two components exhibits a pressure of 4 mm.; at 0° the pressure corresponds to complete dissociation.

Competition reactions were run between ammonia and trimethylamine with tri-*t*-butylboron as the reference acid. From 56.4 cc. of ammonia, trimethylamine and the boron acid was obtained 53.2 cc. of amine which analyzed for 98% trimethylamine. It should be pointed out that in these last experiments involving triisopropylboron and tri-*t*-butylboron, the quantitative recovery of excess amine is a slow process—apparently the addition compounds formed have a marked affinity for excess amine.

Discussion

The data on the relative strength of the bases ammonia and trimethylamine are summarized in Table I. The letters W and S are used to indicate the weaker and stronger of the two amines. The first of the two figures in the parentheses following each letter gives the mole fraction of the amine which combined with the reference acid; the second gives the saturation pressure of the addition compound at 25° in mm. It should be noted that the order of base strength established by the competition experiments is fully confirmed by the saturation pressure data.

TABLE I

RELATIVE BASE STRENGTH OF AMMONIA AND TRIMETHYLAMINE

Reference acid	Ammonia	Trimethylamine
Trimethylboron	W (0.15, 6.4)	S (0.85, 2.1)
Triethylboron	S (.91, 1.4)	W (.09, 12.1)
Triisopropylboron	S (.96, 2.3)	W (.04, N. C.[a])
Tri-*t*-butylboron	S (.98, 13.3)	W (.02, N. C.[a])

[a] No compound formed.

It is evident that the order of base strength observed with the reference acid trimethylboron, $NH_3 < (CH_3)_3N$, is reversed with triethylboron. Moreover, trimethylamine exhibits no basic properties with the highly hindered acids, triisopropyl- and tri-*t*-butylboron. The predictions of the steric strain hypothesis on the effect of F-strain on the relative strength of ammonia and trimethylamine are thus in complete accord with experiment.

Before closing, one further point may be mentioned. There has been considerable discussion as to whether a monotonic series of generalized acids and bases exists.[11] The present investigation offers a clear-cut illustration of the dependence of base strength upon the reference acid and supports the viewpoint that such a monotonic series cannot be set up.[12]

Acknowledgment.—The purchase and construction of the apparatus used in this investigation was made possible by a grant from the Penrose Fund of the American Philosophical Society. This assistance is gratefully acknowledged.

Summary

1. The relative strength of the bases ammonia and trimethylamine was determined using trimethyl-, triethyl-, triisopropyl- and tri-*t*-butylboron as the reference acids.

2. The order $NH_3 < N(CH_3)_3$, observed with the hydrogen acids and with trimethylboron, is reversed with triethylboron and the more hindered acids. These observations are in accord with the predicted effect of F-strain on the relative strength of the two bases.

3. In the course of this study improved procedures for the preparation and purification of trimethylboron and triethylboron were developed; and saturation pressures were measured for the addition compounds of triethyl-, triisopropyl-, and tri-*t*-butylboron with ammonia and trimethylamine.

[11] Luder, *Chem. Rev.*, **27**, 547 (1940).

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

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. VI. The Effect of F-Strain on the Relative Base Strengths of Ammonia and the Methylamines

BY HERBERT C. BROWN

In the absence of steric complications, the strength of ammonia and the methylamines should increase regularly with the number of methyl groups as a result of the inductive effect (+I) of alkyl groups. However, this predicted order, $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ (Fig. 1, curve A), is not observed. B-Strain[1] slightly reduces the strength of dimethylamine and markedly reduces the strength of trimethylamine, so that the order of base strength established by acids with a comparatively low F-strain factor is that represented by curve B, $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$.

It is the object of the present investigation to examine the effect of F-strain on the order shown by these amines. The order represented by curve B is observed both with hydrogen ion and with trimethylboron as the reference acid.[1] Replacement of the methyl groups in trimethylboron by larger, bulkier alkyl groups should lead to an increase in F-strain and thus result in a decrease in the apparent strength of the bases. The higher

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[1] Brown, Bartholomay and Taylor, THIS JOURNAL, **66**, 435 (1944).

methylated bases, however, should be affected to a greater extent than the lower.[2] Indeed, it would be anticipated that a change of this kind in the reference acid (as from trimethylboron to tri-*t*-butylboron) would increase F-strain in the order, $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$, resulting in an apparent decrease in base strength in the same order.

It follows that a progressive increase in F-strain should alter the observed order of base strength to those represented by curves C, D and E. Finally, a reference acid with a very high F-strain factor should yield the order, $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < NH_3$ (curve F). *It is noteworthy that this last sequence is the exact opposite of the order which would be predicted if only the polar effect of the methyl group were taken into consideration. The importance of considering the steric factor as well as the polar factor in theorizing is clearly indicated.*

In order to test these conclusions as to the effect of increased F-strain on the relative strength of ammonia and the methylamines, the strengths of these amines were compared using tri-*t*-butylboron as the reference acid with a high F-strain factor.

Experimental Part

Preparation and purification of compounds used in this investigation and the methods used in their study are either described or referred to in the preceding paper of this series.[2]

Results

Monomethylamine-tri-*t*-butylboron was prepared by combining 0.445 g. (2.45 millimoles) of tri-*t*-butylboron with 55.3 cc. (2.47 millimoles) of monomethylamine. The properties of the addition compound thus formed are quite similar to those of the ammonia derivative previously prepared and described.[2] Like the latter it is liquid at 0° and solidifies to a glass at −80°. All attempts at crystallization failed. The saturation pressures of the compound are slightly lower than those of ammonia-tri-*t*-butylboron and exhibit the same dependence upon the proportion of the substance which is in the vapor phase.[2] The data[3] are listed in Table I.

TABLE I

SATURATION PRESSURES OF METHYLAMINE-TRI-*t*-BUTYLBORON

Temp., °C.	0.0	15.0	25.0	30.0	35.0	40.0
Press., mm.	1.5	4.7	9.1	14.5	18.4	25.0

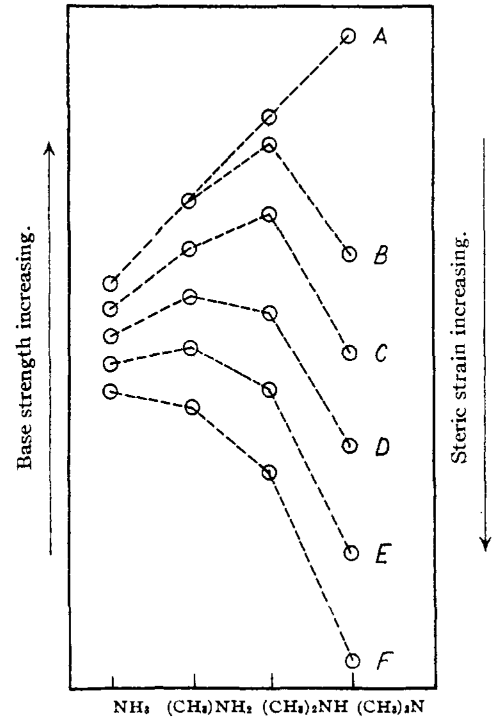

Fig. 1.—Effect of B- and F-strain on the relative strength of ammonia and the methylamines.

Dimethylamine-tri-*t*-butylboron, prepared from 0.374 g. (2.05 millimoles) of tri-*t*-butylboron with 45.9 cc. (2.05 millimoles) of dimethylamine, was also liquid at 0° and solidified to a glass at −80°. The saturation pressures[3] exhibited by the substance are far higher than those of the corresponding ammonia and methylamine derivatives (Table II).

TABLE II

SATURATION PRESSURES OF DIMETHYLAMINE-TRI-*t*-BUTYLBORON

Temp., °C.	−40	−30	−20	−10	0.0
Press., mm.	1.4	3.9	9.3	22.8	44.5

Trimethylamine and tri-*t*-butylboron do not combine to form an addition compound at temperatures as low as −80°.[2]

Competition experiments were carried out to determine the relative strength of the four amines. From a reaction mixture of 42.5 cc. each of ammonia, methylamine and tri-*t*-butylboron (0.345 g.) was obtained 39.8 cc. of uncombined amines. The molecular weight of this amine mixture was 21.3, indicating that it consisted of 69% ammonia and 31% monomethylamine. Similarly, from 46.0 cc. each of ammonia, dimethylamine and the boron acid (0.374 g.) was obtained 43.6 cc. of amines, the average molecular weight of which was 41.5, corresponding to a composition of 9% ammonia and 91% dimethylamine. The relative strength of ammonia and trimethylamine with tri-*t*-butylboron as the reference acid had been determined previously—the recovered amine analyzed for 2% ammonia and 98% trimethylamine.[2]

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[2] Brown, THIS JOURNAL, **67**, 374 (1945).

[3] The pressure measurements on this compound and the corresponding dimethylamine derivative were made under conditions closely similar to those used for the ammonia derivative. The relative values of the observed pressures at a given temperature may therefore be taken as a measure of the relative "volatility" of the addition compounds.

Discussion

The data pertaining to the relative strengths of ammonia and the three methylamines as determined with tri-*t*-butylboron as the reference acid are summarized in Table III. The numerals give the relative order of the amines, the strongest being indicated by 1, the next by 2, etc. The first of the two figures in each parenthesis following the numerals gives the mole fraction of the amine which combined with the reference acid in the competition experiments, the comparison being made against ammonia; the second figure gives the saturation pressure of the addition compound at 25° in mm. It is of interest that the correlation pointed out previously[2] between the relative stability and the magnitude of the saturation pressure values is further substantiated by the results of the present study.

TABLE III

RELATIVE BASE STRENGTH OF AMMONIA AND THE METHYLAMINES WITH TRI-*t*-BUTYLBORON

Ammonia	2 (1.00, 13.3)
Monomethylamine	1 (0.69, 9.1)
Dimethylamine	3 (.09, >200)
Trimethylamine	4 (.02, N. C.[a])

[a] No compound formed.

It is evident that with tri-*t*-butylboron as the reference acid, monomethylamine is a very slightly stronger base than ammonia, whereas dimethyl- and trimethylamine are considerably weaker. The order observed, $(CH_3)_3N < (CH_3)_2NH < NH_3 < CH_3NH_2$, is therefore that represented by curve E of Fig. 1. It follows that to obtain the order of base strength represented by curve F, it will be necessary to use for the reference acid an even more highly hindered acid than tri-*t*-butylboron.[4] However, it is apparent that the change in the relative strength of the methylamines observed with tri-*t*-butylboron is in close agreement with the predicted effect of F-strain on the order of the four bases (Fig. 1).

It is of interest to make some estimates of the magnitude of these strains from the available data, crude though such estimates must be. At 100° the dissociation constants for ammonia–trimethylboron and monomethylamine–trimethylboron differ by a factor of 130; at 0° the disparity between the two constants is even greater—they differ by a factor of 1000 (Table IV).

TABLE IV

DISSOCIATION DATA OF TRIMETHYLBORON ADDITION COMPOUNDS AT 0 AND 100°

Compound	$K_{100°}$	$K_{0°}$	$\Delta F_{0°}$
$NH_3:B(CH_3)_3$	4.6	5.2×10^{-3}	2840
$CH_3NH_2:B(CH_3)_3$	0.0350	5.8×10^{-6}	6530
$(CH_3)_2NH:B(CH_3)_3$	.0214	1.5×10^{-6}	7250
$(CH_3)_3N:B(CH_3)_3$	.472	7.8×10^{-5}	5120

From the results of the competition experiments on these amines, it may be estimated that at 0° the ratio of the dissociation constants of the corresponding addition compounds of tri-*t*-butylboron has been greatly reduced to a figure in the neighborhood of 4. This means that the F-strain between tri-*t*-butylboron and the methyl group in monomethylamine is sufficiently great to reduce the apparent strength of the amine to a point where it is comparable to that of ammonia and has decreased the work required to separate the amine from the boron compound by nearly 3700 calories per mole.

It is reasonable to assume that two methyl groups will have at least twice, and three methyl groups at least three times this effect on the free energy of dissociation. If tri-*t*-butylboron were as strong an acid as trimethylboron, the free energy of dissociation of dimethylamine-tri-*t*-butylboron could be estimated as −100 to −200 cal. per mole, and the corresponding trimethylamine derivative as −5000 cal. per mole.[5] However, since both the inductive effect and B-strain will reduce the strength of tri-*t*-butylboron as an acid relative to trimethylboron, the true values of the free energies of dissociation must be considerably lower than the figures given. In this way the low stability of dimethylamine-tri-*t*-butylboron and the non-existence of the trimethylamine derivative may be accounted for readily.

Acknowledgment.—The purchase and construction of the apparatus used in this investigation was made possible by a grant from the Penrose Fund of the American Philosophical Society. This assistance is gratefully acknowledged.

Summary

1. The relative order of base strength, $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$, observed with hydrogen acids and with trimethylboron is altered to $(CH_3)_3N < (CH_3)_2NH < NH_3 < CH_3NH_2$ with tri-*t*-butylboron as the reference acid.

2. This change in the order is in accord with the predicted effect of increased F-strain on the relative base strengths of ammonia and the methylamines.

3. In the course of this work, the addition compounds monomethylamine-tri-*t*-butylboron and dimethylamine-tri-*t*-butylboron were prepared and characterized.

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(4) Work on this phase of the problem is under way. However, it may be noted at this time that preliminary results indicate that the order represented by curve F is obtained by using certain highly hindered triarylborons as the reference acids.

(5) These estimates are based on the assumptions that the dissociation constants at 0° can be calculated from the dissociation data at higher temperatures and the ratios of the dissociation constants are not greatly altered by the change from the gaseous to the solid phase