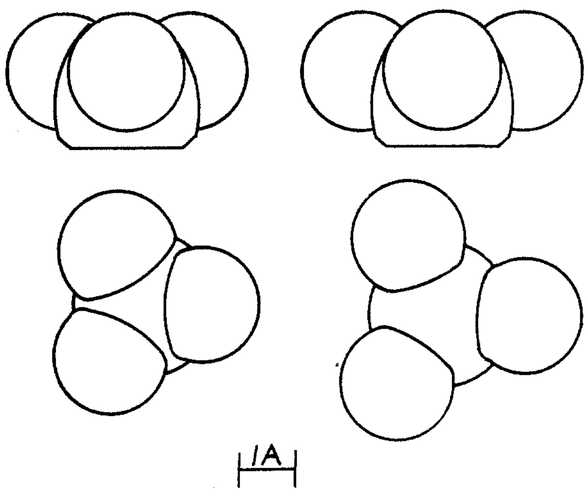

Fig. 6.—Molecular models: borine (left) and boron trifluoride (right).

tolyltrimethylammonium ion (Fig. 5F) is reported[43] to be 21.1 kcal., as compared with the value 15.2 for dimethylaniline. In view of our results, the difference 5.9 kcal. appears somewhat high. However, the aniline bases involve the possibility of an additional complication—steric inhibition of resonance. The precise relationships in these bases between strain in the transition state and increase in energy of activation must await further study.

Finally, it is significant that *o-t*-butylaniline is quite weak in water, pK_a being 3.78 *versus* 4.58 for aniline itself.[44] That is to say, the strained homomorph, *o-t*-butylanilinium ion (Fig. 5C) exhibits an enhanced tendency to transfer its proton to water.

Conclusions.—From this survey it appears that strains of the following magnitudes may be assigned to the model homomorphs:

Hemimellitene	1–2 kcal./mole
o-t-Butyltoluene	4–6
Di-*t*-butylmethane	5.4
2,6-Dimethyl-*t*-butylbenzene	≥ 17
o-Di-*t*-butylbenzene	≥ 25

Completion of present studies[42] on the heats of reaction of diborane and trimethylboron with pyridine bases will permit a more precise assignment of strains to the homomorphs of hemimellitene and *o-t*-butyltoluene. These strains have a pronounced effect on the homomorphs of these hydrocarbons. With the strains of lower magnitude, their effects are observed as decreased ease of formation of the compounds, decreased rates of reactions leading to the formation of the strained system, increased rates of reactions where the reaction leads to a decrease in strain, and decreased base strengths, both toward Lewis acids and hydrogen ion. The strains in the upper range appear sufficiently great as to prohibit practically all reactions which lead to the formation of the strained systems. Finally, it appears that the concept of homomorphs permits a useful correlation between the chemical properties of molecules of widely different functions, but of similar sizes and shapes.

Acknowledgment.—We wish to acknowledge the financial assistance of the Standard Oil Company (Indiana), the Purdue Research Foundation and the Atomic Energy Commission for the support of graduate fellowships which made these studies possible.

Lafayette, Indiana

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[43] D. P. Evans, H. B. Watson and R. Williams, *J. Chem. Soc.*, 1345, 1348 (1939).

[44] Private communication from Dr. B. M. Wepster of Delft Technical University, Delft, The Netherlands.

[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

Dissociation of the Addition Compounds of Trimethylboron with Branched-Chain Primary Amines; the Effects of Chain-Branching[1,2]

By Herbert C. Brown[3] and Geraldine K. Barbaras

Received February 28, 1952

The addition compounds of trimethylboron with isopropyl-, *s*-butyl- and *t*-butylamines were prepared and characterized and their dissociation in the gas phase was examined. At 100° the dissociation constants for the reaction, $RNH_2{:}BMe_3 \rightleftharpoons RNH_2 + BMe_3$, are: R = H, 4.62 atm.; Me, 0.0360; Et, 0.0705; *i*-Pr, 0.368; *s*-Bu, 0.373; *t*-Bu, 9.46. The heats of dissociation show a marked decrease with chain-branching, the effect being especially pronounced in the case of the *t*-butylamine derivative: H, 13.75 kcal.; Me, 17.6; Et, 18.0; *i*-Pr, 17.4; *s*-Bu, 17.3; *t*-Bu, 13.0. Since the *n*-Bu compound has a heat of dissociation of 18.4 kcal., a strain of 5.4 kcal. is assigned to structures related to *t*-butylamine-trimethylboron (homomorphs of di-*t*-butylmethane).

Introduction

Previous qualitative experiments had shown that chain-branching in the alkyl group of the amine leads to a decrease in the stability of addition compounds with trimethylboron.[4] The decrease in stability was ascribed to steric strain arising from the larger steric requirements of the branched alkyl group. As part of our program to obtain quantitative data for the effect of structure on the stability of molecular addition compounds, it was decided to study the dissociation of the addition compounds of such branched-chain amines. Accordingly, the addition compounds of trimethylboron with isopropyl-, *s*-butyl- and *t*-butylamines were prepared and their dissociation in the gas phase studied by the techniques previously described.[5]

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[1] Acid–Base Studies in Gaseous Systems. IX. Strained Homomorphs. II. A preliminary communication of a portion of these results was published in *J. Chem. Phys.*, **14**, 114 (1946).

[2] Based upon a thesis submitted by Geraldine K. Barbaras to the Faculty of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Department of Chemistry, Purdue University.

[4] H. C. Brown, This Journal, **67**, 1452 (1945); H. C. Brown and H. Pearsall, *ibid.*, **67**, 1765 (1945).

[5] H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

Results

Isopropylamine-trimethylboron, $(CH_3)_2CHNH_2:B(CH_3)_3$.—The addition compound, isopropylamine–trimethylboron, was synthesized by the union of equal molar quantities of the two components in the high vacuum apparatus. The product is a colorless liquid at room temperature. It solidifies at low temperatures to a white crystalline solid, which melts sharply at 8.7°. The saturation pressures were studied over the temperature range from 0 to 69.8°. The data, summarized in Table I, are satisfactorily represented by the equation

$$\log P_l = -\frac{3074}{T} + 10.640$$

The "boiling point," obtained by extrapolation of the saturation pressure equation to 760 mm., is 123°. It is of interest that the compound is considerably more volatile than the corresponding derivative with ethylamine (b.p. 137°), in spite of the lower molecular weight of the latter.

TABLE I

SATURATION PRESSURES OF ISOPROPYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	10.0	15.0	19.9	25.4
Press., mm.	0.21	0.57	0.91	1.42	2.20
Temp., °C.	30.6	40.9	49.5	59.8	69.8
Press., mm.	3.32	7.12	13.0	25.9	47.9

The dissociation of the addition compound was studied over the temperature range of 75.2 to 115.2° by the "method of approximations."[5] The dissociation data are listed in Table II and shown graphically in Fig. 1; they can be represented by the equation

$$\log K_p = -\frac{3810}{T} + 9.774$$

TABLE II

DISSOCIATION DATA FOR ISOPROPYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant, K(atm.)
75.2	47.39	27.51	0.7226	0.0682
85.0	51.36	28.28	.8160	.135
90.4	53.37	28.71	.8589	.198
95.1	54.88	29.08	.8872	.267
100.9	56.58	29.54	.9154	.385
105.6	57.90	29.92	.9340	.530
110.0	58.91	30.26	.9470	.671
115.2	60.11	30.67	.9599	.928

[a] Pressure of isopropylamine and of trimethylboron was estimated by the method of approximations as 26.84 mm. at 0.0°.

TABLE III

SUMMARY OF THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF ISOPROPYLAMINE-TRIMETHYLBORON

Detmn.	K_{100}, atm.	ΔF^0_{100}, cal.	ΔH, kcal.	ΔS^0, e.u.
1[a]	0.366	745	17.42	44.7
2	.375	727	17.34	44.5
3	.376	743	17.41	44.7
4	.366	745	17.51	44.7
Mean values	.368	740	17.42	44.7

[a] Experimental data in Table II.

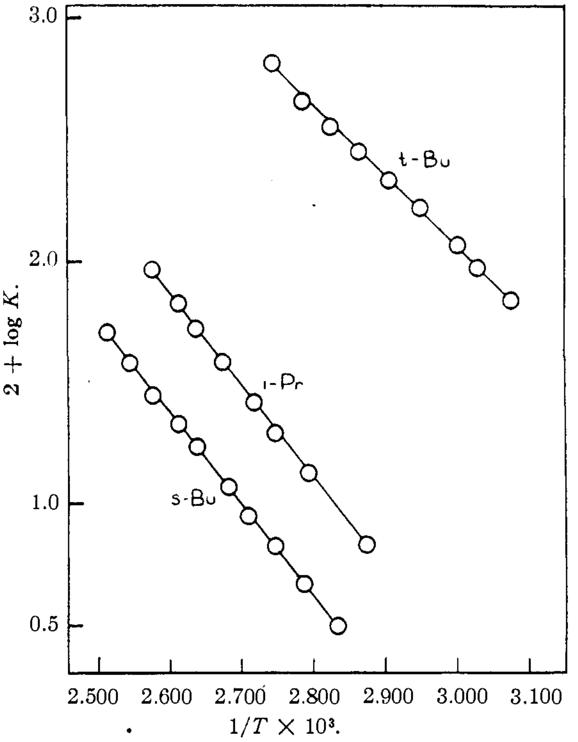

Fig. 1.—Dissociation data for trimethylboron addition compounds of branched-chain primary amines (for s-$BuNH_2:BMe_3$ read 1.5 + log K for ordinate).

Results of additional determinations are summarized in Table III. It is of interest that the heat of dissociation, 17.42 kcal., is 0.6 kcal. smaller than that for the ethylamine derivative.

***s*-Butylamine-trimethylboron,** $(C_2H_5)(CH_3)CHNH_2:B(CH_3)_3$.—The addition compound *s*-butylamine-trimethylboron has not been previously prepared. It is a colorless liquid at room temperature which melts at −7.0°. The vapor pressures were studied over the temperature range from 0° to 70.3°. The data, listed in Table IV, are represented by the equation

$$\log P_l = -\frac{3204}{T} + 10.866$$

The calculated "boiling point" is 128°.

TABLE IV

SATURATION PRESSURES OF *s*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	20.0	27.2	40.2	49.1	58.9	70.3
Press., mm.	0.14	0.86	1.58	4.36	8.38	16.5	34.3

The dissociation of the addition compound was studied over the temperature range of 79.9 to 125.2° by the "method of approximations." The data are given in Table V and Fig. 1; they can be represented by the equation

$$\log K_p = -\frac{3780}{T} + 9.701$$

Thermodynamic constants for this and two other studies are reported in Table VI. The heat of dissociation, 17.26, is only slightly lower than the value for the isopropyl compound,

TABLE V

DISSOCIATION DATA FOR *s*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm Obsd.	Pressure, mm Calcd.[a]	Degree of dissociation, α	Dissociation constant K(atm.)
79.9	48.52	27.27	0.7792	0.0987
85.6	50.66	27.71	.8282	.146
90.6	52.41	28.10	.8651	.205
95.6	53.96	28.49	.8940	.283
100.0	55.22	28.83	.9154	.376
106.1	56.77	29.30	.9375	.542
110.0	57.67	29.60	.9483	.678
114.5	58.66	29.94	.9592	.889
120.0	59.80	30.37	.9690	1.211
125.2	60.81	30.77	.9763	1.630

[a] Pressure of *s*-butylamine and of trimethylboron was estimated by the method of approximations as 21.10 mm. at 0.0°.

TABLE VI

SUMMARY OF THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF *s*-BUTYLAMINE-TRIMETHYLBORON

Detmn. no	K_{100}, atm.	ΔF^0_{100}, cal.	ΔH, kcal.	ΔS^0, e.u.
1[a]	0.374	729	17.29	44.4
2	.371	735	17.30	44.4
3	.373	731	17.20	44.2
Mean values	.373	732	17.26	44.3

[a] Experimental data in Table V.

***t*-Butylamine-trimethylboron,** $(CH_3)_3CNH_2:B(CH_3)_3$.—The addition compound derived from *t*-butylamine is by far the most volatile addition compound of the primary aliphatic amines. It is a colorless liquid at room temperature which melts at 19.1–19.5°. This melting point was observed in a sealed tube with very small vapor space (2 ml.). When the melting point was observed with the same sample in the dissociation tensimeter (380 ml.), the compound liquified at 17.1°. The melting point, calculated from the vapor pressure data for the solid and liquid (Table VII), is 16.7°. The discrepancy is probably the result of the high instability of the addition compound and the resulting high vapor pressure, 7.15 mm., at the melting point.

TABLE VII

SATURATION PRESSURES OF *t*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	5.0	11.1	17.1	20.0
Press., mm.	1.38	2.30	4.20	7.34	9.31
Temp., °C.	25.4	30.6	33.8	40.3	46.0
Press., mm.	14.3	20.5	26.0	40.6	57.4

The saturation pressures of the solid are represented by the equation

$$\log P_s = -\frac{3384}{T} + 12.534$$

and those for the liquid by the equation

$$\log P_l = -\frac{2915}{T} + 10.915$$

The calculated "boiling point" is 89.7°.

The dissociation of the addition compound was studied over the temperature range from 51.4° to 91.3°. The data, in Table VIII and Fig. 1, are represented by the equation

$$\log K_p = -\frac{2850}{T} + 8.618$$

TABLE VIII

DISSOCIATION DATA FOR *t*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation α	Dissociation constant K(atm.)
51.4	60.27	30.95	0.9470	0.690
56.6	61.63	31.45	.9595	0.940
60.2	62.52	31.79	.9664	1.162
66.2	63.95	32.36	.9759	1.687
70.6	64.94	32.78	.9809	2.166
75.8	66.06	33.28	.9849	2.812
80.8	67.11	33.76	.9881	3.644
86.1	68.19	34.26	.9904	4.579
91.3	69.27	34.76	.9930	6.442

[a] The pressure of *t*-butylamine and of trimethylboron calculated by the method of approximations was 26.05 mm. at 0.0°.

Thermodynamic constants derived from this and additional studies are reported in Table IX. The heat of dissociation, 13.0 kcal., makes this addition compound less stable than any of the other related compounds of the primary amines which have been studied and even less stable than ammonia-trimethylboron itself.

TABLE IX

SUMMARY OF THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF *t*-BUTYLAMINE-TRIMETHYLBORON

Detmn.	K_{100}, atm.	ΔF^0_{100}, cal.	ΔH, kcal.	ΔS^0, e.u.
1[a]	9.56	−1673	13.03	39.4
2	9.64	−1680	12.92	39.1
3	9.16	−1641	13.02	39.3
Mean values	9.46	−1665	12.99	39.3

[a] Experimental data in Table VIII.

Discussion

The thermodynamic constants for the dissociation of the addition compounds of trimethylboron with the branched-chain primary amines are summarized in Table X along with pertinent data for several simpler amines.[6,7]

TABLE X

SUMMARY OF DISSOCIATION DATA OF COMPOUNDS $RNH_2:B(CH_3)_3$

R	K_{100}, atm.	ΔF^0_{100}, cal.	ΔH, kcal.	ΔS^0, e.u.
Hydrogen	4.62	−1134	13.75	39.9
Methyl	.0360	2463	17.62	40.6
Ethyl	.0705	7965	18.00	43.0
Isopropyl	.368	740	17.42	44.7
s-Butyl	.373	732	17.26	44.3
t-Butyl	9.46	−1665	12.99	39.3

If we examine the free energies of dissociation for the series: ammonia, methylamine, ethylamine, isopropylamine and *t*-butylamine, we observe a very sharp increase as the hydrogen is replaced by a methyl group, and then an even greater decrease as the group becomes larger and larger (Fig. 2). Such behavior points to the operation of at least two conflicting factors, presumably the inductive and the steric effects. It is noteworthy that the first and second replacements of hydrogen

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(6) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

(7) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).

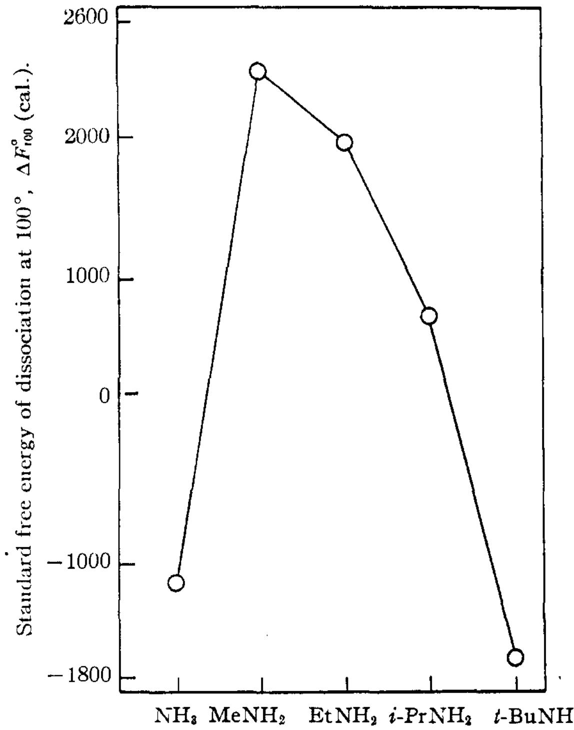

Fig. 2.—Effect of chain branching on the free energy of dissociation of the addition compounds, $RNH_2{:}BMe_3$.

atoms in the methyl group of methylamine produce only minor decreases in stability. The third methyl group causes a decrease in the heat of dissociation from 17–18 kcal. to 13.0 kcal., even lower than for ammonia itself. One can therefore conclude that in this compound steric strains must be larger than the inductive effect of the alkyl group.

The heat of dissociation of *n*-butylamine-trimethylboron is 18.47 kcal.[8] If it is assumed that the inductive effect of the *t*-butyl and *n*-butyl groups are not significantly different,[9] the strain in *t*-butylamine-trimethylboron is 5.4 kcal.

The molecular structure of *t*-butylamine-trimethylboron is closely related to that of di-*t*-butylmethane, di-*t*-butyl ether, di-*t*-butylamine, etc. (Fig. 3).[10] Therefore it is possible to predict that the strains in these related compounds will also be in the neighborhood of 5.4 kcal. and should markedly affect their chemistry.[10]

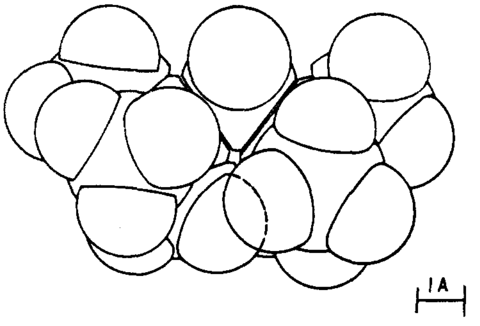

Fig. 3.—Molecular model of *t*-butylamine-trimethylboron.

Finally it is of interest to point out that we have now determined precise dissociation data for all of the amines in the four series—methyl, ethyl, isopropyl and *t*-butyl—which are sufficiently stable to be examined. The results are shown in Fig. 4. The effect of the increasing steric requirements of the alkyl group on the relative base strength of each member of a particular series is apparent.

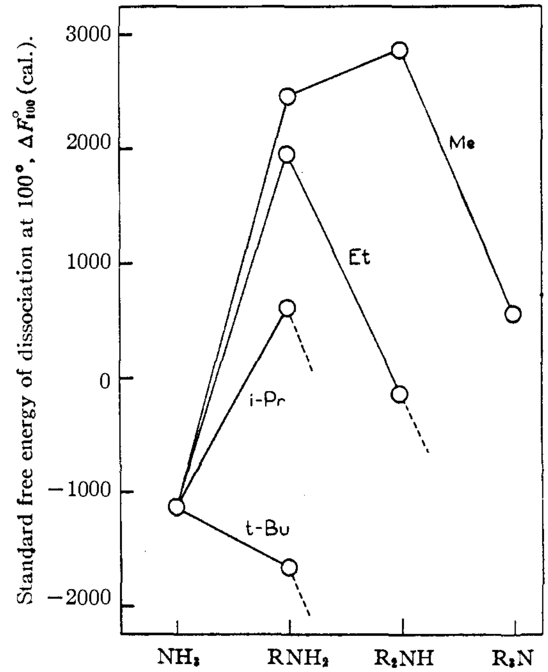

Fig. 4.—Free energies of dissociation at 100° of the amine series: methyl, ethyl, isopropyl and *t*-butyl.

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[8] H. C. Brown, M. D. Taylor and S. Sujishi, THIS JOURNAL, **73**, 2464 (1951).

[9] The base strengths of the two amines in aqueous solution are quite similar: pK_A 10.61 (25°) for *n*-butylamine, 10.82 (16°) for *t*-butylamine: N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3473 (1932); G. Vexlearschi, *Compt. rend.*, **228**, 1655 (1949).

[10] The term "homomorph" is proposed for compounds of similar sizes and shapes: H. C. Brown, *et al.*, THIS JOURNAL, **75**, 1 (1953).