stants found were: log $k_1 = 3.09$, log $k_2 = 3.47$ and log $K_2 = \log k_1k_2 = 6.56$ at 23°. This is in excellent agreement with the value of log $K_2 = 6.51$, which can be calculated from the data on the solubility of silver chloride in tris given by Bates and Pinching.[4]

These data may be compared with the corresponding value for the silver–ammonia complex, determined under the same conditions, *i.e.*, log $K_2 = 7.30$. As would be expected from these values, the half-wave potential at the rotating platinum electrode of the silver–tris complex was found to be only slightly more positive (*ca.* 30 millivolts) than that of the silver–ammonia complex under the same conditions.

In view of the rather bulky substituent groups on the α-carbon atom, it seems surprising at first sight that the reactivity of tris toward silver should be of the same order as that of ammonia. Moreover, its ratio of log $K_{2\text{Ag}^+}/pK_{a\text{H}^+}$ is 0.81, which is almost identical with that of ammonia, *i.e.*, 0.79. Both these values are above those encountered with other primary amines.[5,6] It is suggested that the substituent groups do not interfere with the reactivity of the nitrogen atom because intramolecular hydrogen bonding between the hydroxymethyl groups leads to a highly symmetrical structure as shown in Fig. 1. This structure also is consistent with the crystalline state of this compound in contrast to other primary amines.

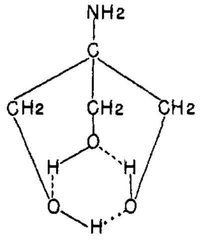

Fig. 1.

Acknowledgment.—This investigation was supported in part by a research grant H-1565 from the National Heart Institute of the National Institutes of Health, Public Health Service and by a grant from the National Science Foundation.

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[5] R. V. Bruehlman and F. H. Verhoek, This Journal, **70**, 1401 (1948).

[6] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., New York, N. Y., 1952.

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Tetrahydrofuran–Borine

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The solid–liquid equilibrium for tetrahydrofuran and diborane has been investigated from zero to 0.34 mole per cent. of diborane. Within the range studied, the system (Fig. 1 and Table I) has a single eutectic with a composition of 9 mole per cent. diborane and a temperature of −117°. The compound tetrahydrofuran–borine, C_4H_8O:BH_3, is clearly indicated at 33 mole per cent. by the sharp maximum. Existence of the compound is further indicated by the homogeneous solid phase which appears at this composition and by the rapid increase in the saturation pressure of diborane at compositions just above 33 mole per cent. diborane. The point at mole per cent. 0.34 is not reliable, but serves to isolate the maximum. The high diborane pressures made extension of the data to higher diborane concentration difficult and suggest that the solubility of diborane in tetrahydrofuran–borine is negligible. The melting point of the compound is about −34° as determined by direct observation and by extrapolation of the melting point–composition curve to 33 mole per cent.

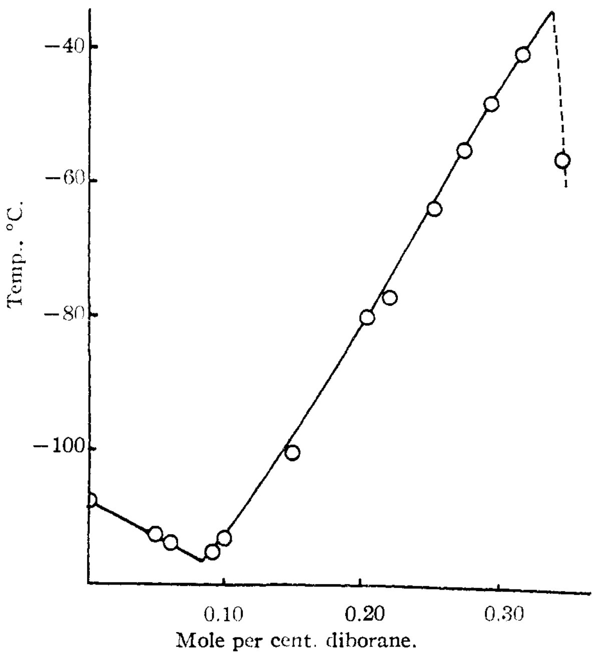

Fig. 1.—The system tetrahydrofuran–diborane.

Table I

Mole % B_2H_6	Temp., °C.	Mole % B_2H_6	Temp., °C.
0.00	−107.8	0.22	−76.7
.05	−112.5	.25	−63.6
.06	−114.0	.27	−54.7
.09	−114.7	.29	−48.2
.10	−113.6	.31	−40.1
.15	−100.2	.34	−56.2
.20	− 79.8		

These results are consistent with the solubility data of Elliot, *et al.*,[2] who interpreted the dependence of the solubility on the square root of the diborane pressure to imply the existence of tetrahydrofuran–borine. These investigators found no indication from solubility data of the existence of diethyl ether–borine and this compound may be presumed much less stable than tetrahydrofuran–borine. Dimethyl ether–borine[3] is the only other compound of this class for which evidence has been advanced. It has been shown to exist below −78° and is evidently much less stable than the compound reported herein. Under comparable conditions, no evidence for diethyl

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[1] Taken from a thesis presented by Jeanette A. Livasy to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Master of Science, June, 1955.

[2] J. R. Elliot, W. L. Roth, G. F. Roedel and E. M. Boldebuck, This Journal, **74**, 5211 (1952).

[3] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 296 (1938).

ether–borine has been obtained. The relative stability of the series of ether–borines is probably: $C_4H_8O:BH_3 > (CH_3)_2O:BH_3 \gg (C_2H_5)_2O:BH_3$, the order which would be expected if steric factors in the $—BH_3$ group were comparable to those in the $—BF_3$ group.[4] The interpretation of the compounds of diborane with ethers as ether–borines and the order of the stability as given above have been further confirmed by a detailed study[5] of the Raman spectra, to be published elsewhere, of ether solutions of diborane at low temperatures.

Experimental

Materials.—Diborane was prepared by the reaction[6] of $LiBH_4 \cdot O(C_2H_5)_2$ and copper(I) chloride in chlorobenzene and purified by fractional condensation at −140°. The product had a sharp melting point at −168.0° and a vapor pressure at −112° of 225 mm. The procedure used has the advantage of minimizing the diethyl ether concentration and thus contamination of the diborane with ether and its cleavage products. Diborane of exceptional purity results. Tetrahydrofuran was purified by refluxing over $LiAlH_4$, followed by fractionation. The purified material gave a sharp melting point at −107.8°.

Procedure.—The freezing points of tetrahydrofuran–diborane solutions were determined from cooling curves in the region 0 to 34 mole per cent. diborane. The quantities of tetrahydrofuran were measured as the liquid in a calibrated tube and the quantities of diborane were measured as the gas in a calibrated volume. The materials were transferred into the freezing point cell by condensation with liquid nitrogen. Liquid nitrogen was used as the coolant and the rate of cooling was regulated by variation of the gas pressure in a jacket interposed between the cell and the cooling bath. Temperatures were determined by a thermocouple calibrated against a platinum resistance thermometer and their over-all reliability is estimated to be ±0.5°. The results are given in the table above and graphically in Fig. 1.

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[4] H. C. Brown and R. M. Adams, This Journal, **64**, 2557 (1942).

[5] H. S. Uchida, Doctoral Dissertation, St. Louis University, June 1954.

[6] R. Toeniskoetter, Master's Thesis, St. Louis University, June 1955.

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Ammoniates of Guanidine and Guanidinium Chloride[1]

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Received December 23, 1954

The experiments described below are concerned with a method for the preparation of pure guanidine, and with the detection of ammoniates of guanidine and guanidinium chloride through the study of pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia.

Experimental

Guanidine was prepared by the interaction of guanidinium carbonate and potassium amide by an adaptation of equipment and procedures described previously.[2] The apparatus was modified to the extent that the reaction vessel was provided with a side-arm addition bulb from which guanidinium carbonate was added in slight excess to potassium amide solution previously prepared in the reaction vessel by the iron-catalyzed interaction of potassium and ammonia. After about two hours, the liquid ammonia solution of guanidine was separated from the insoluble potassium carbonate and excess guanidinium carbonate by filtration, the ammonia was evaporated, and the guanidine was collected in ampoules in the manner previously described.[2] Guanidinium chloride was prepared by treating guanidinium carbonate with hydrochloric acid, and was purified by recrystallization from absolute ethanol.

The purity of both the free base and the salt was determined by precipitation of guanidinium picrate using a procedure based upon the work of Vozarik.[3] To 25 ml. of aqueous solution of guanidinium chloride (or guanidine neutralized to the phenolphthalein end-point with hydrochloric acid), 50 ml. of 1.4% ammonium picrate solution was added slowly and with stirring. The resulting mixture was maintained at 25°, stirred occasionally over a period of at least 30 min., filtered, and the crystals of guanidinium picrate washed with two 5-ml. portions of ice-water, and dried to constant weight at 120°. To the weights of guanidinium picrate thus found there was added a predetermined correction factor to compensate for the solubility of the picrate under the conditions specified. On the basis of analyses of solutions of known guanidinium salt content, the solubility loss was found to be linear with respect to observed weights of guanidinium picrate over the range 120 to 500 mg.; the corresponding corrections amount to 10.6 to 21.0 mg., respectively. The maximum error in the determination of the solubility loss in this range is 0.5 mg. and the maximum percentage error in the analytical determinations would vary from about 0.5 to 0.1% as the observed weight of guanidinium picrate varies from 120 to 500 mg. As determined by this method, the purity of guanidinium hydrochloride was found to be 99.9% while that of guanidine was found to be 98.3 ± 0.6%. The purity of the latter

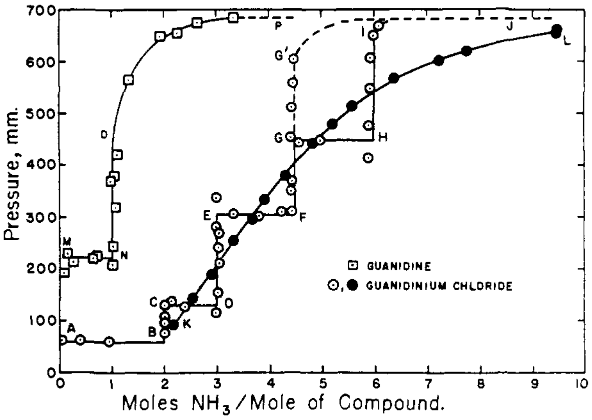

Fig. 1.—Pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia at −35.5°.

Table I

Composition of Phases in Equilibrium

Curve	Phases
AB	$A(s)$,[a] $A \cdot 2NH_3(s)$, $NH_3(g)$
BC	$A \cdot 2NH_3(s)$, $NH_3(g)$
CD	$A \cdot 2NH_3(s)$, $A \cdot 3NH_3(s)$, $NH_3(g)$
DE	$A \cdot 3NH_3(s)$, $NH_3(g)$
EF	$A \cdot 3NH_3(s)$, $A \cdot 4.5NH_3(s)$, $NH_3(g)$
FG	$A \cdot 4.5NH_3(s)$, $NH_3(g)$
GG	$A \cdot 4.5NH_3(s)$, $NH_3(g)$[b]
GH	$A \cdot 4.5NH_3(s)$, $A \cdot 6NH_3(s)$, $NH_3(g)$
HI	$A \cdot 6NH_3(s)$, $NH_3(g)$
IJ	$A \cdot 6NH_3(s)$, satd. soln., $NH_3(g)$
KL	Supersatd. soln., $NH_3(g)$[b]
MN	$B(s)$,[c] $B \cdot NH_3(s)$, $NH_3(g)$
NO	$B \cdot NH_3(s)$, $NH_3(g)$
OP	$B \cdot NH_3(s)$, satd. soln., $NH_3(g)$

[a] A = guanidinium chloride. [b] Metastable. [c] B = guanidine.

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] G. W. Watt and W. R. McBride, This Journal, **77**, 2088 (1955).

[3] A. Vozarik, *Z. angew. Chem.*, **15**, 670 (1902).