would have determined the magnitude of any diffusion error the small differences between results calculated for these runs is taken as proof that such error is insignificant. Considerable care was exercised to exclude from the various parts of the apparatus any material which could absorb or exchange with carbon dioxide.

There is the possibility that the medium employed here, 80% sulfuric acid, has caused important changes in the solution decarboxylation mechanism as found by Hall.[15] Average first-order rate constants obtained from kinetic analysis of the sample collection data for pairs of runs at two temperatures are compared in Table IV with those calculated from Hall's results. Our constants must be regarded as approximate because sweep collection of gas samples is a rather poor technique if really precise kinetic information is sought. We believe, however, that the data shown in Table IV indicate strongly that the rate and heat of activation of the decarboxylation in 80% sulfuric acid are the same as in 0.381 *M* hydrochloric acid,[15] and that it is likely that the mechanism is the same, *i.e.*, decomposition of the undissociated diacid.[16]

TABLE IV

RATE CONSTANTS FOR DECARBOXYLATION

T, °C.	Runs	$k \times 10^6$, sec.$^{-1}$ Calcd.	Obsd.
56	26, 27	0.82	0.95
79	14, 15	2.0	1.8

We are now investigating the isotope effects and kinetics of this reaction in other solvent media.[17]

Acknowledgments.—This research was supported by the A.E.C. We are indebted to Mrs. R. W. Hill, who performed the mass spectrometer analyses.

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(15) G. A. Hall, THIS JOURNAL, **71**, 2691 (1949).

(16) Preliminary experiments in this Laboratory have shown that the rate of the decarboxylation in 96% sulfuric acid is nearly the same as in the 80% solution, while that in 100% sulfuric acid is larger by a factor *ca.* 20.

(17) Tentative results for quinoline solutions indicate that the rate of decarboxylation in that solvent is very nearly the same as that in 100% sulfuric acid. At 79°, $(k_1/2k_2)$ = 1.0468 ± 0.0003, in quinoline.

URBANA, ILL.

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

Reactions of Lithium Aluminum Hydride with Representative Elements of the Main Groups of the Periodic System[1]

BY THOMAS WARTIK AND H. I. SCHLESINGER

RECEIVED JULY 14, 1952

Whereas treatment of alkyl derivatives of the alkali metals and of the metals of the main and sub-groups II with lithium aluminum hydride leads almost exclusively to the formation of the corresponding metal hydrides, the trialkyls of boron, aluminum and gallium react as represented by the equation: $LiAlH_4 + R_3M \rightarrow LiMH_3R + R_2AlH$. The unexpected character of the reaction is pointed out and briefly discussed. As judged by the behavior of a limited number of examples, alkyls of main groups IV, V and VI do not react with lithium aluminum hydride. The behavior of the alkyls is contrasted with the behavior of the corresponding halides. Vapor tensions of dimethylaluminum hydride at several temperatures have been determined, as have its apparent molecular weights. In the gas phase at temperatures between 83 and 167° it appears to be a mixture of trimer and dimer in varying proportions; in isopentane solutions it seems to be largely trimeric at 20°.

In an earlier paper[2] dealing with the reactions between lithium aluminum hydride and metal alkyls, it was shown that alkyl derivatives of the first main group of the periodic system (as illustrated by methyl lithium) and those of the second group (as illustrated by beryllium, magnesium, zinc and cadmium alkyls) are transformed to the hydrides of these elements. Only when dimethylaluminum hydride was used as the hydrogenating agent in place of lithium aluminum hydride, was definite evidence obtained of the formation of mixed hydride alkyls (*i.e.*, of compounds of the type $CH_3M^{II}H$ in which M^{II} is a metal of the second group). In contrast to this behavior, the methyl derivatives of the third group elements, boron, aluminum and gallium, produce dimethylaluminum hydride and the compounds $LiM^{III}CH_3H_3$, in which M^{III} represents any one of the elements in question.

So far as our present information goes, lithium aluminum hydride does not react with alkyls of the fourth, fifth and sixth main groups. This statement is based on the behavior of the reagent toward alkyl silanes, alkyl germanes, alkyl stannanes, tetramethyllead, trimethylamine, and toward ethers or diethyl sulfide.

Thus it appears that the more electropositive the element with which the alkyl groups are associated, the more readily are the latter replaced by hydrogen in these reactions. The reverse of this statement applies to the hydrogenation of halides. Thus the chlorides of elements of the first main group do not react with lithium aluminum hydride, and the chlorides of second group elements either do not react or react incompletely, giving mixtures from which pure compounds could not be isolated. The halides of the third,[3a] of the fourth,[3b] and of the fifth main groups[4] readily give the corresponding

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(1) Taken from Final Reports submitted to the Navy on Contracts N173-10421, NRL-C-3147, N6ori-20 for the years 1945-1948, and from a thesis submitted by Thomas Wartik to the Department of Chemistry of the University of Chicago in part fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **73**, 4585 (1951).

(3) (a) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947). (b) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).

(4) H. I. Schlesinger, *et al.*, Final Report on Contract N173s-10421, for the year 1945-1946, p. 8, in which it was shown that arsenic trichloride and antimony pentachloride in ether solution react with lithium aluminum hydride to produce arsine and stibine, respectively. Halides of sixth group elements have not been studied.

hydrogen compounds. Alkyl halides (which are reduced to hydrocarbons) may be considered halides of carbon rather than alkyl derivatives of halogens.

It is surprising that the reactions of lithium aluminum hydride with trimethylboron and with trimethylgallium do *not* lead merely to substitution of hydrogen by methyl groups (R) in the lithium aluminum hydride, and to substitution of methyl groups by hydrogen in the metal alkyls, as represented by the equations

$$LiAlH_4 + R_3B \longrightarrow LiAlH_3R + R_2BH$$
$$LiAlH_4 + R_3Ga \longrightarrow LiAlH_3R + R_2GaH$$

Instead, all of the reactions in question result in the formation of dimethylaluminum hydride

$$LiAlH_4 + R_3B \longrightarrow LiBH_3R + R_2AlH$$
$$LiAlH_4 + R_3Al \longrightarrow LiAlH_3R + R_2AlH$$
$$LiAlH_4 + R_3Ga \longrightarrow LiGaH_3R + R_2AlH$$

For the purpose of seeking factors which might be responsible for the course of the reactions (and not as a definite suggestion for a reaction mechanism), the reaction between lithium aluminum hydride and trimethylboron may be considered as occurring in two steps, of which the first is represented by the equation[5]

$$LiAlH_4 + R_3B \longrightarrow LiH + R_xBH_{3-x} + R_yAlH_{3-y}$$

The several chemical species represented by the formulas R_xBH_{3-x} and R_yAlH_{3-y} (in which $x + y = 3$ but neither x nor y is zero) would presumably constitute the equilibrium system

$$R_2BH + RAlH_2 \rightleftarrows RBH_2 + R_2AlH$$

If, of the four species participating in the equilibrium, the monomethylboron hydride (RBH_2) should add preferentially to the lithium hydride assumed to be formed as an intermediate, the overall result of the reaction in question would be the formation of the products actually observed, namely, the compound $LiBH_3R$ and dimethylaluminum hydride.

The preceding discussion represents a possible description of how the observed chemical change may come about, and not an effort to explain why it occurs.[6] The reaction is a complex one, which involves the formation of one solid from another. Furthermore, the postulated methyl boron hydrides do not exist as monomers, but are known only as methyldiboranes; aluminum hydride and its methyl derivatives appear to be even more highly polymerized. Hence a full understanding of the reactions requires knowledge of relative lattice and polymerization energies and other thermodynamic data, as well as of relative reaction rates, none of which information is available.

The description of the way in which the reaction may occur is, however, consistent with other aspects of the behavior of compounds closely related to those in question. Thus compounds of the type $R_3N:BH_xR_{3-x}$ are the less stable the more methyl groups they contain.[7] Similarly, whereas diborane reacts rapidly and completely with lithium hydride in the presence of ether to form lithium borohydride irreversibly, the corresponding reactions between trialkyl borons and lithium hydride lead to very unstable addition products.[8] These facts are consistent with the assumption that the monomethyl boron hydride is more likely to form a Lewis acid-base adduct with lithium hydride (*i.e.*, with hydride ion) than is dimethylboron hydride. Furthermore the assumption that methyl derivatives of borine, BH_3, are more likely to form adducts with hydride ion than do the corresponding aluminum compounds, is consistent with the observation that diborane reacts with lithium aluminum hydride to form lithium and aluminum borohydrides

$$LiAlH_4 + B_2H_6 \longrightarrow LiBH_4 + Al(BH_4)_3$$

As has already been mentioned there are not sufficient thermodynamic data to answer the question about which of the several factors involved in determining the course of the reaction are the more important ones. Perhaps a clue to the answer lies in the fact that trimethylgallium behaves toward lithium aluminum hydride as does trimethylboron. The tendency to polymerization of boron and gallium compounds of the type involved seems to be less than that of the aluminum compounds, as judged by the fact that both trimethylboron and trimethylgallium vapors are monomeric at ordinary temperatures, whereas the vapor of the corresponding aluminum compound is dimeric even at moderately high temperatures. The parallelism suggests, though it does not prove, that the polymerization energy is a more important factor than the other thermodynamic properties involved.

The reactions of lithium aluminum hydride with the alkyl derivatives of the first and second groups of the periodic system[2] had to be carried out in ether solution, because all of the reactants are nonvolatile or nearly so. The resulting lithium salts could not be freed from the solvent, and reliable analyses could not readily be obtained. The alkyl derivatives of boron, aluminum and gallium were used in the gaseous or liquid condition, and reacted smoothly in the absence of solvent. As a result it became possible to obtain an analysis of the resulting lithium salt, as is described in the Experimental part. The latter also contains data supporting the statement that lithium aluminum hydride does not react with alkyls of fourth, fifth and sixth group elements, as well as data about the properties of dimethylaluminum hydride. Reactions with alkyl halides are not described because other reports on this topic have appeared since our work was done.

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(5) The assumption of the formation of lithium hydride as an intermediate is not entirely arbitrary, as shown by the fact that this hydride is actually obtained in the reaction between lithium aluminum hydride and methyl lithium (Ref. 2).

(6) Another way in which the end result may be thought of as being achieved, is discussed in the Ph.D. thesis of Thomas Wartik, University of Chicago, 1949. This alternative description is represented by the equations

$$LiAlH_4 + R_3B \longrightarrow LiAlH_3R + R_2BH$$
$$LiAlH_3R + R_2BH \longrightarrow LiBH_3R + R_2AlH$$

The two approaches are basically the same. We have herein stressed the somewhat more elaborate one because it indicates more clearly what are the fundamental problems involved.

(7) H. I. Schlesinger, N. W. Flodin and A. B. Burg, This Journal, **61**, 1078 (1939).

(8) (a) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953); (b) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *ibid.*, **75**, 192 (1953).

Experimental

Materials.—**Trimethylboron** was prepared by the interaction of boron fluoride on methylmagnesium iodide.[9] The product had a vapor tension of 683 mm. at −22.9°.

Trimethylaluminum, obtained by allowing liquid dimethylmercury to remain in contact with aluminum foil for 24 hours, was condensed in a trap at −45.2°, through which the unchanged mercury alkyl passed. The vapor tension of the material used was 14.9 mm. at 25.5°.

Trimethylgallium was prepared by treating resublimed gallium trichloride with a slight deficiency of dimethylzinc for four hours at 120° in a sealed tube.[10] Its 0° tension was 65.9 mm. in agreement with the value previously reported.[10]

Tetramethyl tin was a stock sample purified by passing it through a trap at −45.2° into one at −78.5°. Its 0° tension was 33.3 mm., as compared with a reported value of 31.4 mm.[11]

Tetraethyllead, diethyl sulfide and methyl chloride were commercial samples obtained from the Ethyl Corporation, the Eastman Kodak Co. and the Matheson Co., respectively. The first of these was freed from more volatile contaminants by pumping on the sample for one hour at 0°; the second, without further purification, had a 20° tension of 46.7 mm. (reported value[12] 50 mm.); the third, after purification by fractional condensation, had a −22.9° tension of 804 mm., as contrasted with the reported value of 793 mm.[13] The other reagents used were purified by methods previously described[2].

The Reaction of Trimethylboron with Lithium Aluminum Hydride.—The reaction was carried out in a weighed, evacuated flask, the neck of which carried a break-off side arm and a standard joint. Between the latter and the side-arm there was a constriction, narrow enough for convenient sealing, but wide enough to permit the introduction of a diethyl ether solution of lithium aluminum hydride into the nitrogen filled flask by means of an all-glass syringe. After introduction of the solution, the flask was connected to the vacuum line, the ether was removed *in vacuo* at 70°, and nitrogen was readmitted. The flask with its contents was then weighed. A measured volume of trimethylboron was introduced into the flask after the nitrogen had again been removed through the vacuum system.

The flask, now sealed off, was allowed to stand at room temperature for about 24 hours. Through the side arm and vacuum tube opener the volatile products were removed and collected in a liquid nitrogen trap. Dimethylaluminum hydride was separated from excess trimethylboron by condensation at −78.5°, and was then condensed into a small weighing tube. In the meantime, nitrogen had again been admitted to the reaction flask, from the weight of which (with all its original parts) the weight of the solid reaction product was ascertained.

A number of experiments carried out in this way gave uniform results which are adequately represented by the following example: A sample containing 0.3273 g. (8.65 mmoles) of lithium aluminum hydride,[14] was treated with 547.1 cc. of trimethylboron, of which all but 193.2 cc. (8.63 mmoles) was recovered. The weight of volatile reaction product (0.4894 g.) corresponded to 8.42 mmoles of dimethylaluminum hydride, and that of the non-volatile residue (0.3122 g.) corresponded to 8.72 mmoles of a compound of the formula $LiB(CH_3)H_3$. These results are in excellent agreement with the equation given earlier for the reaction.

Analysis of Dimethylaluminum Hydride.—The volatile product of the preceding reaction was identified as dimethylaluminum hydride by hydrolysis and measurement of the volume of hydrogen and methane obtained. The hydrolysis was carried out with water vapor, since liquid water reacts so violently that charring occurs and the container may be cracked. To achieve the desired result, the compound was condensed in the lower part of a tube attached to the vacuum system. The liquid nitrogen bath was raised to a higher level in order that the water, to be introduced next, solidified at the top of the vessel, which was then sealed. The vessel was inverted, thus retaining the ice in a portion below the compound, the viscosity of which prevented it from reaching the liquid water before interaction with the vapor had progressed far enough to prevent violent reaction. The vessel was gradually warmed to room temperature, and then heated for 2 hours on a steam-bath.

The resulting hydrogen and methane were freed from water vapor, measured and then repeatedly passed through a quartz tube filled with copper oxide and heated to 900°. Aluminum, brought into solution by treatment with hydrochloric acid followed by fusion with sodium carbonate, was determined as the 8-hydroxyquinolate.

Table I gives the results of such analyses carried out on three samples. The observed amount of hydrogen is divided by two since one-half of it is supplied by the water; all of the analytical data are, for convenience, reported in milligrams or mmoles of the components rather than in terms of the actually measured weights or volumes. Dimethylaluminum hydride clings tenaciously to glass surfaces. The gaseous volume, rather than the weight of reaction product was, therefore, measured at 90°. To obtain the weight of the sample, the volume was multiplied by the molecular weight, 141, which as described later is its experimentally determined value at 90°.

TABLE I

ANALYSIS OF DIMETHYLALUMINUM HYDRIDE

	Wt. sample		H	CH_3		Al	
	Mg.	Mmoles	meq.	Mg.	Mmoles	Mg.	M.at.wt.
Sample 1	64.5	1.21	1.196	33.82	2.255	29.94	1.109
Sample 2	28.7	0.50	0.491	13.95	0.930	12.72	0.471
Sample 3	118.9	2.11	2.089	61.20	4.080	54.84	2.031

On the average, the ratio, $H:CH_3:Al = 1.05:2.00:1.00$; furthermore the observed sums of the weights of the constituents are 64.97, 27.17 and 118.1, respectively, as compared with the weights of sample recorded in the table. The identity of the volatile reaction product is thus clearly established as dimethylaluminum hydride.

Analysis of the Compound $LiBCH_3H_3$.—For determination of lithium and of active hydrogen the solid reaction product was hydrolyzed, the evolved hydrogen was measured, and the lithium determined as periodate in the solution.[15] The procedure used in the hydrolysis step was similar to that described in the case of dimethylaluminum hydride, since the lithium salt also reacts violently with liquid water.

For determination of carbon (methyl groups) and boron, separate samples of the product were oxidized with fuming nitric acid in the apparatus which is shown in Fig. 1.[16] The acid was introduced into the lower part of the apparatus by means of an all-glass syringe without wetting the upper portions. The upper tube was closed with a rubber stopper, the acid was frozen at liquid nitrogen temperature, the apparatus was evacuated and then filled with dry nitrogen. A "piggy" (A), filled with a weighed sample of the solid in a dry-box, was inserted, as shown in the figure, while a continuous stream of nitrogen flowed out of C. After the cap of the "piggy" had been removed with a long forceps, the upper part of the tube was sealed, the apparatus was evacuated, and the side arm was closed at the constriction. The apparatus was slowly heated to 350° and there maintained for 4 hours.

After the tube had cooled, its volatile contents were removed in the usual manner, and were passed through −120° and −196.5° traps. The nitrous oxide and carbon dioxide, retained in the colder trap, were vaporized and passed over copper turnings at 700° to reduce the nitric oxide to nitrogen, from which the carbon dioxide could be removed by condensation, and measured. Water was added to the non-

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[9] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 436 (1944).

[10] C. A. Kraus and F. E. Toonder, *Proc. Nat. Acad.*, **19**, 292 (1933).

[11] R. H. Bullard and A. C. Haussman, *J. Phys. Chem.*, **34**, 741 (1930).

[12] H. W. Thompson and J. W. Linnett, *Trans. Far. Soc.*, **31**, 1743 (1935).

[13] Landolt-Börnstein, "Phys. Chem. Tab.," 5th ed., Vol. 2, 1923, p. 1359.

[14] This weight, as well as that of the solid reaction product, is the observed weight corrected for a known amount of non-volatile impurity present in the sample.

[15] L. B. Rogers and E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, **15**, 209 (1943).

[16] The contents of the tubes were limited to quantities which, as shown by previous calculations, would not produce pressures great enough to be hazardous.

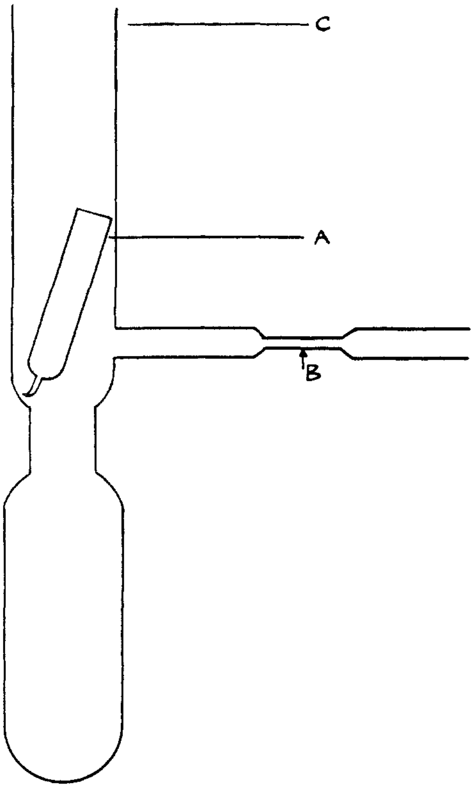

Fig. 1.

volatile products for determination of boron by the usual titration.

The results of the analyses are as follows: Found: Li, 19.75; B, 28.9, 28.5; C, 36.6, 32.6; H, 8.34, 8.57. Calcd. for $LiB(CH_3)H_3$: Li, 19.37; B, 28.7; C, 33.53; H, 8.41. In view of the small quantities of material available for analysis (from 0.0673 to 0.1071 g. for the several separate steps) and of the complexity of the analytical procedure, the results adequately confirm the proposed formula.

The Reaction of Trimethylgallium with Lithium Aluminum Hydride.—Because of the small amount of the gallium compound available, the lithium salt was used in excess. Thus a mixture of 2.99 mmoles of the latter and 1.34 mmoles of the former was prepared as described for the preceding reaction, and was allowed to stand for 24 hours at room temperature. During this interval the white solid had begun to turn gray, as is characteristic of lithium gallium hydride.[3] The volatile contents of the flask consisted mainly of a slightly volatile liquid, together with 0.05 cc. of a more volatile material, probably unchanged trimethylgallium, and a small amount of non-condensable gas, presumably hydrogen. The slightly volatile liquid was identified as dimethylaluminum hydride by its vapor tensions, which were 3.7, 12.0 and 23.5 mm. at 35.8°, 54.6° and 67.2°, respectively, as compared with the values 3.6, 11.7 and 22.9 mm. for the pure compound.

The liquid was then completely volatilized at 90°, and was found to occupy a volume corresponding to 10.6 cc. at standard conditions. This quantity represents an 86% yield on the basis of the suggested equation and on the value 141 for the observed apparent molecular weight of dimethylaluminum hydride at 90°. In view of the small quantity of material, no better confirmation of the course of the reaction could have been expected.

The Reaction of Trimethylaluminum with Lithium Aluminum Hydride.—The procedure was the same as that for the two preceding cases. The reaction was, however, much slower and was not complete in 24 hours. As a result the solid was contaminated with difficultly separable liquid material. The volatile product was, however, identified as dimethylaluminum hydride by comparison of its vapor tensions with those of a known sample. It was considered unnecessary to carry the experiment further.

The Behavior of Lithium Aluminum Hydride Toward Tetramethyltin, Tetraethyllead, Trimethylamine and Diethyl Sulfide.—From a mixture of tetramethyltin and lithium aluminum hydride in the presence of diethyl ether, stirred for 30 minutes at room temperature, all of the original lithium salt was recovered unchanged. In another experiment, carried out in the absence of solvent at 80° in a sealed tube for 2 hours, over 99% of the tin alkyl was recovered.

From a mixture of a diethyl ether solution of the reagent and tetraethyllead, 95% of the original alkyl was recovered. Similar results were obtained when ether solutions of the reagent were treated with trimethylamine or with diethyl sulfide at room temperature. No experiments were carried out at higher temperatures or in the absence of solvents.

Properties of Dimethylaluminum Hydride.—For purposes of identification of this compound accurate values of its vapor tensions were needed. These were determined in the apparatus described by Brown and his collaborators.[17] The values obtained are recorded in Table II. As shown by the values listed under (P_{calcd}), the data fall satisfactorily on a straight line represented by the equation

$$\log P = -2575/T + 8.92$$

according to which the normal boiling point is 154°.

TABLE II

VAPOR TENSIONS OF DIMETHYLALUMINUM HYDRIDE

t, °C.	24.7	25.9	35.8	39.4	47.5	49.1	54.6	57.1
P_{mm} (obsd.)	1.8	2.1	3.6	4.7	7.7	8.4	11.7	13.2
P_{mm} (calcd.)	1.9	2.0	3.2	4.7	7.6	8.4	11.4	13.2
t, °C.	61.8	66.5	69.2	72.0	75.2	80.4	86.2	91.0
P_{mm} (obsd.)	16.7	22.4	25.1	29.6	34.0	43.4	57.4	70.7
P_{mm} (calcd.)	16.9	21.7	24.8	28.4	33.5	43.0	56.5	70.3

As was previously mentioned some of the calculations in this paper also required knowledge of the molecular weight of the vapor of dimethylaluminum hydride at various temperatures. Since the molecular weight of monomeric dimethylaluminum hydride is about 58, the values given in Table III show that, at the lowest temperature used, the vapor density indicates a mixture of equal amounts of dimer and trimer, whereas the dimer is the predominating species at higher temperatures.[18]

TABLE III

APPARENT MOLECULAR WEIGHTS OF DIMETHYLALUMINUM HYDRIDE VAPOR AT SEVERAL TEMPERATURES

t, °C.	P, mm.	Vol., cc.	Wt., g.	Obsd. mol. wt.
82.9	55.80	11.32	0.0714	141.6
88.15	47.80	11.93	.0754	141.6
89.0	34.60	8.63	.0537	139.5
90.8	50.90	12.64	.0809	143.3
95.05	69.10	16.89	.1077	142.6
160.1	92.50	20.18	.1068	118.8
167.0	50.10	10.30	.0544	118.5

A disturbing feature of the data is the fact that the apparent molecular weights undergo little variation in the range 83–95°. For this reason it was thought desirable to determine the molecular weights in solution at lower temperatures by the lowering of the vapor tension of isopentane used as a solvent.

The apparatus, which followed closely that described by Stock and Pohland,[19] consisted of two similarly constructed tubes, one of which contained the solvent and the other the solution. These tubes were connected to the two arms of a differential mercury manometer, the levels in which were read to the nearest 0.05 mm. by means of a cathetometer.

There was one uncertainty in the data, namely that dimethylaluminum hydride, as already mentioned, is difficult to transfer quantitatively from a weighing tube to the apparatus in which it is to be used. For this reason, a measured volume of the vapor, rather than a measured weight

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[17] H. C. Brown, M. D. Taylor and M. Gerstein, THIS JOURNAL **66**, 432 (1944).

[18] According to a private communication, Professor E. Wiberg (Munich) had previously obtained results similar to ours. See also O. Stecher and E. Wiberg, *Ber.*, **75B**, 2003 (1942).

[19] A. Stock and E. Pohland, *ibid.*, **58**, 681 (1925).

of the liquid, is the experimental basis for the calculations. Since the volume of the vapor was measured at about 90°, the value 141 (see Table III) was used for the molecular weight. Any change in that value would alter the value for the molecular weight in solution, but the indications are that the resulting correction is relatively small.

The observations on which the molecular weight is based are reproduced in Table IV.

TABLE IV

MOLECULAR WEIGHT OF DIMETHYLALUMINUM HYDRIDE IN ISOPENTANE SOLUTION AT 20.3°

ΔP, mm.	55.45	30.00	17.40
$P°$, mm.	580.0	580.0	580.0
Mole fraction solute ($\Delta P/P°$)	0.0956	0.0517	0.0300
Weight solvent, g.	0.2315	0.493	0.891
Weight solute, g.	0.0697	0.0697	0.0697
Mol. wt. solvent	72.15	72.15	72.15
Calcd. mol. wt. solute	206	187.5	182.0

To correct for deviations from Raoult's law, the observed molecular weights at various concentrations were extrapolated to zero concentrations by use of the equation

$$C^{1.41} = -767.7 + 4.318M$$

in which C is the number of grams of solute per 100 g. of solvent, and M is the apparent molecular weight at the concentration in question. So plotted, the experimental values fall on a straight line which, extrapolated to zero concentration, gives a limiting value of 178 for the molecular weight. The theoretical value for the trimer is 174.[20]

Acknowledgment.—We wish to acknowledge gratefully the financial support and the continued interest of the Office of Naval Research under whose auspices the work herein reported was carried out. We also acknowledge our indebtedness to Dr. A. E. Finholt who carried out exploratory experiments on the reaction of lithium aluminum hydride with trimethylaluminum.

CHICAGO 37, ILLINOIS

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[20] That the change of apparent molecular weight with mole fraction is not due to an equilibrium between two polymers, *e.g.*, a dimer and a tetramer, was shown by one or two additional measurements made for us at low concentrations by Dr. Riley Schaeffer, whose contribution we hereby acknowledge.

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption of Nitrogen and Argon on Porous and on Non-porous Carbon Adsorbents at −195°[1]

BY R. A. BEEBE, B. MILLARD AND J. CYNARSKI

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By means of an isothermal calorimeter, heats of adsorption at −195° have been determined for nitrogen and argon on Spheron and Graphon carbon blacks, on two samples of Saran charcoal previously studied by Pierce, *et al.*, and on carbon wear dust prepared by Savage. In the course of these measurements we have found that certain anomalies both in the isotherm and the heat-coverage curve, observed by Joyner and Emmett for the system nitrogen–Graphon, are likewise present in the results for the system argon–Graphon. The magnitude of the heats obtained with the porous Saran charcoals is discussed in relation to pore diameters. The heat data indicate that the carbon wear dust does not present as homogeneous a surface as might have been predicted.

Introduction

Previous work in this Laboratory has dealt with the calorimetric measurement of heats of adsorption on carbon blacks having an essentially non-porous structure.[2] In particular with nitrogen as the adsorbate gas on these non-porous adsorbents at −195°, it has been demonstrated that there is a marked difference between the heat-coverage curves on the heterogeneous surface of a commercial channel carbon black designated as Spheron 6 and the much more homogeneous surface of a black designated as Graphon and produced by a sintering of the above channel black at electric furnace temperatures. Following the publication of the results of our original calorimetric measurements for nitrogen on the Spheron and Graphon carbon blacks, Joyner and Emmett[3] determined the isosteric heats on these adsorbents. In their work on Graphon, the measurements, which were extended through the second layer, revealed an anomalous hump in the isotherm and a corresponding second maximum in the heat curve at about 1.75–2.0 B.E.T. layers. The nitrogen isotherm hump had also been observed in this Laboratory. However, it had not been practicable with our apparatus to extend the heat measurements with nitrogen much beyond the first layer, and as a result we had failed to observe the second maximum in the heat curve. Because of the lower value of the saturation pressure (p_0) of argon at −195°, it was more practicable with this gas than with nitrogen for us to carry the measurements to higher relative pressures (p/p_0). Moreover, preliminary experiments on Graphon showed that the hump in the isotherm was at least as pronounced with argon, as with nitrogen. In the present work we have extended the calorimetric measurements on the system argon–Graphon to over four times the monolayer as calculated by the B.E.T. method.

Having completed the calorimetric measurements on these essentially non-porous carbon adsorbents,

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[2] (a) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, THIS JOURNAL, **69**, 95 (1947); (b) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 2294 (1947); (c) R. A. Beebe, G. L. Kington, M. H. Polley and W. R. Smith, *ibid.*, **72**, 40 (1950); (d) G. L. Kington, R. A. Beebe, M. H. Polley and W. R. Smith, *ibid.*, **72**, 1775 (1950); (e) W. R. Smith and R. A. Beebe, *Ind. Eng. Chem.*, **41**, 1431 (1949).

[3] L. G. Joyner and P. H. Emmett, THIS JOURNAL, **70**, 2353 (1948).