc. of trimethylamine in the high temperature bulb; after heating to ensure the attainment of equilibrium, the mixture was separated into a residual solid, and a gas at room temperature. The solid melted sharply at 105°, which is correct for trimethylamine-trimethylaluminum. The pressure of the gas was 40 mm. (standard volume, 3.4 cc.); when condensed at -45° in the same U-tube, the vapor tension was 13.5 mm. (for trimethylphosphine, $p = 13.0$ mm. at -45°; for trimethylamine, $p = 91$ mm. at -45°). It is safe to conclude that the reaction proceeded at least 95% to the right.



A 15.0-cc. sample of trimethylamine was condensed upon 15.4 cc. of dimethylether-trimethylaluminum; the solid trimethylamine-trimethylaluminum formed immediately upon warming. After the mixture had stood overnight, the volatile material was removed; it was a tensimetrically homogeneous sample of dimethyl ether ($p = 33$ mm. at -78.4°).



A 4.2-cc. sample of the etherate was treated with 4.2 cc. of trimethylphosphine; the solid $Me_3P:AlMe_3$ formed immediately. After heating the reaction bulb to 70°, the volatile products were removed; these consisted of 4.0 cc. of dimethyl ether and 0.2 cc. of trimethylphosphine (separated by distillation from a -110° bath).

No reactions were carried out with the sulfide since it is clear from its dissociation that it is the least stable of the

(34) It is hardly necessary to point out that this reaction has been assumed and not demonstrated, since only one pressure measurement has been made at each temperature. Barring the very improbable possibility that the addition compound is a polymer, $(Me_2S:AlMe_3)_x$, there is no other possible reaction to be considered.

addition compounds described. The stabilities of several of the addition compounds of dimethylaluminum chloride relative to the corresponding addition compounds of trimethylaluminum also were studied.

The exchange reaction $(\text{Me}_2\text{AlCl})_2 + 2\text{Me}_2\text{O}:\text{AlMe}_3 \rightleftharpoons 2\text{Me}_2\text{O}:\text{AlMe}_2\text{Cl} + \text{Al}_2\text{Me}_6$ was investigated by treating a 20.5-cc. sample of $\text{Me}_2\text{O}:\text{AlMe}_3$ with 7.9 cc. of $(\text{Me}_2\text{AlCl})_2$. After the mixture had been heated to 100° , it was separated into two fractions by distillation at room temperature.

That the reaction proceeds quantitatively to the right is demonstrated by the fact that a first fraction of the distillate gave no chloride upon hydrolysis. Any free dimethylaluminum chloride would have been in this first fraction. Furthermore, the vapor tensions of the residue were practically identical with those of pure $\text{Me}_2\text{O}:\text{AlMe}_2\text{Cl}$. The quantity of residue (7.4 cc.) was slightly smaller than the quantity of $\text{Me}_2\text{O}:\text{AlMe}_2\text{Cl}$ calculated for 100% reaction. This was not unexpected, since dimethyl ether-dimethylaluminum chloride is slightly volatile at room temperature.

The exchange reaction $2\text{Me}_2\text{N}:\text{AlMe}_3 + (\text{Me}_2\text{AlCl})_2 \rightleftharpoons 2\text{Me}_2\text{N}:\text{AlMe}_2\text{Cl} + \text{Al}_2\text{Me}_6$, appears to proceed largely but not exclusively to the right; the reaction was not studied quantitatively.

Attempted Formation of $\text{Al}(\text{BMe}_2)_3$.—The molecular weight of trimethylaluminum dissolved in trimethylboron was determined tensimetrically in an apparatus very much like that described by Stock and Pohland.³⁵ The trimethylboron was prepared from methyl borate³⁶ and the methyl Grignard reagent in butyl ether,³⁷ and was purified by distillation through a fractionating column.

The measurements were made at -21.2° (ice-salt eutectic), where the vapor tension of trimethylboron is 728 mm. The results are summarized in Table XIX.

TABLE XIX

MOLECULAR WEIGHT DATA FOR TRIMETHYLALUMINUM IN TRIMETHYLBORON

V , cc., Al_2Me_6	3.56	1.63	0.57
V , cc., BMe_3	264	264	270
p , mm., obsd.	10.4	5.5	2.40
p , mm., calcd. ^a	9.80	4.75	1.67
p , mm., obsd./ p , mm. calcd.	1.07	1.15	1.44

^a Obtained, assuming the molecular formula, Al_2Me_6 .

The data indicate some dissociation in the more dilute solutions, but the experimental error in these dilute solutions is too great to permit reliable conclusions to be drawn. There is certainly no evidence for a stable $\text{Al}(\text{BMe}_2)_3$.

Acknowledgment.—The authors are especially indebted to Professor H. I. Schlesinger for his encouragement, advice, and criticism.

Summary

1. The substances of empirical formula $\text{Me}_2\text{AlNMe}_2$ and Me_2AlSMe have been prepared by the reactions of trimethylaluminum with dimethylamine and methyl mercaptan. They are dimeric in the vapor state, as are Me_2AlCl and Me_2AlBr .

(35) Stock and Pohland, *Ber.*, **58**, 657 (1925).

(36) Webster and Dennis, *This Journal*, **55**, 3233 (1933).

(37) This (unpublished) method was developed by Dr. A. B. Burg.

The substances Me_2AlOMe and $\text{Me}_2\text{AlPMe}_2$, prepared by treating trimethylaluminum with methyl alcohol and dimethylphosphine, are trimeric.

2. $(\text{Me}_2\text{AlCl})_2$ and $(\text{Me}_2\text{AlBr})_2$ react with both trimethylamine and dimethyl ether to form stable one to one addition compounds; the mercaptyl derivative reacts with trimethylamine to form an addition compound, but it does not react with dimethyl ether; and $(\text{Me}_2\text{AlOMe})_3$, $(\text{Me}_2\text{AlPMe}_2)_3$ and $(\text{Me}_2\text{AlNMe}_2)_2$ do not react with these coordinating agents. This trend is interpreted to mean that the halogen compounds are the least strongly polymerized of these various substances, the mercaptyl derivative is of intermediate stability, and the oxygen, phosphorus and nitrogen compounds are the most stable polymers.

3. The monomeric addition compounds of trimethylaluminum with the coordinating agents trimethylamine, trimethylphosphine, dimethyl ether and dimethyl sulfide have been prepared. The relative stabilities of these substances decrease in the order $\text{Me}_3\text{N}:\text{AlMe}_3$, $\text{Me}_3\text{P}:\text{AlMe}_3$, $\text{Me}_2\text{O}:\text{AlMe}_3$ and $\text{Me}_2\text{S}:\text{AlMe}_3$, but only the latter substance is measurably dissociated as a vapor at 150° and 40 mm. pressure.

4. The correlation between the relative stabilities of the dimeric substances $(\text{Me}_2\text{AlNMe}_2)_2$, $(\text{Me}_2\text{AlSMe})_2$ and $(\text{Me}_2\text{AlCl})_2$ containing the elements nitrogen, sulfur and chlorine and the relative stabilities of the addition compounds of trimethylaluminum with the methyl derivatives of these elements supports the bridged structures for the dimeric substances. The high stability of the trimeric phosphorus and oxygen compounds is in accord with six-membered ring bridged structures.

5. Incidental to the main purposes of the investigation, a number of observations were made: (a) the addition compounds of trimethylaluminum with dimethylamine and dimethylphosphine were isolated and characterized; (b) dimethylaluminum chloride was shown to be a stronger acid (in the Lewis sense) than trimethylaluminum (c) investigation of the trimethylboron-trimethylaluminum system at -20° indicated the absence of a compound formation; (d) the melting point of trimethylphosphine was determined; and (e) previously reported values for the vapor tensions of dimethyl sulfide and methyl mercaptan were corrected.³⁸

CHICAGO, ILL.

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(38) Precise vapor tension data for these two substances have been reported quite recently by Yost and his co-workers, *This Journal*, **64**, 165, 169 (1942).