ratus at the usual pressure. The results are given in Tables I and II, determinations 4 and 5. It is apparent that within the lower precision of these results, there is no significant difference between the constants thus obtained and those observed in runs 1, 2 and 3. It may be concluded that the accuracy of the constants is not seriously affected by deviations from the perfect gas laws. Although errors due to this factor might be reduced by using an extrapolation procedure, the sensitivity of the dissociation data obtained in the lower pressure range to variations in the initial pressures[7] suggests that very little would be gained by recourse to such a method.

Summing up, then, it appears that the method described in this paper for measuring the dissociation of addition compounds yields dissociation data with the desired accuracy: the dissociation constants are estimated to be reliable to 2% and the heat of dissociation to 0.1%. The optimum pressure range (initial pressure of each component) is 20–30 mm. Operating below this range (*e. g.*, 10 mm.) does not noticeably affect the experimental values of the constants, but it greatly increases the probable error.

There is little doubt that the precision of the measurements could be further improved by additional refinements. However, the uncertainty introduced by neglect of the gas law deviations suggests that higher precision is of uncertain value. Certainly, the field is so new and the questions to be answered are so many that it appears more important now to concentrate on the more urgent problems and to leave further refinements to such a time as the need for even more accurate data becomes apparent.

Summary

Accurate dissociation data of addition compounds in gaseous systems are of considerable interest and value for theoretical organic chemistry. A simple technique for precise measurement of such dissociations has been developed and tested by a series of studies on the dissociation of trimethylamine–trimethylboron. The tests indicate that by this method the dissociation constants can be determined to 2% and the heat of dissociation to 0.1%.

DETROIT, MICHIGAN RECEIVED AUGUST 7, 1943

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[7] Comparison of the calculated values in runs 5 and 5′ illustrates this sensitivity. In the 5′ series of calculations, 10.07 mm. was used for the initial pressure instead of the 10.04 (±0.04) actually observed.

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

Acid–Base Studies in Gaseous Systems. II. The Anomalous Base Strength of the Methylamines; A New Manifestation of Steric Strain[1,2]

BY HERBERT C. BROWN,[3] HERMAN BARTHOLOMAY, JR., AND MODDIE D. TAYLOR

Organic acids and bases have played a significant role in the development of modern physical theories.[4] The influences which structure and substituents exert on the relative strengths of acids and bases are an important part of the foundations upon which such present-day theories as those of the "inductive effect" and the "resonance effect" are constructed. Although much research has been devoted to this subject, a number of interesting phenomena have not yet received satisfactory explanations.

One such phenomenon is the well-known anomalous behavior of the methylamines. The introduction of a methyl group into the ammonia molecule produces an increase in base strength which is ascribed to the positive inductive effect (+I) of the methyl group. The introduction of a second methyl group causes a further increase which is ascribed to the same effect. Introduction of a third methyl group, however, markedly reduces the strength of the tertiary amine formed[5] (Table I).

TABLE I

BASE DISSOCIATION CONSTANTS FOR AMMONIA AND THE METHYLAMINES AT 25°

Amine	$K_b \times 10^5$
NH_3	1.79
$CH_3 \rightarrow NH_2$	42.5
$\begin{matrix} CH_3 \searrow & \\ & NH \\ CH_3 \nearrow & \end{matrix}$	59.9
$\begin{matrix} CH_3 \searrow & \\ CH_3 \rightarrow & N \\ CH_3 \nearrow & \end{matrix}$	6.31

The behavior of the normal aliphatic acids and amines furnishes other puzzling problems. Acetic acid is considerably weaker than formic acid, a result which might be expected in view of the inductive (+I) effect postulated for the methyl group. Propionic acid is still weaker, a fact which is also in accord with the theory. Butyric acid, however, is stronger than propionic.[6]

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[1] This publication is also paper IV in the series, Studies in Stereochemistry; for paper no. III in this series, see THIS JOURNAL, **64**, 2563 (1942).

[2] Presented before the Division of Physical and Inorganic Chemistry at the Detroit Meeting of the American Chemical Society. A preliminary communication was published in *J. Chem. Phys.*, **11**, 43 (1943).

[3] Present address: Department of Chemistry, Wayne University, Detroit, Mich.

[4] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940; Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, Oxford, 1941.

[5] Everett and Wynne-Jones, *Proc. Roy. Soc.* (London), **177A**, 449 (1941). Earlier values for the dissociation constants of the methylamines are summarized in this paper.

[6] Dippy, *Chem. Rev.*, **25**, 151 (1939). Particular attention is called to the graph on page 189 of this review. The increase in the acid strength of butyric acid has been ascribed to hydrogen bond formation between the end methyl group and the carboxyl group. Since we have observed similar phenomena in compounds where such hydrogen bond formation is impossible, this explanation is no longer satisfactory. The subject will be discussed in subsequent papers of this series.

The normal aliphatic amines exhibit a similar phenomenon. The data, although less precise than those for the carboxylic acids, clearly show that the base strength rises in the series ammonia, methylamine, ethylamine, but drops with propylamine.[7]

Before attempting to explain these facts, it is important to know whether the phenomena are due primarily to the substances themselves or to indirect solution effects. The nature of the hydrogen acids has made their study difficult except by working with solvents of relatively high dielectric constant. Unfortunately, these are just the solvents which are the most complex and the least understood. By adopting the viewpoint advanced by G. N. Lewis[8] that the proton is but one out of many acids, it has become possible to draw conclusions regarding the relative strength of acids and bases from the dissociative characteristics of selected groups of addition compounds. By a suitable choice of the reference compounds, it is possible to make these dissociation studies in non-polar solvents, or even in the gas phase. The complexities of the polar solvents may thus be avoided. Such studies of generalized acids and bases in the comparative simplicity of the gas phase are now under way. The results already obtained not only furnish strong support for the Lewis concept of acids and bases, but they also throw light on the interesting problems previously mentioned. In the present paper, an investigation dealing with the first of these problems—the anomalous behavior of the methylamines—is reported. In this study, trimethylboron serves as the reference acid.

$$R_3N{:}B(CH_3)_3 \rightleftarrows R_3N{:} + B(CH_3)_3$$

$$R = CH_3 \text{ and/or } H$$

Purification of Compounds

In order to obtain constants of the desired accuracy (heat of dissociation good to 0.1 or 0.2 kcal.; the dissociation constants correct to 1–2%), it was necessary rigorously to purify the substances used in the investigation.[9] Since the experimental technique used is sensitive to impurities of the order of 0.1%, efforts were directed to preparing materials containing this quantity of impurity as the upper limit.

Trimethylboron was prepared by the action of boron trifluoride on methylmagnesium bromide in butyl ether. The crude trimethylboron was distilled (under nitrogen) directly out of the reaction flask; the yields were over 80%. The substance was introduced into the high vacuum apparatus and subjected to a prior distillation, from a U-tube at −112° to a U-tube at −130°. The ammonia addition compound, prepared from the distillate, was purified by distillation from a tube held at 0°. The fraction used was cut when the saturation pressure had become constant and agreed with the known value for the pure compound. This fraction was then distilled into a flask and treated with a deficiency of pure dry hydrogen chloride in order to liberate the trimethylboron.

$$NH_3{:}B(CH_3)_3 + HCl \longrightarrow NH_4Cl + B(CH_3)_3$$

The trimethylboron thus obtained was again distilled from a −112° bath and trapped by a −130° bath. The material exhibited a vapor pressure which was independent of the vapor volume; the pressure observed was 680 mm. at −22.9° (m. p. of carbon tetrachloride). The product combined with pure ammonia exactly in the molecular ratio 1:1 to form an addition compound with the correct saturation pressure. The pure trimethylboron was stored in large flasks as a gas. No change in its properties has been observed over a period of many months of storage.

Ammonia, obtained from a commercial tank of the anhydrous material, was treated with metallic sodium[10] until a permanent blue color was observed. A small middle fraction, sublimed at −80°, was collected in the vacuum apparatus. This ammonia was tensiometrically homogeneous; the vapor pressure was independent of the vapor volume; the value agreed with that of the ammonia vapor tension thermometer used.

Methylamine was generated from hydrochloride purified in the following manner. The hydrochloride (Eastman Kodak Co.) was washed several times with chloroform to remove traces of dimethylamine hydrochloride; then it was twice recrystallized from butanol. Finally, it was freed from possible traces of ammonia and trimethylamine by the process of Sharp and Solomon.[11] The free amine, obtained from the purified hydrochloride, was introduced into the vacuum line and placed over sodium. It was distilled from the sodium at −80°. The vapor pressure of the product was 422 mm. at −18.6° (measured with an ethyl ether vapor tension thermometer); this vapor pressure was independent of the vapor volume.

Dimethylamine was also generated from the hydrochloride (Eastman Kodak Co.) purified in the manner just described. The amine, after being treated with sodium, showed a vapor pressure of 561 mm. at 0°.

Trimethylamine was generated from an aqueous solution (Commercial Solvents Corp.); it was purified by treatment with freshly sublimed phosphorus pentoxide. This simple process, developed by Burg and Ingram,[12] removes ammonia and all primary and secondary amines. The pure trimethylamine thus obtained had a vapor pressure of 680.5 mm. at 0°

In all of the purifications, the vapor pressure measurements were used only to check the absence of any gross impurity present in an amount greater than 1 mole per cent. The absence of impurities larger than 0.1 mole per cent. was assured by careful measurement of the saturation pressures of the addition compound at 0° and by observations on the constancy of the pressure while the addition compound was distilled.[9]

Results

Ammonia–trimethylboron,[13] $NH_3{:}B(CH_3)_3$.—The addition compound formed by ammona and trimethylboron was described first by Frankland[14] and later by Stock.[15] The melting point reported by these authors,[16] 56°, is much lower than the

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[7] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1929.

[8] Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[9] It was also necessary to devise improved methods for studying dissociations in the gas phase. These methods are described in the first paper of this series. THIS JOURNAL, **66**, 431 (1944).

[10] The sodium for drying the ammonia and the amines was prepared in the following manner to avoid possible contamination of the amines by hydrocarbon vapors. Molten sodium was kept under high vacuum until gases were no longer evolved. Hydrogen was then introduced and the sodium drawn up into 4-mm. glass tubes, which dipped beneath the surface of the metal. After the sodium had solidified, the tubes were removed. Short lengths of this tubing were cut off as the sodium was needed.

[11] Sharp and Solomon, *J. Chem. Soc.*, 1477 (1931).

[12] Ingram, M. S. Dissertation, University of Chicago, Chicago, 1940.

[13] For a discussion of the nomenclature used for these addition compounds, see Davidson and Brown, THIS JOURNAL, **64**, 316 (1942), footnote 11.

[14] Frankland, *Ann.*, **124**, 129 (1862).

[15] Stock and Zeidler, *Ber.*, **54**, 531 (1921).

[16] It is not entirely clear whether the melting point reported by Stock and Zeidler is their own observation or is merely a republication of Frankland's value.

value, 73.2–73.7°, observed in the present investigation for the carefully purified product.

The saturation pressure[17] of the compound was studied over the temperature range from 0 to 59.7°. The data are listed in Table II and represented graphically in Fig. 1-A. The saturation pressure exhibits a behavior which appears to be general for addition compounds of the type under discussion. The values at low temperatures show a definite curvature in a log $P - 1/T$ graph; at higher temperatures they fall on a straight line.[18] The straight portion of the curve (20.0° and above) is represented satisfactorily by the equation

$$\text{Log } P = (-3095/T) + 11.229$$

The pressure above the solid would reach 760 mm. at 97.6° if the equation were valid to this temperature. However, since the compound melts at 73°, the "boiling point"[19] must lie somewhat higher than the above calculated value. Frankland[14] reports the boiling point as 110°.

TABLE II

SATURATION PRESSURES OF AMMONIA-TRIMETHYLBORON

Temp., °C.	0.0	4.2	10.5	15.0	20.0	28.0
Press., mm.	.95	1.33	2.12	3.16	4.70	8.81
Temp., °C.	30.0	40.0	46.1	50.0	55.0	59.7
Press., mm.	10.17	21.7	33.9	44.4	62.0	76.1

Stock and Zeidler report the compound to be highly dissociated (above 90%) at room temperature. In the present investigation, the dissociation of the substance over the temperature range from 54.8 to 130° was studied. The results are given in Table III and Fig. 1-B. The variation in the dissociation constants with temperature is represented by the equation

$$\text{Log } K_p = (-3007/T) + 8.723$$

TABLE III

DISSOCIATION PRESSURES OF AMMONIA-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Observed	Pressure, mm. Calculated[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
54.8	57.62	30.20	0.908	0.356
60.1	59.22	30.68	.930	.501
65.4	60.69	31.17	.947	.695
70.8	62.06	31.67	.960	.951
75.0	63.06	32.06	.967	1.19
77.4	63.64	32.28	.972	1.41
79.9	64.18	32.51	.974	1.57
86.0	65.52	33.07	.981	2.23
91.5	66.67	33.58	.985	2.94
99.6	68.26	34.32	.989	4.18
114.6[b]	71.15	35.70	.993	6.59
130.0[b]	74.10	37.12	.996	12.9

[a] Pressure of ammonia and trimethylboron (calculated to 0°) was 25.15 mm. [b] Values are not included in Fig. 1-B.

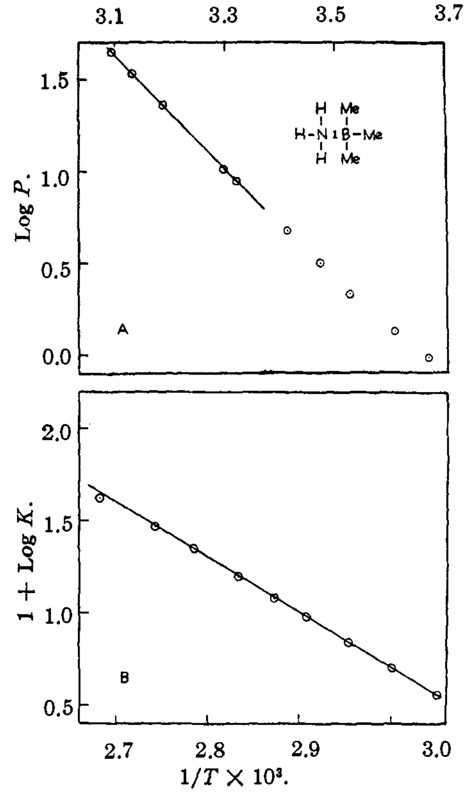

Fig. 1.—Ammonia-trimethylboron: A, saturation pressure data; B, dissociation data.

The dissociation constant at 100° is 4.6 and the heat of dissociation is 13.75 ± 0.3 kcal. A comparatively large probable error (0.2% as compared with 0.1% for the derivatives of the other amines) is assumed because of the particularly difficult region (α = 0.90 to 0.99) in which the dissociation of the compound was studied. (The methods used for determining the accuracy of the dissociation data are described in the first paper of this series.)

Methylamine-trimethylboron, $CH_3NH_2:B(CH_3)_3$.—The preparation and properties of methylamine-trimethylboron have not been previously reported. The addition compound is a white solid which melts at 26.9–27.2°; it is considerably less volatile than the corresponding

TABLE IV

SATURATION PRESSURES OF METHYLAMINE-TRIMETHYLBORON

Temp., °C.	0	15.0	20.0	25.0	34.7	43.4
Press., mm.	.16	0.62	0.87	1.31	2.49	4.34
Temp., °C.	50.1	60.6	71.6	81.4	85.6	93.1
Press., mm.	7.34	13.61	25.31	42.41	54.01	78.8

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(17) For reasons which are discussed in the first paper of this series, the precision of the saturation pressure measurements below 20 mm. is considerably lower than the precision of the saturation and dissociation pressures above that value.

(18) The clarification of this unusual behavior does not fall within the limits prescribed for the present series of investigations. It is hoped, however, that the problem will be examined by investigators interested in the physical properties of these addition compounds.

(19) Since the compound is almost completely dissociated at this temperature, this is not a true boiling point.

ammonia derivative. The saturation pressure was studied over a temperature range from 0 to 93.1°. The observed values are listed in Table IV and are represented graphically in Fig. 2-A. Above 34.7° the data fall on a straight line which is given by the equation

$$\text{Log } P = (-2829/T) + 9.611$$

The extrapolated "boiling point" is 147°.

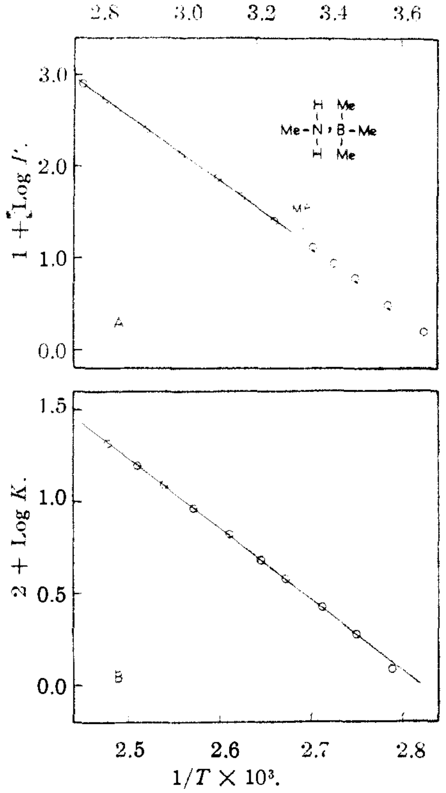

Fig. 2.—Methylamine-trimethylboron: A, saturation pressure data; B, dissociation data.

Under comparable conditions, the compound is considerably less dissociated than the ammonia derivative. The dissociation data observed over the temperature range from 85.4 to 132.9° are listed in Table V and represented graphically in Fig. 2-B. The dissociation constants can be represented by the equation

$$\text{Log } K_p = (-3856/T) + 8.880$$

The value of the dissociation constant at 100° is 0.0350 and the heat of dissociation of the compound is 17.64 ± 0.2 kcal.

TABLE V

DISSOCIATION PRESSURES OF METHYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Observed	Calculated[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
85.4	52.46	37.78	0.3886	0.0123
90.6	55.67	38.33	.4524	.0188
95.6	58.57	38.86	.5072	.0267
101.1	61.68	39.43	.5643	.0379
104.9	63.85	39.83	.6031	.0480
110.1	66.84	40.38	.6553	.0662
115.8	69.96	40.98	.7072	.0921
120.7	72.65	41.50	.7506	.123
125.3	74.93	41.99	.7847	.158
130.6	77.42	42.55	.8195	.208

[a] Pressure of methylamine and trimethylboron (calculated to 0°) was 28.69 mm.

Dimethylamine-trimethylboron, $(CH_3)_2NH{:}B(CH_3)_3$.—The addition compound formed by dimethylamine and trimethylboron also has not previously been described. It is a white solid which melts at 35.0–35.5° and resembles the methylamine derivative in volatility. The saturation pressure data (over the range from 0 to 74.6°) are given in Table VI and represented graphically in Fig. 3-A. The compound behaves like the corresponding methylamine derivative. Above 45.7° the saturation pressures can be represented by the equation

$$\text{Log } P = (-2902/T) + 9.860$$

The extrapolated "boiling point" is 143°.

TABLE VI

SATURATION PRESSURE OF DIMETHYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	10.0	19.8	31.8	37.8	40.2
Press., mm.	.20	0.40	0.91	2.32	3.63	4.11
Temp., °C.	45.7	50.1	55.2	65.3	70.0	80.0
Press., mm.	5.76	7.75	10.6	19.3	25.1	41.9

The dissociation of the compound was studied over the temperature range from 85.1 to 125.6°. The substance is somewhat less dissociated than the corresponding methylamine derivative under comparable conditions. It is the least dissociated of the four derivatives studied in the present investigation. The dissociation data are given in Table VII and illustrated in Fig. 3-B. The variation of the dissociation constant with temperature can be represented by the equation

$$\text{Log } K_p = (-4211/T) + 9.595$$

The value of the dissociation constant at 100° is

TABLE VII

DISSOCIATION PRESSURES OF DIMETHYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Observed	Calculated[a]	Degree of dissociation, α	Dissociation constant K (atm.)
85.1	44.97	34.18	0.316	0.00655
89.3	47.04	34.58	.360	.00924
90.9	47.91	34.73	.379	.0106
94.4	49.66	35.07	.416	.0137
99.8	52.47	35.58	.475	.0201
104.8	55.17	36.06	.530	.0283
110.3	58.18	36.58	.590	.0410
116.1	61.34	37.14	.652	.0595
121.2	64.01	37.62	.701	.0816
125.6	66.25	38.04	.742	.106

[a] Pressure of dimethylamine and trimethylboron (calculated to 0°) was 26.06 mm.

0.0214 and the heat of dissociation of the complex is 19.26 ± 0.2 kcal.

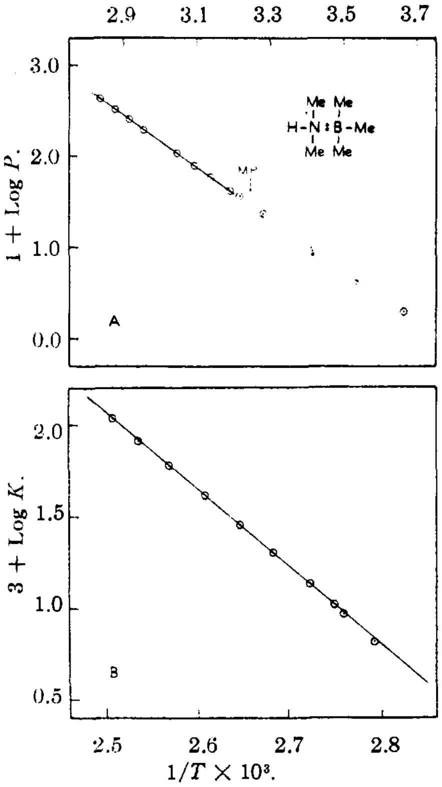

Fig. 3.—Dimethylamine-trimethylboron: A, saturation pressure data; B, dissociation data.

Trimethylamine–trimethylboron, $(CH_3)_3N:B(CH_3)_3$.—The complex, trimethylamine–trimethylboron, has been previously prepared and studied by Schlesinger and co-workers.[20] In view of the high accuracy demanded by the present study, the properties and the dissociation of the compound in the gas phase were reinvestigated. Trimethylamine–trimethylboron is a white crystalline solid which softens at 120° and melts at 128°. It is the second most volatile of the addition compounds under consideration, being exceeded in this respect only by the ammonia derivative.[21] Saturation pressure measurements are listed in Table VIII and illustrated in Fig. 4-A. Above 29.8° the saturation pressure data may be represented by the equation

$$\text{Log } P = -(3467/T) + 11.949$$

Below this temperature the graph shows the curvature to which attention has previously been called. The extrapolated "sublimation point" is 109.6°.

TABLE VIII

SATURATION PRESSURES OF TRIMETHYLAMINE–TRIMETHYLBORON

Temp., °C.	0.0	6.2	10.3	14.9	20.1	24.2	29.8
Press., mm.	0.24	0.42	0.60	0.90	1.41	2.00	3.17
Temp., °C.	34.8	39.1	44.2	50.5	55.8	59.8	65.1
Press., mm.	4.91	7.05	10.47	17.10	25.8	33.9	48.6

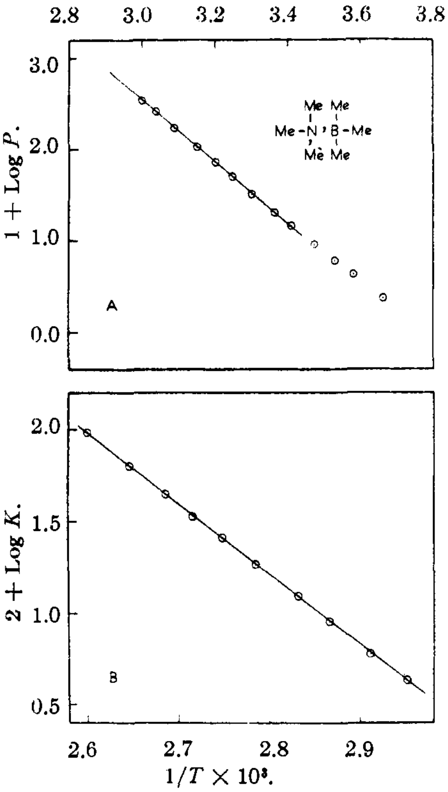

Fig. 4.—Trimethylamine-trimethylboron: A, saturation pressure data; B, dissociation data.

The dissociation of the compound was studied over the temperature range from 65.8 to 111.3°. It is less than that of the ammonia, but more than that of the methylamine, derivative. The dissociation data are listed in Table IX and repre-

TABLE IX

DISSOCIATION PRESSURES OF TRIMETHYLAMINE–TRIMETHYLBORON

Temp., °C.	Pressure, mm. Observed	Pressure, mm. Calculated[a]	Degree of dissociation, α	Dissociation constant K (atm.)
65.8	47.54	29.02	0.638	0.0430
70.4	49.77	29.42	.692	.0601
75.8	52.35	29.88	.752	.0897
80.0	54.35	30.24	.797	.125
85.8	56.70	30.74	.844	.185
90.6	58.48	31.15	.877	.257
95.0	59.90	31.53	.900	.335
99.0	61.18	31.87	.920	.441
104.7	62.79	32.36	.940	.631
111.3	64.47	32.92	.960	.956

[a] Pressure of trimethylamine–trimethylboron (calculated to 0°) was 23.39 mm.

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(20) Schlesinger, Flodin and Burg, THIS JOURNAL, **61**, 1078 (1939).

(21) The volatility appears to be closely connected with the relative degree to which the compounds are dissociated under comparable conditions.

sented in Fig. 4-B.[22] The dissociation constants can be represented by the equation

$$\text{Log } K_p = -(3852/T) + 9.998$$

The value of the dissociation constant at 100° is 0.472 and the heat of dissociation is 17.62 ± 0.2 kcal.

Discussion

The dissociation data in Table X (*cf.* also Fig. 5) reveal that the relative affinities of ammonia and its methyl derivatives for trimethylboron are almost identical with the relative affinities o these amines for the proton. In both instances the affinity increases with the introduction of the first methyl group, increases still further with the introduction of the second, but drops sharply with the introduction of the third. That these amines, when investigated by two radically different procedures, fall into the same order can hardly be a matter of chance. There is probably one fundamental explanation for the two phenomena.[23]

TABLE X

SUMMARY OF DISSOCIATION DATA

Compound	K_{100}	ΔF_{100}	ΔH	ΔS
$NH_3{:}B(CH_3)_3$	4.6	−1134	13,750	39.9
$CH_3NH_2{:}B(CH_3)_3$	0.0350	2472	17,640	40.6
$(CH_3)_2NH{:}B(CH_3)_3$	.0214	2885	19,260	43.6
$(CH_3)_3N{:}B(CH_3)_3$	.472	557	17,620	45.7

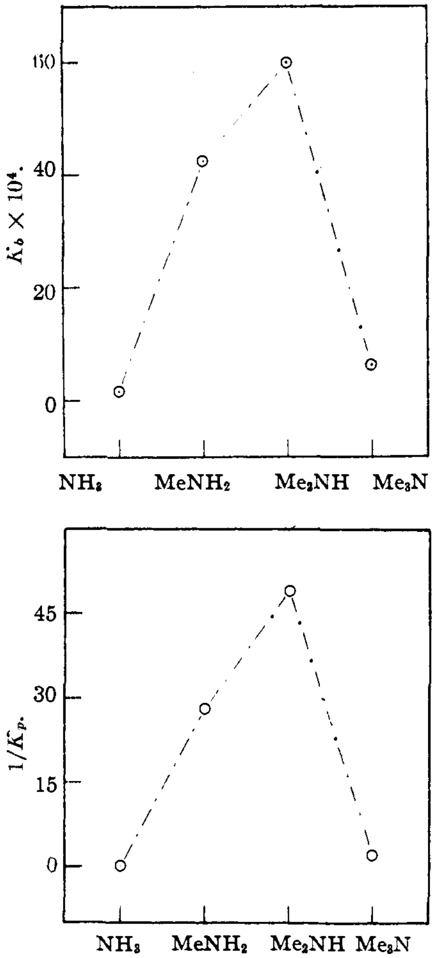

Fig. 5.—Base dissociation constants (K_p) at 25° of ammonia and the methylamines (top); dissociation constants (K_p) at 100° of the addition compounds of ammonia and the methylamines with trimethylboron (bottom).

According to current theories, introduction of a given substituent influences the properties of the parent molecule in two ways: firstly by changing the charge distribution, secondly by changing the steric relationships within the molecule. The first of these effects is due primarily to the electric properties of the substituent; the second, to its space requirements. The former effect has been called the "polar factor" associated with a given substituent; the second is here termed the "steric factor." The influence of the polar factor on the strength of acids and bases has long been realized; the importance of the steric factor with respect to these properties has only recently been recognized.

The increase in base strength of methylamine over ammonia and the further increase of dimethylamine over methylamine are plausibly ascribed to the polar factor. The inductive effect of two successive methyl groups (+I) increases the electron density on the nitrogen atom, and thus augments the ability of that atom to donate an electron pair to an acceptor, such as the proton or the boron atom in trimethylboron. There is, however, no apparent explanation in terms of the polar factor for the marked decrease in the donor properties of the nitrogen atom associated with the introduction of the third methyl group. It is plausible, therefore, to seek the reason for the phenomenon in the steric factor.

Previous investigations have shown that steric strain is important in determining the strength of acids and bases.[24] Thus pyridine is weaker than

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[22] Other dissociation measurements of this compound are reported in the first paper of this series, where the dissociation of the complex was used to test the reliability of the experimental technique.

[23] A rough idea of the extent to which the base is weakened by the introduction of the third methyl group may be obtained as follows. The free energy of dissociation (at 100°) of methylamine-trimethylboron is approximately 3600 cal. greater than that of ammonia-trimethylboron. That is, the replacement of a hydrogen atom in ammonia by a methyl group increases by 3600 cal. the work required to separate the trimethylboron from the amine. Replacement of the second and third hydrogen atoms by methyl groups might be expected to increase the free energy of dissociation by approximately the same amounts. The free energy of dissociation (at 100°) of the dimethylamine compound would then be about 6000 cal., and that of the trimethylamine derivative about 9600 cal. The observed values, 2885 and 557 cal. respectively, indicate that some influence lowers the ΔF_{100} of the dimethylamine derivative by about 3500 cal. and that of the trimethylamine derivative by about 9000 cal.

It is interesting that the variation in the base strength of the amines is not due primarily to entropy effects. The interesting behavior of the ΔS term in the dissociation of these and related addition compounds will be discussed in a later paper.

[24] Brown, Schlesinger and Cardon, THIS JOURNAL, 64, 325 (1942).

trimethylamine when such acids as the proton (hydrogen chloride or hydrogen bromide), boron trifluoride, or borine are used to make the comparison, whereas the reverse is true when trimethylboron is so used. The weakness of trimethylamine when trimethylboron is the reference acid is ascribed to steric interference between the three methyl groups attached to the boron atom and the three methyl groups attached to the nitrogen atom.[25] The interference results in a force which tends to separate the two parts of the addition compound and thereby to increase its dissociation.

Another example of this type of strain is furnished by pyridine and α,α'-lutidine. The latter is a considerably stronger base than pyridine if the proton is used as the comparison acid. (The increase in base strength can readily be accounted for by the inductive effect of the methyl groups.) On the other hand, the comparatively large acid, boron trifluoride, reverses the order of these base strengths. Furthermore, α,α'-lutidine exhibits no basic properties whatsoever when the very bulky trimethylboron is the acid.[25]

These examples furnish clear cut illustrations of the type of steric strain under discussion—a face-to-face interference which markedly increases rissociation. For convenience, this type of steric dasain will be called "F-strain."

F-strain cannot be used as the basis of a satisfactory explanation of the behavior of the methyltmines. It is characteristic of F-strain that its magnitude depends on the steric requirements of both components. Thus, in the previously mentioned illustrations, the relative strengths of the amines differ, depending upon which acid, the proton, boron trifluoride, or trimethylboron, is used for the comparison. In the methylamines, however, the relative base strengths must be largely independent of the acid component since identical orders of base strengths are observed with both the proton and trimethylboron. The close similarity (Fig. 5) in the behavior of the dissociation constants, K_b, and the association constants, $1/K_p$, of the amines,[26] suggests that the correct explanation for this phenomenon must somehow be connected with the transformation of the trivalent nitrogen compound into an ammonium derivative. That is, the steric cause of the phenomenon under investigation must be in some way related to the fourth nitrogen bond; it must be of such a nature as to render relatively unimportant the steric factor of the group adding.

A simple explanation filling these requirements is available provided a not unreasonable assumption be made regarding the configuration of the free trimethylamine molecule.

There are theoretical reasons for believing that the three bonds of a trivalent nitrogen atom should be directed in space at angles of 90° to each other. In all cases which have been investigated, however, the angles are considerably greater, probably because they must be increased to accommodate the attached groups.[27] An electron diffraction investigation of trimethylamine led Brockway and Jenkins to the conclusion that the C–N–C angle in this molecule is $108 \pm 4°$.[28] In the explanation here proposed, it is assumed that the bond angle in trimethylamine is somewhat greater than the normal tetrahedral angle, probably close to the upper limit set by Brockway and Jenkins. In other words, the three rather bulky methyl groups spread the bonds of the nitrogen atom from their preferred configuration (90°) to a value greater than the tetrahedral angle.

In the trivalent nitrogen derivative, such spreading of the bond angles is relatively easy since the fourth position in the valence shell is not occupied. However, the addition of a fourth group to the vacant position, be it a proton or a trimethylboron molecule, forces the nitrogen atom toward a tetrahedral configuration and results in a reduction of the expanded angles. The methyl groups are, therefore, crowded toward each other, setting up a strain which reduces the stability of the addition compound.

The term "B-strain" is proposed for this effect. (The letter B is used to indicate that the interference which causes the strain is localized at the "back" of the molecule—trimethylamine in the case under discussion—away from the entering group; it is thus contrasted to F-strain which results from interference at the "front" of the molecule, at the interface between the two components of the addition compound.) B-strain should depend greatly upon the size of the groups attached to the nitrogen atom or any other small central atom, but should be relatively independent of the size of the adding group. The absence or relative unimportance of B-strain in ammonia and methylamine is accounted for by the fact that the small hydrogen atoms attached to the nitrogen atom permit the bond angle to approach the tetrahedral value without appreciable B-strain. On the other hand, the two methyl groups in dimethylamine and the three methyl groups in trimethylamine cannot adapt themselves so easily to the space available. The B-strain, in fact, is sufficient to reduce slightly the strength of dimethylamine and to reduce greatly that of trimethylamine.

The suggestion that B-strain is the primary cause of the anomalous behavior of the methyl-

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(25) See Fig. 2, p. 327, of reference 24.

(26) The magnitude of the base dissociation constant, K_b, is a measure of the affinity of the free amine for a proton. Actually, K_b/K_w should be compared, since that quantity is the equilibrium constant for the reaction

$$R_3N: + H^+ \rightleftarrows R_3N{:}H^+$$

However, no error is introduced in neglecting the constant factor, $1/K_w$, in making comparisons.

Similarly, the association constant, $1/K_p$, measures the affinity of the free amine for trimethylboron

$$R_3N: + B(CH_3)_3 \rightleftarrows R_3N{:}B(CH_3)_3$$

(27) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 78.

(28) Brockway and Jenkins, THIS JOURNAL, 58, 2036 (1936).

amines does not mean that F-strain is absent. Indeed, the results previously reported[24] show that F-strain must be present. However, it probably increases regularly with the introduction of one, two or three methyl groups into the amine. The absolute magnitudes of the amine strengths are thus affected; their relative order, however, is not altered.

The proposed explanation leads to a number of interesting predictions; these are now being tested.

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Summary

1. The trimethylboron addition compounds with ammonia, methylamine, dimethylamine and trimethylamine have been prepared and characterized.

2. The dissociation of these compounds in the vapor phase ($R_3N{:}BMe_3 \rightleftarrows R_3N{:} + BMe_3$) has been studied; ΔH, ΔF and ΔS for the reactions have been measured.

3. The relative affinity of the methylamines for trimethylboron (measured by the dissociation constant of the complex) is identical with their affinity for the proton (measured by the dissociation constant of the base). In both instances, the base strength rises from ammonia to methylamine and to dimethylamine, but drops sharply from dimethylamine to trimethylamine.

4. To account for this observed order the strain resulting from the "steric factor" is divided into two kinds, "B-strain" and "F-strain." The anomalous behavior of the methylamines is ascribed to B-strain.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressure of Beryllium at 1170–1340°K.

BY ROBERT SCHUMAN AND A. B. GARRETT

The vapor pressure of beryllium was determined by measuring the rate of vaporization in a vacuum. The theory and application of this method are adequately described by other investigators.[1,2,3,4] In the case of beryllium, the accommodation coefficient appears (qualitatively) to be unity within the limits of experimental error. This was true for iron,[2] copper,[2] nickel,[3] nickel oxide,[3] and for liquid and solid mercury.[5,6]

Experimental

The procedure was that of determining the loss of weight due to evaporation of a beryllium ring of known surface area; the ring was held at a constant known temperature by an induction furnace for a known length of time.

The beryllium was a very pure sample supplied by the Brush Beryllium Company with the analysis: 0.03% Fe, 0.008% Al, 0.004% Mg, 0.022% Si. The ring was made from the sample and had an effective area of evaporation of about 8.5 sq. cm.

The water-cooled cell was a modification of the one used by Marshall, Dornte and Norton,[2] but was made of Pyrex glass. The cell was constructed with two small-diameter water-cooled glass tubes sealed just inside the inner tube to prevent the formation of a continuous film of metal on the inside of the tube. The ring was supported by a tungsten tripod. The optical window at the top of the cell was protected from the metal vapors by a glass shutter.

The temperature was measured by a Leeds and Northrup No. 8622-C optical pyrometer with which the readings were easily reproducible to within 5°. The pyrometer was calibrated against the apparent black body temperature of melting silver, the silver being melted in a groove in an iron ring into which small holes had been drilled to serve as black bodies. The pyrometer was checked three times against the melting point of silver, the apparent melting points having a variation of 3°. The temperature of the beryllium ring used for determining the rate of evaporation was taken as the apparent emission temperature, and then corrected to black body temperatures by values of beryllium emissivities determined. The beryllium emissivities were obtained by comparing the apparent temperature readings of a polished beryllium surface and those of 1-mm. diameter, 4-mm. deep holes drilled in the specimen.

A pressure below 10^{-5} mm. of mercury was maintained throughout the run to prevent oxidation. In several runs in which the vacuum was poor, surface oxidation prevented or slowed up evaporation. A period of outgassing at dull red heat was also found valuable to eliminate adsorbed gases.

The weighings were made on a balance accurate to about ±0.05 mg.

Data.—The experimental results are recorded in Table I and Fig. 1 for the rate of vaporization. The temperatures given are the average temperature during the runs, and thus take into account small fluctuations in temperature during the run. The times are the effective times at the temperature indicated. The apparent emission temperatures for $\lambda = 6500$ Å. are given in terms of the black body temperatures by the equation

$$t_e = 0.904 t_{bb} + 54.5 \quad (\pm 5^\circ\ 800\text{-}1000^\circ)$$

where t_e is the apparent polished surface temperature in °C. and t_{bb} is the corresponding black body temperature, °C. Runs 9 and 12 were of no value owing to surface oxidation.

Thermodynamic Considerations.—In order to check the validity of the vapor pressure results,

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(1) Langmuir, *Phys. Rev.*, **2**, 329 (1913).

(2) Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

(3) Johnston and Marshall, *ibid.*, **62**, 1382 (1940).

(4) Marshall and Norton, *ibid.*, **55**, 431 (1933).

(5) Knudsen, *Ann. Physik*, **29**, 179 (1909).

(6) Volmer and Estermann, *Z. Physik*, **7**, 1 (1921).