[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Dissociation of the Addition Compounds of Trimethylboron with the Ethylamines; Configuration of the Ethylamines[1]

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In aqueous solution, *i. e.*, with the proton as the reference acid, the methylamines and the ethylamines exhibit similar behavior—an increase in strength with the first alkyl substituent, a further increase with the second, followed by a sharp decrease with the third[3]

$$NH_3 < CH_3NH_2 < (CH_3)_2NH \gg (CH_3)_3N$$
$$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH \gg (C_2H_5)_3N$$

The relative tendency of the amines to add hydrogen ion should correlate closely with their relative tendency to add trimethylboron.

$$R_3N: + H^+ \rightleftharpoons R_3N:H^+$$
$$R_3N: + B(CH_3)_3 \rightleftharpoons R_3N:B(CH_3)_3$$

No change in the order is observed in the methylamines[4] when trimethylboron is used as the reference acid in place of hydrogen ion. However, the ethylamines[5] show a marked alteration in sequence.

$$NH_3 < C_2H_5NH_2 > (C_2H_5)_2NH \gg (C_2H_5)_3N$$

The difference in the results obtained with the two reference acids has been ascribed to differences in their steric requirements.[6] This hypothesis receives substantiation from the further changes in sequence shown by these bases with the exceedingly bulky reference acid, tri-*t*-butylboron.[5,6]

$$NH_3 < CH_3NH_2 > (CH_3)_2NH \gg (CH_3)_3N$$
$$NH_3 > C_2H_5NH_2 \gg (C_2H_5)_2NH > (C_2H_5)_3N$$

These sequences were largely established with the aid of an expedient competitive method[6a] which is not entirely free from possible theoretical objections. Moreover, precise quantitative data are required for the development of a fully satisfactory theory of steric effects. For these reasons, it was decided to study the dissociation of the addition compounds of trimethylboron with the ethylamines by the precise technique described earlier.[7]

Discussion

The results are summarized in Table I together with some earlier data[4] on the dissociation of the corresponding derivatives of ammonia and the methylamines.

Ethylamine is a slightly stronger base than methylamine ($K_b = 4.7 \times 10^{-4}$ *versus* 4.4×10^{-4}).[3] The addition compound, ethylamine-trimethylboron, would therefore be expected to be slightly more stable than the corresponding derivative of methylamine. However, the opposite is observed: the dissociation constant at 100° for ethylamine-trimethylboron is 0.0705 as compared to the value 0.0350 for methylamine-trimethylboron. This reversal in the apparent strength of the two amines is attributed to the greater steric requirements of the ethyl group as compared to the methyl group.

TABLE I

SUMMARY OF DISSOCIATION DATA ON THE ADDITION COMPOUNDS OF TRIMETHYLBORON WITH AMMONIA, THE METHYLAMINES AND THE ETHYLAMINES[a]

Amine component	K_{100}	ΔF°_{100}	ΔH	ΔS
Ammonia	4.6	−1,134	13,750	39.9
Methylamine	0.0350	2,472	17,640	40.6
Dimethylamine	.0214	2,885	19,260	43.6
Trimethylamine	.472	557	17,620	45.7
Ethylamine	.0705	1,965	18,000	43.0
Diethylamine	1.22	− 147	16,310	44.1
Triethylamine	Too highly dissociated to be measured			

[a] These dissociation data were obtained by measuring the pressures of an equilibrium mixture, *e. g.*, $C_2H_5NH_2:B(CH_3)_3 \rightleftarrows C_2H_5NH_2 + B(CH_3)_3$, in which all of the reactants and products were gaseous.

The configuration of the ethyl group in such molecules as ethyl ether and diethyl ketone has been discussed by Stuart.[8] From the Kerr constants for these substances, he concludes that the preferred configurations are those in which the methyl groups are near the open positions of the oxygen atom and undergo but relatively minor vibrations from their equilibrium position. He attributes the stability of this configuration to attractive forces between the dipoles of the carbon-hydrogen bonds of the methyl groups and the dipole of the carbon-oxygen bonds of the ether or carbonyl linkages.

Similar attractive forces should be present in the ethylamine molecule. Assumption of a similar configuration by the ethyl group would place the methyl portion of this group in a position greatly to hinder the addition of the trimethylboron molecule (compare A and B, Fig. 1).[9] The

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[1] Acid-Base Studies in Gaseous Systems. IV. Paper no. XI in the series, Studies in Stereochemistry; for preceding paper, see THIS JOURNAL, **68**, 1137 (1947).

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[3] Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

[4] Brown, Bartholomay and Taylor, *ibid.*, **66**, 435 (1944).

[5] Brown, *ibid.*, **67**, 1452 (1945).

[6] (a) Brown, *ibid.*, **67**, 374 (1945); (b) **67**, 378 (1945).

[7] Brown, Taylor and Gerstein, *ibid.*, **66**, 431 (1944).

[8] Stuart, "Molekülstruktur," Julius Springer, Berlin, 1934, pp. 236–240.

[9] Note that in this configuration the methyl group is in the same relative position to the vacant position of the nitrogen atom as is the methyl group in α-picoline. In the latter substance, in which the position of the methyl group is fixed by the geometry of the molecule, the addition of trimethylboron is markedly hindered. Indeed, the heat of formation of the addition compound is reduced by some 6 to 8 kcal.; see Brown and Barbaras, THIS JOURNAL, **69**, 1137 (1947).

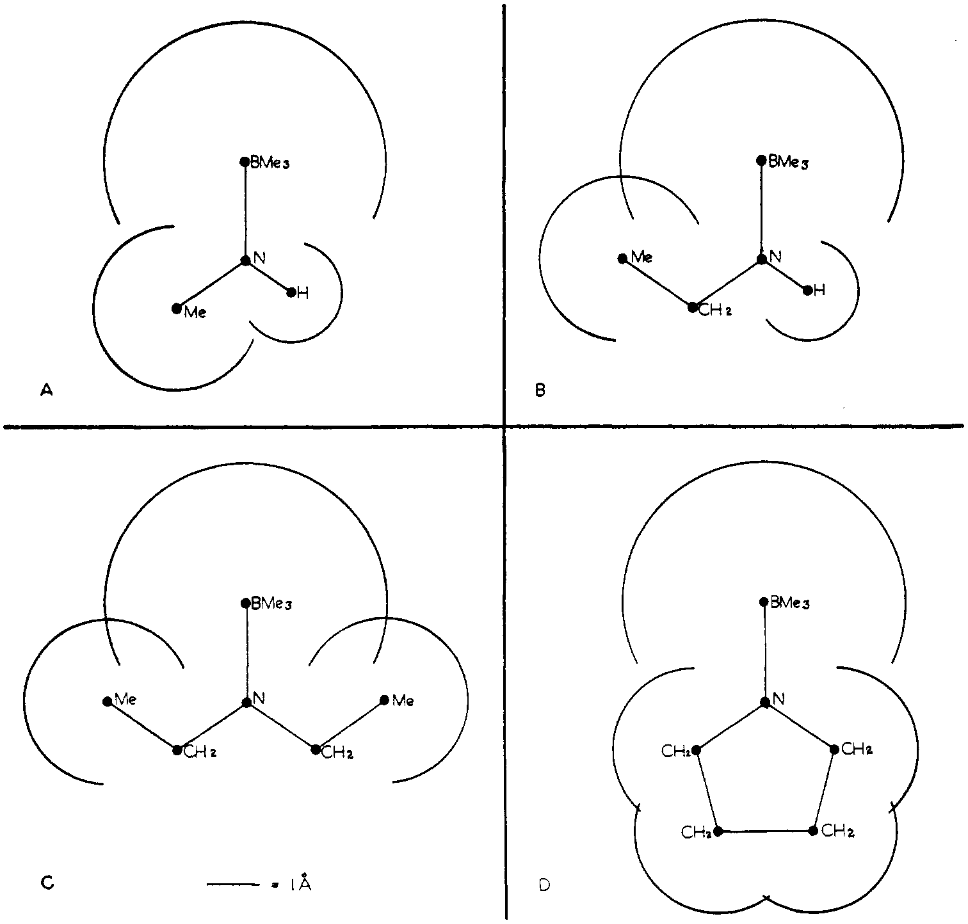

Fig. 1.—Schematic representation of molecular models. The values of the interatomic distances and van der Waals radii are those given by Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York. The van der Waals radii are reduced somewhat (25%) in order to show the steric effect more clearly: A, methylamine-trimethylboron; B, ethylamine-trimethylboron; C, diethylamine-trimethylboron; D, pyrrolidine-trimethylboron.

comparatively small decrease in the stability of the ethylamine addition compound over the corresponding methylamine derivative suggests that this configuration, though it may be preferred, is not much more stable than other possible configurations involving greater distances between the methyl group and the unshared electron pair of the nitrogen atom.

In ethylamine the ethyl group can probably rotate more or less freely with the carbon–nitrogen bond as axis. If it is assumed that in common with other molecules of this general type there are potential minima at angles of 120°, there are three stable configurations that can be assumed by the ethyl group. The first of these involves the close approach of the methyl group to the free electron pair of the nitrogen atom (Fig. 1,B); the second involves a rotation of the ethyl group about the carbon–nitrogen bond through an angle of 120°; the third involves a similar rotation in the opposite direction.

In the addition compound the first of these configurations is prohibited by the trimethylboron molecule. This leaves only the last two configurations as possible ones for the ethyl group. Such restriction of the motion of the ethyl group would be expected to lead to an increase in the entropy of dissociation. Such an increase is observed (Table I). It may therefore be suggested that the increased dissociation of the ethylamine addition compound is probably largely an entropy effect resulting from a conflict between the steric requirements of the trimethylboron molecule and the steric requirements of the ethyl group.

In contrast to the effect of the second alkyl group in dimethylamine (Table I), the second ethyl group in diethylamine further decreases the stability of the addition compound. Moreover, the decrease is large and markedly affects both the dissociation constant and the heat of dissociation.

In the addition compound formed from this amine, (Fig. 1,C) the arguments used earlier for ethylamine lead to the conclusion that the only possible configuration is that in which one ethyl group is rotated 120° in one direction from the nitrogen atom and the other is rotated 120° in the opposite direction. A rigid structure results in which the molecule possesses practically no freedom of motion and is under considerable strain. Relief of the strain would involve separation of the trimethylboron molecule and rotation of one or both of the ethyl groups into the space vacated. It is therefore not surprising that the addition compound exhibits such a low degree of stability and a heat of dissociation some 3000 cal. lower than the corresponding derivative of dimethylamine.

According to this argument, tying the ethyl groups back in such a way as to relieve the strain in the addition compound should result in a marked increase in its stability (Fig. 1,D). In effect this is accomplished in the cyclic imine, pyrrolidine, which forms an addition compound with trimethylboron of high stability, exceeding that of the dimethylamine derivative.[10]

In triethylamine-trimethylboron, two of the ethyl groups can be accommodated in the manner suggested for the diethylamine derivative. However, the only possible position for the third ethyl group is that involving projection of the methyl portion of the group into the region immediately adjacent to the nitrogen atom (Fig. 2). It must be concluded that one methyl group is more or less rigidly fixed in this position which in its general relationship to the nitrogen atom is quite similar to the position of the methyl group of α-picoline to the ring nitrogen atom (Fig. 2). It is therefore not surprising that the stabilities of the addition compounds of triethylamine and α-picoline are both too low for these derivatives to be studied by the present technique. However, the magnitude of the strain introduced by accommodating the third ethyl group of triethylamine in the position described may be judged from the fact that the heat of dissociation of the trimethylboron addition compound is definitely less than 13 kcal. and probably less than 10 kcal.,[11] instead of a value in the neighborhood of 18-19 kcal. which might have been anticipated from the behavior of trimethylamine and a comparison of the base dissociation constants of the two tertiary amines.

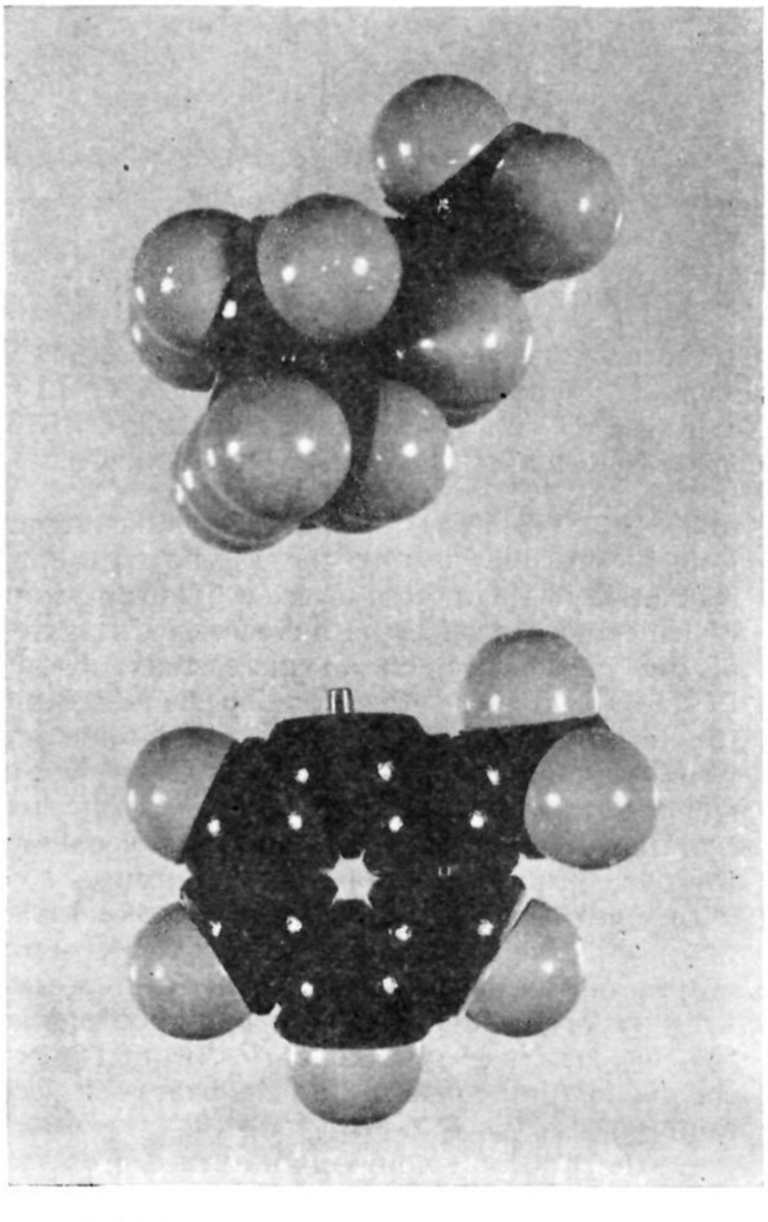

Fig. 2.—Molecular models: above, triethylamine; below, 2-picoline.

It should be pointed out that the postulated position of the third ethyl group in triethylamine should not hinder the addition of a proton more than such addition is hindered by the methyl group in α-picoline.[9] It is the much larger steric requirements of the trimethylboron molecule which result in marked strain and increased dissociation. In displacement reactions of the S_N2 type, particularly in cases where the other reactant has large steric requirements, triethylamine should act as a typical "hindered" amine.[12]

Finally, it is of interest to note that the data fully support the earlier conclusions as to the relative strengths of ammonia and the ethylamines[5] which were based on the competition method. The close agreement suggests that with reasonable caution the competition method can serve to give reliable qualitative information on the relative strengths of a series of bases.

Results[13]

Ethylamine-trimethylboron, $C_2H_5NH_2{:}B(CH_3)_3$.—The addition compound, prepared by combining equimolar quantities of ethylamine and trimethylboron, is a white solid which melts sharply at 24.5°. It is slightly less volatile than methylamine-trimethylboron[4] at lower temperatures, but above 80° it becomes more volatile, probably because it is more highly dissociated. The saturation pressure data over the temperature range from 0 to 81.0° are given in Table II and are represented graphically in Fig. 3-A.

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[10] Unpublished work with Dr. Melvin Gerstein.

[11] A calorimetric method is being developed for the study of the heats of dissociation of the less stable addition compounds which cannot be handled by the present technique.

[12] Studies of the behavior of triethylamine and related bases in displacement reactions are under way at this University (with Mr. Nelson Eldred).

[13] The preparation and purification of the various intermediates and the experimental techniques are described in previous publications in this series. See particularly references **5**, 6 and 7. For a brief outline of the experimental method see accompanying paper THIS JOURNAL, **69**, 1137 (1947).

TABLE II

SATURATION PRESSURES OF ETHYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	9.7	19.9	24.4	29.8	39.7
Press., mm.	0.10	0.23	0.64	0.95	1.53	3.09
Temp., °C.	49.4	60.7	66.2	71.4	75.0	81.0
Press., mm.	6.21	13.3	18.7	25.5	31.6	43.1

The saturation pressures of the solid describe a line whose slope is distinctly different from that of the liquid. However, the range of temperature is so short and the values of the saturation pressures are so low that no attempt has been made to represent the solid–vapor data by an equation. Above the melting point the saturation data are represented by the equation

$$\log P = -(3152/T) + 10.568$$

The extrapolated "boiling point" is 137°.

The dissociation of the addition compound was studied over the temperature range from 91.0 to 131.0°. The dissociation data are given in Table III and represented graphically in Fig. 3-B. The values for the dissociation constants are represented by the equation

$$\log K_p = -(3942/T) + 9.408$$

The value of the dissociation constant at 100° is 0.0695 and the calculated heat of dissociation is 18.03 ± 0.2 kcal.

In a duplicate determination made over the temperature range from 92.3 to 135°, the values of the dissociation constants are represented by the equation

$$\log K_p = -(3929/T) + 9.385$$

In this run the value of the dissociation constant at 100° is 0.0716 and the calculated heat of dissociation is 17.97 ± 0.2 kcal. The average values for these two determinations are listed in Table I.

TABLE III

DISSOCIATION DATA FOR ETHYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obs.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant K (atm.)
91.0	58.80	37.41	0.5718	0.0376
94.9	61.13	37.81	.6168	.0494
95.6	61.57	37.88	.6254	.0520
99.9	64.04	38.32	.6712	.0691
105.0	66.87	38.85	.7212	.0954
110.1	69.61	39.37	.7681	.132
115.5	72.26	39.93	.8097	.181
120.8	74.78	40.47	.8478	.251
125.6	76.79	40.96	.8748	.329
131.0	78.95	41.52	.9015	.451

[a] Pressure of ethylamine and of trimethylboron in the dissociation tensimeters was 28.06 mm. (calculated to 0°).

Diethylamine-trimethylboron, $(C_2H_5)_2NH:B(CH_3)_3$.—The addition compound, synthesized by the combination of equimolar quantities of the two components, is a white solid which melts from 26–28°. The relatively wide range in melting point probably results from the appreciable dissociation of the complex at the melting point. Its relatively high saturation pressure, listed in Table IV and represented graphically in Fig. 4-A, also is to be attributed to its comparatively low stability. Above the melting point, these data are represented by the equation

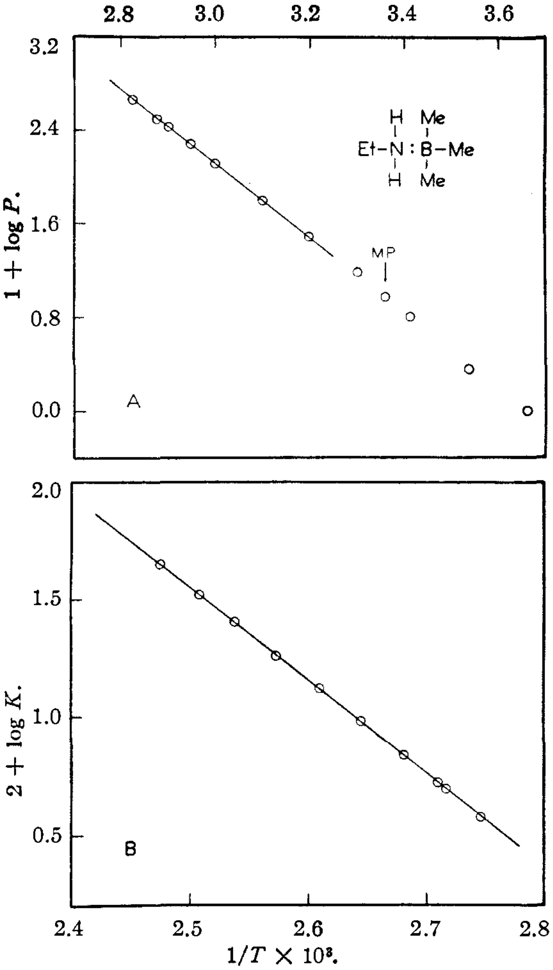

Fig. 3.—Ethylamine-trimethylboron: A, saturation pressure data; B, dissociation data.

$$\log p = -(3111/T) + 10.913$$

The extrapolated "boiling point" is 114°, some 33° below the "boiling point" of the corresponding ethylamine derivative, a substance of considerably lower molecular weight.

TABLE IV

SATURATION PRESSURES OF DIETHYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	5.5	10.4	15.1	19.6	24.8	28.9
Press., mm.	0.27	0.42	0.69	1.13	1.67	2.81	4.00
Temp., °C.	35.0	40.3	46.1	51.0	54.1	60.7	66.7
Press., mm.	6.46	9.67	14.8	20.7	24.9	39.2	55.1

The dissociation of the compound was studied over the temperature range from 71.0 to 115.3°. The data are listed in Table V and represented

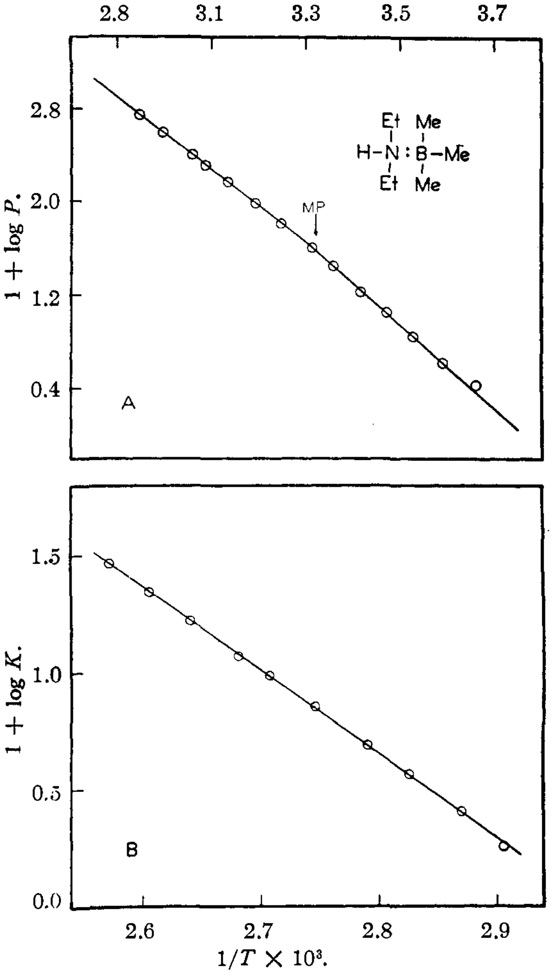

Fig. 4.—Diethylamine-trimethylboron: A, saturation pressure data; B, dissociation data.

graphically in Fig. 4-B. The values of the constants are given by the equation

$$\log K_p = -(3580/T) + 9.677$$

At 100° the dissociation constant is 1.21; the calculated heat of dissociation is 16.37 ± 0.2 kcal.

A duplicate determination over the range from 60.5 to 111.3° yielded values of the dissociation constants which are represented by the equation

$$\log K_p = -(3551/T) + 9.609$$

with a value of 1.23 for the dissociation constant at 100° and 16.24 ± 0.2 kcal. for the calculated heat of dissociation.

Average values for these quantities are given in Table I.

TABLE V

DISSOCIATION DATA FOR DIETHYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
71.0	60.08	32.78	0.8328	0.179
75.3	62.03	33.19	.8689	.251
80.8	64.10	33.72	.9009	.364
85.2	65.59	34.14	.9212	.484
91.1	67.42	34.70	.9429	.711
96.2	68.83	35.19	.9559	.960
99.9	69.76	35.54	.9628	1.17
105.5	71.17	36.07	.9731	1.67
110.5	72.34	36.55	.9792	2.21
115.3	73.40	37.00	.9838	2.90

[a] Pressure of diethylamine and of trimethylboron in the dissociation tensimeters was 26.02 mm. (calculated to 0°).

Triethylamine-trimethylboron, $(C_2H_5)_3N:B(CH_3)_3$.—Equimolar quantities of triethylamine and trimethylboron combine at −80° to form a solid addition compound which is quite unstable and melts with considerable dissociation in the neighborhood of −18 to −13°. Both the melting point and the saturation pressures depend upon the relative size of the sample and volume of the container, an indication of a high degree of dissociation even at these low temperatures. At room temperature a sample with a total pressure of 33 mm. was at least 97% dissociated[14]; at 100° it is practically 100% dissociated. It was therefore impossible to obtain data which could be used for the calculation of the heat of dissociation.

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Summary

1. The dissociation in the vapor phase of the addition compounds of trimethylboron with ethylamine, diethylamine and triethylamine has been studied.

2. Values of ΔH, ΔF and ΔS for the dissociation of the ethyl- and diethylamine derivatives have been determined. Triethylamine-trimethylboron is too highly dissociated to be studied by the technique used.

3. The observed changes in the magnitude of ΔH, ΔF and ΔS are attributed to the conflicting steric requirements of the trimethylboron molecule and the ethyl groups of the amines.

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[14] High van der Waals deviations at this temperature suggest that the compound is probably nearer 100% dissociated under these conditions.