

about 9% of the entropy expected for a doubly-degenerate ground state.

Discussion

The heat capacity anomaly and the corresponding decrease in $\chi_m T$ below 2°K. suggest that a cooperative or "exchange" interaction between the magnetic ions becomes important at these temperatures. Such an interaction had previously been deduced from the paramagnetic resonance spectrum of $K_3Fe(CN)_6$ at low temperatures.¹¹ The heat capacity anomaly is much too small to account for the $R \ln 2$ magnetic entropy of the spin doublet ground state at high temperatures. The high heat capacity observed by Stephenson and Morrow between 50° and 160°K. was attributed to magnetic interactions, who estimated the entropy associated with this anomaly as 0.09 ± 0.02 e.u.¹² It does not appear that their anomaly is due to removal of the spin degeneracy, since even below 20°K. $K_3Fe(CN)_6$ still possesses a magnetic susceptibility nearly the same as that expected for a single unpaired electron. The "high-temperature" anomaly may be associated with a "quenching" of the orbital magnetic moment, which contributes significantly to the susceptibility at higher temperatures and may be appreciable even at 20°, according to the calculations of Howard.⁸ Whatever the cause, it is evident that even the sum of the entropy decreases associated with the two regions of high heat capacity is insufficient to account for all the magnetic entropy. It seems likely that there is a peak in the heat capacity below 0.6°, the beginning of which may be the observed rise in the heat capacity curve at 0.75°.

Both the heat capacity and the magnetic susceptibility indicate that there are pronounced interactions between the magnetic ion and its surroundings. In the first place, the observed structure of the heat capacity curve and the hint of additional structure below 0.7°K. indicate the presence of fairly complicated cooperative effects. Second, the fact that no dispersion effects were

observed in the 400 cycle susceptibility indicates that any relaxation time present is substantially below a millisecond even below 1°K. This is in marked contrast to the behavior of such salts as the paramagnetic alums, whose relaxation times are typically above 0.01 second at liquid helium temperatures.¹⁷ The existence of cooperative interactions might indeed be expected to reduce the relaxation times.

Our susceptibilities above 4°K. agree, within experimental error, with the equation given by McKim and Wolf⁹ for their experimental data on potassium ferricyanide. Below 3°K. our results are from 3 to 7% higher than theirs. The difference is reflected mainly in a less rapid drop in $\chi_m T$ for our measurements. (McKim and Wolf use an equation of different form from ours, but with a correction term corresponding approximately to a Weiss Δ of 0.200, compared with our 0.140.) The differences between our results and theirs are of the same order of magnitude as the differences they observed between the susceptibility of the powdered specimen and values calculated for the powder from the principal susceptibilities of crystalline specimens.

McKim and Wolf⁹ estimated the magnetic heat capacity in zero field as $0.08/T^2$ ($\pm 20\%$) on the basis of a measurement of the adiabatic susceptibility at 1,000 gauss, 1.05°K. The heat capacity at 1.05°K. is in fact slightly over 0.11 (their estimate 0.07). However, this temperature is below the maximum in the heat capacity, and the actual magnetic heat capacity in the $1/T^2$ region is more than twice their estimate.

Acknowledgments.—We wish to thank Professor J. G. Aston for helpful discussions, Mr. L. Shultz for production of the refrigerants used in this investigation and Mr. R. G. Taylor for preparation of the specimen. We are grateful to the Research Corporation and Westinghouse Electric Corporation for provision of funds for construction of the iron-free solenoid magnet.

(17) C. J. Gorter, "Paramagnetic Relaxation," Elsevier Publishing Co., New York, N. Y., 1947, pp. 77 ff.

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA]

The Preparation and Reactions of Dialkylamino Derivatives of Aluminum

By JOHN K. RUFF

RECEIVED DECEMBER 19, 1960

Two different types of dialkylamino derivatives of aluminum, $(R_2N)_2AlX$ and $(R_2N)_3Al$, were prepared. Apparent molecular weights of the products were determined and their structures discussed. Exchange reactions with boron trichloride were interpreted in terms of reactivity of the different types of dialkylamino groups.

Dialkylamino derivatives of aluminum have been discussed only briefly in the literature. Davidson and Brown¹ first reported the preparation of dimethylamino dimethyl aluminum from dimethylamine and trimethyl aluminum. In 1955 tris-dimethylamino alane, bis-dimethylamino alane and dimethylamino alane² were reported by

(1) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

Wiberg.³ Recently several other aluminum derivatives containing one dimethylamino group were prepared.⁴ This paper presents further results on the preparation and reactions of aluminum derivatives containing two or more dialkylamino groups.

(2) The nomenclature used in this paper is an extension of that proposed previously; *ibid.*, **82**, 2141 (1960).

(3) E. Wiberg and A. May, *Z. Naturforsch.*, **10b**, 234 (1955).

(4) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).

Experimental

Since the products and starting materials react with moisture and oxygen, all handling of samples for analysis was performed in a nitrogen filled dry box.

Analyses.—The preparation of samples for aluminum, chlorine and active hydrogen analyses was described previously.⁵ Nitrogen was determined by a modified Kjeldahl procedure. The Kjeldahl apparatus was first flushed with nitrogen gas and then the weighed sample contained in a small round-bottomed flask was attached. The sample was hydrolyzed with water and then a 20% sodium hydroxide solution was added. The amine liberated was determined in the usual manner.

Materials.—Trimethylamine alane and dimethylamino alane were prepared as described previously.³ Lithium aluminum hydride obtained from Metal Hydrides, Inc., was used after extraction with diethyl ether.⁴ Di-isopropylamine was distilled from sodium hydroxide before use and dimethylamine obtained from Matheson Co. was used without further purification. Boron trichloride was purified by passing it through two mercury-filled bubblers to remove chlorine.

Tris-Dimethylamino Alane: Method A.—A 5.5 g. sample of trimethylamine alane was treated with 100 ml. of dried benzene or diethyl ether. Dimethylamine was passed through the solution until hydrogen evolution ceased. The solvent was removed under reduced pressure and the solid residue was loaded into a cold finger sublimator. Tris-dimethylamino alane sublimed readily at 90°. The product weighed 8.7 g., m.p. 87–89° (lit.³ 87–88°). The yield was 90%.

Anal. Calcd. for $\text{Al}[\text{N}(\text{CH}_3)_2]_3$: Al, 16.98; N, 26.4. Found: Al, 16.76; N, 26.6.

Method B.—A 5.0 g. sample of lithium aluminum hydride was dissolved in 150 ml. of tetrahydrofuran. Dimethylamine was passed into the mixture until hydrogen evolution ceased. A solution of 4.5 g. of aluminum chloride, in 50 ml. of tetrahydrofuran, was added slowly to the flask. The reaction mixture was refluxed for 1 hr., and then the tetrahydrofuran was displaced with benzene by distillation. The mixture was filtered and the filtrate was treated as described in Method A. A yield of 16.1 g. or 76% was obtained, m.p. 86–87°.

Lithium Tetrakis Dimethylamino Aluminate.—A solution of 4.0 g. of lithium aluminum hydride in 200 ml. of tetrahydrofuran was allowed to react with dimethylamine as described above. The solution was filtered and the solvent removed *in vacuo*. The solid residue was dried at 60° overnight under high vacuum.

Anal. Calcd. for $\text{LiAl}[\text{N}(\text{CH}_3)_2]_4$: Al, 12.85; Li, 3.31. Found: Al, 11.81; Li, 2.94; Li/Al = 1.04.

Bis-dimethylamino Alane.—Trimethylamine alane, 3.6 g., was dissolved in 100 ml. of ether. The flask was evacuated on the vacuum line. Dimethylamine, 8.1×10^{-2} mole, was condensed into the flask and the mixture was allowed to warm slowly to ambient temperature. Hydrogen was evolved. When gas evolution had ceased, the hydrogen was removed through two liquid nitrogen traps. Any unreacted dimethylamine was then re-condensed into the reaction vessel. After no further hydrogen evolution was observed, the solvent was removed under vacuum and the solid residue was sublimed at 40°. A yield of 4.2 g. or 91% was obtained, m.p. 62° (lit.³ 63°).

Anal. Calcd. for $\text{HAl}[\text{N}(\text{CH}_3)_2]_2$: Al, 23.28; active hydrogen, 0.862. Found: Al, 23.39; active hydrogen, 0.856.

Tris-di-isopropylamino Alane.—Approximately 50 ml. of dried di-isopropylamine was condensed into 3.6 g. of trimethylamine alane with liquid nitrogen. Upon warming, evolution of hydrogen occurred. The mixture was refluxed under nitrogen for 20 hr. It is important that no oxygen be allowed to enter the system during the reflux period or dark yellow to red oils will result when the excess amine is removed *in vacuo*. The solid residue usually obtained was sublimed at 70°. The product weighed 8.9 g., 68% yield, m.p. 58–59°.

Anal. Calcd. for $[(\text{CH}_3)_2\text{CH}]_2\text{N}_3\text{Al}$: Al, 8.26; N, 13.2. Found: Al, 8.42; N, 13.1.

(5) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 535 (1961).

Dimethylamino Di-isopropylamino Alane.—The above procedure was repeated with 3.6 g. of dimethylamino alane and 40 ml. of di-isopropylamine. After refluxing the mixture for 36 hr. the excess amine was removed and the solid residue was sublimed at 95°. A yield of 7.2 g. of the product was obtained.

Anal. Calcd. for $[(\text{CH}_3)_2\text{CH}]_2\text{NAlHN}(\text{CH}_3)_2$: Al, 15.58; active hydrogen, 0.581. Found: Al, 15.50; active hydrogen, 0.562.

Di-isopropylamino Alane.—Di-isopropylamino alane was prepared from 4.0 g. of di-isopropylammonium chloride and 1.5 g. of lithium aluminum hydride as described previously.² The crude product was purified by sublimation at 90°. The product weighed 2.4 g., m.p. 130–131°.

Anal. Calcd. for $\text{H}_2\text{AlN}[\text{CH}(\text{CH}_3)_2]_2$: Al, 20.93; active hydrogen, 1.55. Found: Al, 21.24; active hydrogen, 1.55.

Reaction of Aluminum Chloride with Tris-dimethylamino Alane.—A. A 3.2 g. sample of tris-dimethylamino alane and 1.35 g. of aluminum chloride were placed in a sublimator. The solid mixture was heated for 1 hr. under a nitrogen atmosphere at 90°. The sublimator was evacuated and the product sublimed at 55°. A yield of 3.2 g. of the product was obtained, m.p. 55–57°.

Anal. Calcd. for $\text{ClAl}[\text{N}(\text{CH}_3)_2]_3$: Al, 17.95; Cl, 23.60; Al/Cl = 1.01. Found: Al, 17.96; Cl, 23.48.

B. The same procedure was repeated using 2.7 g. of aluminum chloride and 1.6 g. of *tris*-dimethylamino alane. The product was sublimed at 90°. The product weighed 3.6 g., m.p. 151°.

Anal. Calcd. for $\text{Cl}_2\text{AlN}(\text{CH}_3)_2$: Al, 19.03; Cl, 50.01. Found: Al, 19.11; Cl, 50.22.

Reaction of Trimethylamine Alane with Tris-dimethylamino Alane.—A 0.8 g. sample of tris-dimethylamino alane and 0.9 g. of trimethylamine alane were heated together under nitrogen at 80° for 2 hr. Trimethylamine was evolved (9.8×10^{-3} moles). The dimethylamino alane sublimed at 40°, m.p. 89° (lit.² 89–90°).

Anal. Calcd. for $\text{AlH}_2\text{N}(\text{CH}_3)_2$: Al, 37.0; active hydrogen, 2.74. Found: Al, 36.3; active hydrogen, 2.66.

Reaction of Dimethylamine with Tris-di-isopropylamino Alane.—A. A tensiometric titration was performed in an apparatus previously described.⁵ A solution of 0.201 g. of tris-di-isopropylamino alane in 2 ml. of *n*-decane was prepared in the dry box. The reaction flask was attached to the monometer system and thoroughly evacuated. Known amounts of trimethylamine were then condensed into the flask which was warmed to room temperature and a 25° water bath was placed around it. The pressure was read when no further change was detected. The endpoint occurred at a ratio of dimethylamine to the amino alane of 2.05.

B. A 1.40 g. sample of tris-di-isopropylamino alane was placed in a flask, and 1.02×10^{-2} mole of dimethylamine were condensed onto the sample. Upon warming to ambient temperature a liquid phase formed. Fractionation of the volatile components yielded 1.51×10^{-3} mole of dimethylamine and a clear liquid. The vapor pressure of this liquid was 83 mm. at 25.3° and that of a pure sample of di-isopropylamine was 81 mm. at the same temperature. The infrared spectrum of the liquid was identical to that of pure di-isopropylamine.

Reaction of Boron Trichloride with Tris-dimethylamino Alane.—A. A 0.3621 g. sample of tris-dimethylamino alane in 2 ml. of *n*-decane was titrated tensiometrically with boron trichloride. Apparent equilibrium was attained approximately fifteen minutes after removal of the cold bath. The observed pressure was recorded. The end-point occurred at a mole ratio of boron trichloride to tris-dimethylamino alane of 2.10.

B. Tris-dimethylamino alane, 1.6 g., in 25 ml. of pentane was treated with 1.99×10^{-2} mole of boron trichloride. Upon warming, a white solid formed. The solid was isolated by filtration and sublimed at 75°, m.p. 149–150°. Analysis showed it contained no boron. The solvent was removed from the filtrate. A clear liquid remained. It was purified by fractionation through a –63° bath, m.p. –46°. Upon standing at room temperature for several days the liquid turned into a white crystalline solid, m.p. 41°. The melting points and the phase transition identify the liquid as dimethylamino boron dichloride.⁶

(6) E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 77 (1933).

C. Tris-dimethylamino alane 0.163 g. was placed in a seal-off bulb with 3 ml. of *n*-decane. Boron trichloride, 5.47×10^{-3} mole, was added and the flask was sealed off. After standing 24 hr. at ambient temperature, the bulb was opened and the volatile components were fractionated. A 2.34×10^{-3} mole sample of boron trichloride was recovered. The ratio of boron trichloride consumed to tris-dimethylamino alane was 3.05.

Reaction of Boron Trichloride with Bis-dimethylamino-chloro Alane.—A. A tensiometric titration of 0.2885 g. of bis-dimethylaminochloro alane in 2 ml. of *n*-decane with boron trichloride was performed as described above. The end-point occurred at a mole ratio of reactants (B/Al¹⁰) of 1.02.

B. A solution of 2.0 g. of bis-dimethylaminochloro alane in 70 ml. of pentane was allowed to react with 1.35×10^{-2} mole of boron trichloride. Upon warming, a white solid formed. After purification by sublimation the solid had a m.p. of 150°. A clear liquid, m.p. - 44°, was isolated from the filtrate as described above. It crystallized upon standing several days.

Tensiometric Titration of Tris-di-isopropylamino Alane with Boron Trichloride.—A solution of 0.696 g. of tris-di-isopropylamino alane in 2 ml. of *n*-decane was titrated with boron trichloride. The end-point occurred at a mole ratio of boron to aluminum of 2.90.

Molecular Weight Determination.—The apparent molecular weights were determined cryoscopically in benzene, in an apparatus previously described.⁵ A sample of benzene and the cell were taken into the drybox where a solution of the desired compound was prepared. The solution contained one to three grams of the compound per thirty-five grams of benzene. The cell was loaded and the freezing point of the solution was determined. The freezing point of the solvent was determined both before and after that of the solution. The values for benzene were reproducible to $\pm 0.01^\circ$.

Table I presents the apparent molecular weights of the compounds prepared. Included in the table are some values obtained by Wiberg² using the ebullioscopic method in diethyl ether. The large difference in the two sets of values may be due in part to the difference in the solvent employed.

TABLE I
APPARENT MOLECULAR WEIGHT OF SOME DIALKYLAMINO
DERIVATIVES OF ALUMINUM

	Mol. wt. (obsd.)	\bar{n}	\bar{n} (Wiberg ²)
Al[N(CH ₃) ₂] ₃	353	2.22	1.02
HAl[N(CH ₃) ₂] ₂	289	2.49	1.71
H ₂ AlN(CH ₃) ₂	219	3.00	2.08
Al[N[CH(CH ₃) ₂] ₃	347	1.06	..
[(CH ₃) ₂ N] ₂ AlCl ^a	294	1.95	...
(CH ₃) ₂ NAiCl ₂ ^a	301	2.12	..
[(CH ₃) ₂ CH] ₂ NAiH ₂	274	2.16	..
[(CH ₃) ₂ CH] ₂ NAiHN(CH ₃) ₂	346	1.98	...

^a By boiling point elevation in benzene.

N.m.r. Spectrum.—The proton nuclear magnetic resonance spectrum of tris-di-isopropylamino alane was taken on a benzene solution with a Varian Model V4300 B spectrometer operating at forty megacycles. The spectrum consisted of a large doublet and a much smaller septuplet. It was not possible to compare the relative areas of the two, however the observed spin-spin coupling is consistent with an isopropyl group.

Results and Discussion

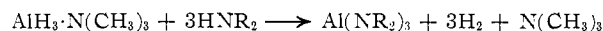
Dialkylamino derivatives of aluminum may be prepared by the reaction of a secondary amine with a suitable aluminum hydride derivative. Sodium aluminum hydride, for example, was reported to yield the completely substituted sodium *tetrakis* dialkylamino aluminate when allowed to react with a dialkylamine.⁷ This reaction was utilized in this study as a part of a convenient preparation of tris-dimethylamino alane from

available starting materials

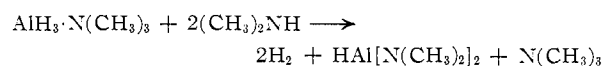


Lithium *tetrakis* dimethylamino aluminate was readily prepared from dimethylamine and lithium aluminum hydride. If desired, this compound can be obtained in a fair state of purity by evaporation of the solvent. However, in the preparation of tris-dimethylamino alane, isolation of the lithium salt was not necessary as aluminum chloride could be added directly to the reaction flask containing the freshly prepared solution.

A more general method of preparation of tris-dialkylamino alanes was found in the reaction of secondary amines with trimethylamine alane



This method is an adaptation of one suggested by Wiberg.² The use of trimethylamine alane in place of aluminum hydride permits a wider choice of solvent and reaction temperature. When dimethylamine was employed, the reaction proceeded rapidly in ether or benzene at room temperature. It was possible, as Wiberg observed, to halt the reaction after either one or two dimethylamino groups were substituted by limiting the amount of amine used. The reaction of two moles of dimethylamine with one mole of trimethylamine alane constitutes one of the best methods of preparation of bis-dimethylamino alane.



When other dialkylamines were used in the reaction, complete substitution of the hydride required more drastic conditions. For example, in the preparation of tris-di-isopropylamino alane, the trimethylamine alane was refluxed for 20 hr. with a large excess of di-isopropylamine before complete substitution of the hydride by di-isopropylamino groups was achieved. The infrared spectrum of the product confirmed the completeness of the substitution, and the proton n.m.r. spectrum indicated that no isomerization of the isopropyl groups had occurred.

It has been observed by several workers^{1,2,4} that substitution of a dimethylamino group for an alkyl, aryl, halide or hydride on aluminum results in the formation of dimers or trimers. Association is generally believed to occur through the formation of nitrogen bridges. Both tris-dimethylamino alane and bis-dimethylamino alane were found to be associated in benzene. Tris-di-isopropylamino alane, however, was monomeric in the same solvent. The inability of this compound to polymerize is believed to be due to steric hindrance. Two possible factors are assumed to be important in preventing dimer formation. Either the di-isopropylamino group is not capable of forming a stable bridge due to steric interaction of the two isopropylamino groups with the adjacent aluminum atoms, or the shielding of the aluminum by the six isopropyl groups surrounding it prevents bridge formation. Di-isopropylamino alane synthesized from lithium aluminum hydride and di-isopropylammonium chloride was found to be dimeric in benzene. This indicates that the

(7) A. E. Finholt, et al., *J. Inorg. and Nuclear Chem.*, **1**, 317 (1955).

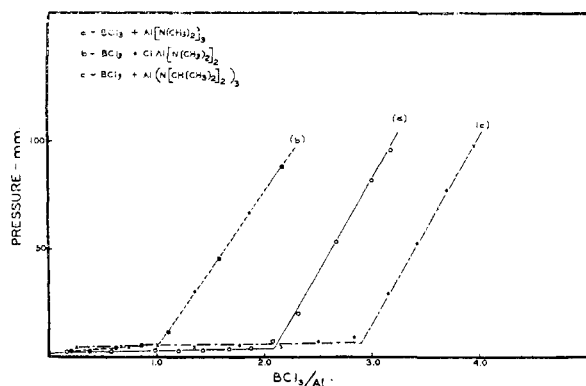
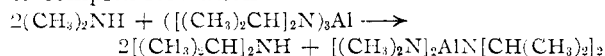


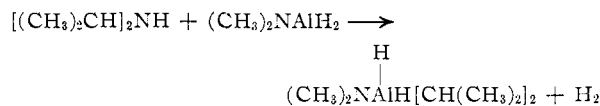
Fig. 1.—Tensiometric titration of some dialkylamino aluminum compounds with boron trichloride.

shielding of the aluminum by the six isopropyl groups is the most important factor. The great difference in the conditions under which tris-dimethylamino alane and tris-di-isopropylamino alane are formed might in part be due to a depolymerization process. Since di-isopropylamino alane is dimeric, the rupture of a nitrogen bridge must occur in the preparation of tris-di-isopropylamino alane.

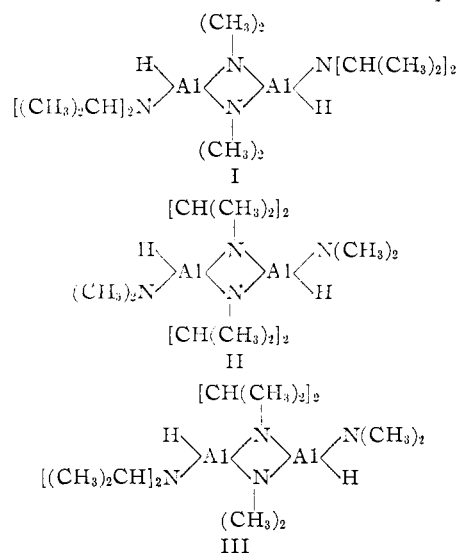
The stability of the nitrogen bridge in the dimethylamino derivatives of aluminum was demonstrated by the quantitative displacement of trimethylamine from trimethylamino alane by a single dimethylamino group, in the preparation of dimethylamino alane.⁵ No interaction has been observed between trimethylamine and other mono dimethylamino derivatives of aluminum.^{1,4} However, the apparent stability of a monomeric form of tris-dimethylamino alane in ether³ and a dimeric form in benzene indicates that the tris-dimethylamino alane may form the etherate, $\text{Al}[\text{N}(\text{CH}_3)_2]_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The possible existence of such a species suggested treatment of tris-dimethylamino alane with trimethylamine. No indication of interaction was observed at ambient temperature when the amino alane was titrated tensiometrically with trimethylamine. Tris-di-isopropylamino alane is monomeric and might therefore be expected to form a mono amine complex, if the amine meets the steric requirements of the amino alane. No interaction was observed in a tensiometric titration with trimethylamine, however. Because of the lower steric requirements of dimethylamine a reaction might be expected. After the addition of two moles of dimethylamine per mole of tris-di-isopropylamino alane, a sharp linear pressure increase was noted. Di-isopropylamine was isolated in good yield from the reaction. It is apparent that an exchange reaction occurred instead of complex formation



Although the dialkylamino aluminum derivative formed in the reaction above was not isolated, an effort was made to prepare bis-di-isopropylamino dimethylamino alane. Di-isopropylamine was allowed to react with dimethylamino alane. Using conditions identical to those used in the preparation of tris-di-isopropylamino alane, only one hydride could be replaced by an amino group.

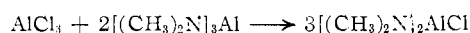


Dimethylamino di-isopropylamino alane is dimeric in benzene. If association occurs through nitrogen bridges, three structures of the dimer are possible.

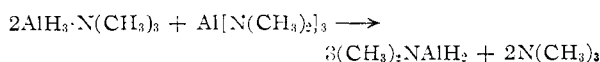


Structure I is favored for steric reasons; also, if the di-isopropylamino group should be the bridging group, it is difficult to explain why reaction with the remaining hydride does not occur, since dissociation of a diisopropylamino bridge occurs in the preparation of tris-di-isopropylamino alane. It is felt that the increased stability of a "dimethylamino bridge" (as opposed to a "di-isopropylamino bridge") prevents further substitution.

The stability of a bridging dialkylamino group might make it less reactive towards exchange with other groups than a non-bridging dialkylamino group. In order to determine whether exchange reactions would occur, tris-dimethylamino alane was allowed to react with either aluminum chloride or trimethylamine alane. An exothermic reaction occurred between the amino alane and aluminum chloride in the absence of solvent to give aminochloro alanes in good yield. Either bis-dimethylaminochloroalane or dimethylaminodichloro alane was obtained depending upon the mole ratio of the reactants.

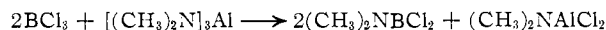


The products are white crystalline solids which are readily hydrolyzed by traces of water. Both are dimeric in benzene. Similarly, a reaction between trimethylamine alane and tris-dimethylamino alane produced dimethylamino alane. The trimethylamine was displaced during the reaction and was recovered quantitatively.



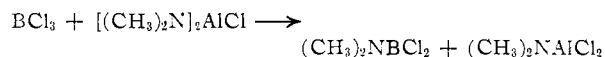
It was not possible to detect any differences in reactivity of the dialkylamino groups under the conditions used in the above reactions. A volatile

metal chloride would permit the use of the tensiometric titration technique to follow the stoichiometry. Tris-dimethylamino alane was allowed to react with boron trichloride since one of the expected products, dimethylamino boron dichloride, has been well characterized.⁹ When tris-dimethylamino alane was titrated tensiometrically with gaseous boron trichloride, a sharp increase in pressure was noted after the addition of two moles of boron trichloride per mole of the amino alane. (See Fig. 1a.) Approximately fifteen minutes was required to reach apparent equilibrium. Both dimethylamino boron dichloride and dimethylamino dichloro alane were isolated.



However, if an excess of boron trichloride was allowed to react with tris-dimethylamino alane in a sealed bulb for 24 hr., three moles of boron trichloride was consumed per mole of the amino alane. The observed effect is most probably due to a difference in the rate of exchange between the non-bridging dimethylamino groups and the dimethylamino group involved in the bridge. Such a difference in reactivity is not unexpected, since two of the six nitrogens in dimeric tris-dimethylamino alane must be tetra co-ordinated. It is felt that under the conditions of the tensiometric titration only the non-bridging amino groups were exchanged. In dimeric bis-dimethylaminochloro alane, two of the four nitrogens are believed to be involved in bridge formation. Therefore, only

one mole of boron trichloride ought to be consumed per mole of bis-dimethylaminochloro alane monomer. This was confirmed by a tensiometric titration (see Fig. 1b). Dimethylamino boron dichloride was again isolated from the reaction mixture.



Tris-di-isopropylamino alane is monomeric in benzene and thus has three non-bridging amino groups. Although a di-isopropylamino group is not strictly comparable to a dimethylamino group, especially in view of the steric requirements of boron, the reactivity of the di-isopropylamino groups should be equivalent if reaction does occur. When tris-di-isopropylamino alane was titrated tensiometrically with boron trichloride, a sharp linear pressure increase was noted after the mole ratio of boron to aluminum exceeded three (see Fig. 1c).

The lability of the non-bridging dialkylamino groups on aluminum in exchange reactions may result in new synthetic routes to dialkylamino derivatives of other elements, as well as, to new dialkylamino derivatives of aluminum itself.

Acknowledgments.—The author wishes to thank Dr. M. F. Hawthorne for many helpful suggestions during the course of this work and Mr. R. D. Strahm for the chemical analyses. This work was performed under contract D.A. 01-021-ORD-784.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE]

The Hydrolysis of Octahedral Complexes of Arsenic(V) : The Kinetics of Hydrolysis of the Catechol Complex

BY JOHN H. CRADDOCK AND MARK M. JONES¹

RECEIVED NOVEMBER 25, 1960

A study of the kinetics of hydrolysis of the arsenic(V)-catechol complex has been carried out to provide information on the behavior of a typical inert outer-orbital complex of a non-transition element. Examination of the levo complex indicates that it does not racemize or hydrolyze in strongly basic solutions even at elevated temperatures. As the pH drops, the rate of hydrolysis becomes measurable in the region of pH values from 3, where it is slow, to about 1.2, where it is rather fast. In this region, the rate of hydrolysis is given by the second-order expression $-d[I(-)\text{-complex}]/dt = k_2[H^+][I(-)\text{-complex}]$. The temperature dependence of the rate in various buffered solutions over the range 25–35° leads to the following values for the free energy, enthalpy and entropy of activation: $\Delta F^\ddagger = 20$ kcal., $\Delta H^\ddagger = 24$ kcal., and $\Delta S^\ddagger = 15$ e.u. The rate of hydrolysis is unaffected by added arsenite or arsenate. The addition of catechol is found to increase the rate of hydrolysis slightly. The over-all results indicate that the gross mechanism of the hydrolytic process may not be radically different from that found for some complexes of transition element ions.

Although a great deal of work has been done on the racemization and hydrolysis of transition element complexes, very little information is available on the racemization of complexes of non-transition elements. The present work was undertaken to provide information of this sort on the inert outer-orbital complex of arsenic(V) and catechol. It was hoped that such evidence would allow a decision to be made concerning possible differences in mechanisms of racemization which may be found for transition and non-transition element complexes. Inasmuch as the inner d orbitals of arsenic(V) are completely filled by non-bonding elec-

trons, the octahedral complexes of arsenic(V) must involve sp^3d^2 hybridization. In the resultant complexes, arsenic has *not* achieved the electronic configuration of the next highest inert gas (krypton) but has more electrons than are required by the effective atomic number rule.

The complex selected for this study is the one formed by the reaction of aqueous solutions of catechol and arsenic acid. The free acid was first prepared by Weinland and Heinzler² by the addition of catechol to a boiling aqueous solution of arsenic acid. Upon cooling, colorless crystals separated which had the composition $\text{HAS}(\text{C}_6-$

(1) To whom correspondence concerning this paper should be addressed.

(2) R. F. Weinland and J. Heinzler, *Ber.*, **52**, 1316 (1919).