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

Dissociation of the Addition Compounds of Trimethylboron with the Normal Primary Aliphatic Amines; the Straight-chain Anomaly[1]

BY HERBERT C. BROWN, MODDIE D. TAYLOR[2] AND SEI SUJISHI[3]

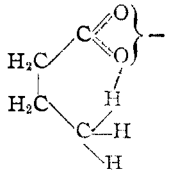
The addition compounds of trimethylboron with *n*-propyl-, *n*-butyl-, *n*-amyl- and *n*-hexylamine were prepared and characterized, and their dissociation in the gas phase was studied. At 100° the dissociation constants for the reaction, $RNH_2{:}BMe_3 = RNH_2 + BMe_3$, are: R = H, 4.62 atm.; Me, 0.0360; Et, 0.0705; *n*-Pr, 0.0598; *n*-Bu, 0.0470; *n*-Am, 0.0415; *n*-Hex, 0.0390. The heat of dissociation increases fairly regularly with chain length to a limit of approximately 18.5 kcal.: R = H, 13.75 kcal.; Me, 17.62; Et, 18.00; *n*-Pr, 18.14; *n*-Bu, 18.41; *n*-Am, 18.71; *n*-Hex, 18.53. Thus the heats of dissociation show no major irregularity, although the dissociation constants show a marked irregularity for ethylamine. The irregularity is attributed to an entropy effect arising from restricted rotation of the ethyl and longer groups in the addition compounds, a consequence of the conflicting steric requirements of the ethyl and trimethylboron groups. In the series of normal carboxylic acids in aqueous solution the ionization constant for *n*-butyric acid exhibits a similar abnormality. Moreover, in the series of aliphatic amines, the ionization constant of *n*-propylamine is also irregular. It is suggested that the explanation proposed for the behavior of the addition compound in the gas phase may also be applicable to the normal aliphatic acids and bases in aqueous systems.

Introduction

In an homologous series lengthening of the carbon chain is usually considered to result in a fairly regular change in chemical behavior, with a rapid approach to an asymptotic limit. However, examination of rate and equilibrium data suggests the possible existence of a fairly general irregularity in the neighborhood of the 3- to 4-carbon atom chain derivative. This phenomenon has been discussed in the case of the aliphatic carboxylic acids,[4] but attention does not appear to have been directed previously to the generality of the effect.

In the normal aliphatic acids, it is observed[4] that acetic acid is considerably weaker than formic acid, a result which is attributed to the inductive affect of the methyl groups. Propionic is still weaker, a fact which can also be justified in terms of the inductive effect. Butyric acid, however, is stronger than propionic, while the higher acids decrease in strength in a regular manner with increasing length of the chain (Fig. 1-A).

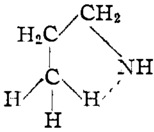
Dippy[4] has suggested that the abnormal increase in strength noted in butyric acid is to be attributed to hydrogen bonding. Such hydrogen bonding, presumably most effective in the anion (I), stabilizes the anion and results in an increase in the ionization constant.



I

The normal primary aliphatic amines exhibit a similar phenomenon. The data (Fig. 1-B) clearly show that the base strength rises in the series ammonia, methylamine and ethylamine, but drops with *n*-propylamine.[5]

Here also the weakness of *n*-propylamine might be attributed to hydrogen bonding (II) and the resulting increased stability of the amine relative to the ammonium ion.



II

However, in this case the geometry of the molecule is much less favorable for hydrogen bonding to be an important contributing factor.

Indeed, it is doubtful that hydrogen bonding, involving a hydrogen atom of a hydrocarbon chain, can ever be a significant factor in aqueous solution, where the carbon–hydrogen bond is in direct competition with the tremendously greater hydrogen-bonding tendencies of water molecules in the very high concentrations afforded by aqueous solutions.

The effect is a relatively small one. It therefore seemed desirable to observe whether it persists in the gas phase, away from the complexities of solvent effects. Accordingly, the addition compounds of trimethylboron with *n*-propyl-, *n*-butyl-, *n*-amyl- and *n*-hexylamine were synthesized and their dissociation in the gas phase studied.

$$RNH_2{:}BMe_3(g) \rightleftarrows RNH_2(g) + BMe_3(g)$$

The techniques previously described[6] were used.

The results, together with earlier data on the corresponding compounds of methylamine[7] and ethylamine,[8] permit a critical examination of the phenomenon and suggest a reasonable explanation which does not involve hydrogen bonding.

Results

n-Propylamine-trimethylboron, n-$C_3H_7NH_2{:}B(CH_3)_3$.—The addition compound, *n*-propylamine-trimethylboron, was synthesized by the combination of equal molar quantities of the two components in the high vacuum apparatus. The product is a liquid at room temperature, but solidifies at low

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(1) Acid-base Studies in Gaseous Systems. VIII.

(2) Department of Chemistry, Howard University, Washington, D. C.

(3) Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois.

(4) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938); *Chem. Revs.*, **25**, 151 (1939).

(5) N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932); C. W. Hoerr, M. R. McCorkle and A. W. Ralston, *ibid.*, **65**, 328 (1943).

(6) (a) H. C. Brown, M. D. Taylor and M. Gerstein, *ibid.*, **66**, 431 (1944); (b) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(7) H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944).

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

temperature to a white solid which melts at −5.5 to −6.0°. The addition compound is less volatile than the corresponding derivative formed by ethylamine. Saturation pressure data are listed in Table I. A graph of the data shows a slight curvature in the lower range but becomes linear above 40°. The linear portion of the curve is represented by the equation: $\log P = -3187/T + 10.479$. The "boiling point," obtained by extrapolation of the saturation pressure equation to 760 mm., is 146°.

TABLE I

SATURATION PRESSURES OF *n*-PROPYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	5.5	10.7	14.9	19.8	25.1	34.7
Press., mm.	0.09	0.12	0.18	0.24	0.37	0.60	1.26
Temp., °C.	39.9	49.6	60.8	71.1	80.7	85.8	90.2
Press., mm.	1.94	3.98	8.49	16.5	29.5	39.2	50.1

The dissociation of the compound was studied by the method of matched samples[6a] over the temperature range from 94.9 to 134.6°. The data are summarized in Table II. It is of interest that *n*-propylamine-trimethylboron is less dissociated than the ethylamine addition compound, although the latter is more highly dissociated than the methylamine derivative.

TABLE II

DISSOCIATION DATA FOR *n*-PROPYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation α	Dissociation constant K (atm.)
94.9	59.74	37.65	0.5867	0.0413
99.0	62.30	38.07	.6365	.0558
104.6	65.47	38.64	.6944	.0802
110.0	68.54	39.19	.7489	.115
114.6	70.84	39.66	.7862	.151
120.4	73.54	40.26	.8266	.209
125.6	75.91	40.79	.8610	.286
130.5	77.91	41.29	.8870	.377
134.6	79.47	41.71	.9053	.475

[a] The addition compound was synthesized in the dissociation tensimeter from equimolar amounts of trimethylboron and *n*-propylamine, measured as gases at temperatures where gas deviations are negligible. The pressure of the two substances, calculated to 0°, was 27.94 mm. The "Calcd. Pressure" column gives the pressure for the addition compound calculated on the assumption of no dissociation ($27.94 \times T/273.1$). The degree of dissociation, α, is readily calculated from this value and the observed pressure.

The change of the dissociation constants with temperature can be reproduced by the equation: $\log K_p = -3952/T + 9.371$. The dissociation constant at 100.0° is 0.0603 atm., and the heat of dissociation is 18.08 ± 0.2 kcal.

***n*-Butylamine-trimethylboron,** $n\text{-}C_4H_9NH_2{:}B(CH_3)_3$.—*n*-Butylamine-trimethylboron, like the corresponding *n*-propylamine derivative, is a liquid at room temperature and exhibits a melting point at 3.4–3.7°. Saturation pressure data are listed in Table III.

TABLE III

SATURATION PRESSURES OF *n*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	0.0	10.1	19.8	30.4	41.0	49.7	59.3
Press., mm.	0.03	0.07	0.22	0.43	1.10	2.17	4.24
Temp., °C.	70.2	79.8	86.3	91.2	94.9	97.6	99.0
Press., mm.	8.99	16.7	24.3	32.3	39.6	46.2	49.4

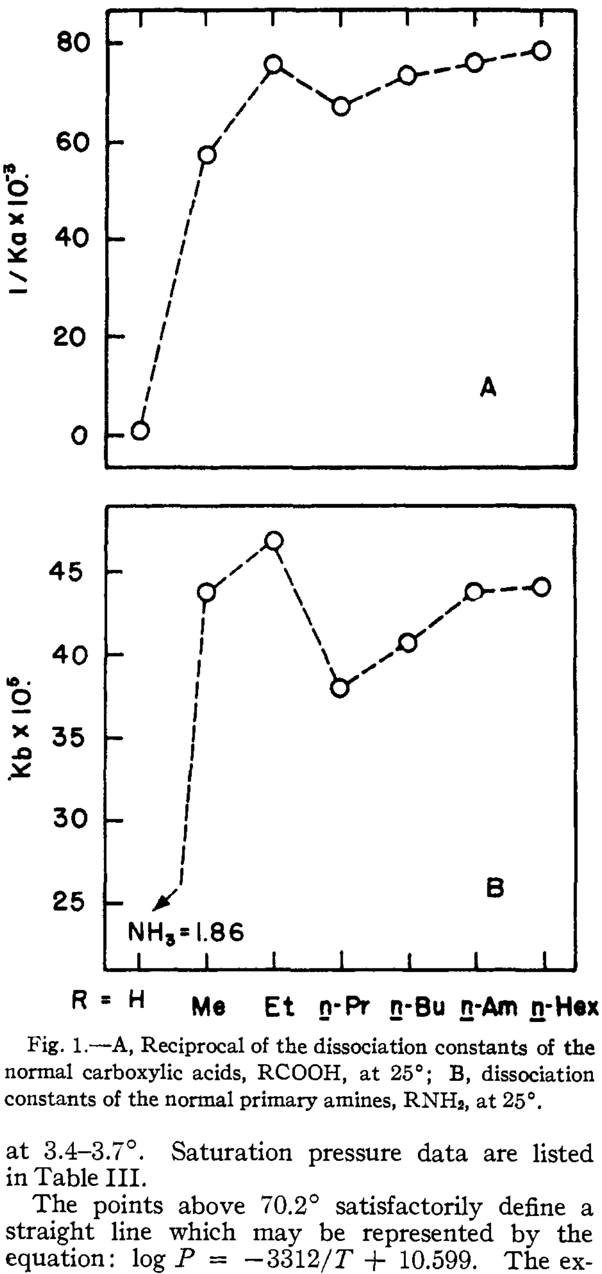

Fig. 1.—A, Reciprocal of the dissociation constants of the normal carboxylic acids, RCOOH, at 25°; B, dissociation constants of the normal primary amines, RNH_2, at 25°.

The points above 70.2° satisfactorily define a straight line which may be represented by the equation: $\log P = -3312/T + 10.599$. The extrapolated "boiling point" is 156°.

The compound is somewhat less dissociated than the *n*-propylamine derivative. The dissociation of

TABLE IV

DISSOCIATION DATA FOR *n*-BUTYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant K (atm.)
102.2	53.75	32.53	0.6523	0.0524
106.3	55.87	32.88	.6992	.0703
110.7	57.91	33.26	.7411	.0929
115.8	60.24	33.71	.7874	.129
120.4	62.12	34.10	.8217	.170
125.9	64.24	34.58	.8577	.235
131.2	66.08	35.04	.8858	.317
136.2	67.67	35.47	.9078	.417
142.3	69.56	36.00	.9322	.607

[a] Pressure of *n*-butylamine and of trimethylboron was 23.67 mm. (calcd. to 0°).

the substance was studied by the method of matched samples[6a] over the temperature range 102.2° to 142.3°. Dissociation data are summarized in Table IV.

The equation $\log K_p = -4038/T + 9.490$ satisfactorily reproduces the change in the equilibrium constant with temperature. The dissociation constant is 0.0467 atm. at 100°, and the heat of dissociation is 18.47 ± 0.2 kcal.

***n*-Amylamine-trimethylboron,** $n\text{-}C_5H_{11}NH_2{:}B(CH_3)_3$.—The addition compound was synthesized from equimolar amounts of *n*-amylamine and trimethylboron. The product is a liquid of low volatility at room temperature. It was subjected to fractional distillation in the high vacuum apparatus and the middle fraction was utilized for saturation pressure measurements. The values are summarized in Table V. The data may be represented by the expression: $\log P = -3360/T + 10.530$. The extrapolated "boiling point" is 166°.

TABLE V

SATURATION PRESSURES OF *n*-AMYLAMINE-TRIMETHYLBORON

Temp., °C.	70.2	75.1	81.4	85.2	90.0	94.7	100.6	104.8
Press., mm.	5.54	7.67	11.3	14.3	19.1	24.9	34.6	43.5

A duplicate series of measurements of the dissociation of the compound led to values for the equilibrium constants at 100° of 0.0416 and 0.0431 atm., respectively, and values for the heat of dissociation of 18.84 and 18.95 kcal. These values for the heat of dissociation are some 0.5 kcal. greater than the corresponding values for the *n*-butyl derivative. This is somewhat disturbing, since one would anticipate that the value of the heat of dissociation should tend toward a limit. For this reason publication was delayed for several years until the opportunity arose to re-examine the dissociation of *n*-amylamine-trimethylboron. Six different determinations were made by the method of approximations.[6b] The results of these determinations are summarized in Table VI.

TABLE VI

SUMMARY OF RESULTS FOR DISSOCIATION OF *n*-AMYLAMINE-TRIMETHYLBORON

Determination[a]	ΔH kcal.	ΔF°_{100} cal.	ΔS°_{100} e.u.	P_0[b]
1	18.95	2331	44.5	22.85
2	18.84	2356	44.2	19.77
3	18.80	2330	44.3	20.95
4	18.85	2370	44.3	10.75
5	18.53	2405	43.3	9.28
6	18.58	2348	43.6	28.08
7	18.76	2348	44.1	26.84
8	18.72	2354	44.0	21.27
Average 1–2	18.89	2343	44.3	
Average 3–8	18.71	2359	43.9	

[a] No. 1 and 2 by method of matched samples; No. 3–8 by method of approximations. [b] Pressure of *n*-amylamine and trimethylboron calculated to 0°.

The data obtained in a typical series of measurements (Table VI, No. 7) are summarized in Table VII. The change of equilibrium constant with temperature may be reproduced by the equation: $\log K_p = -4101/T + 9.617$.

TABLE VII

DISSOCIATION DATA FOR *n*-AMYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant K (atm.)
120.2	69.58	38.65	0.8004	0.163
124.7	71.68	39.09	.8338	.215
130.2	74.07	39.63	.8690	.301
134.5	77.75	40.06	.8911	.384
139.8	77.63	40.57	.9132	.513
144.8	79.28	41.07	.9306	.674
149.9	80.82	41.57	.9444	.877
154.8	82.26	42.05	.9562	1.16
159.7	83.60	42.53	.9656	1.52

[a] Pressure of *n*-amylamine and of trimethylboron was approximated as 26.84 mm. (calcd. to 0°).

As a result of this extended study we were forced to the conclusion that the heat of dissociation does show an appreciable rise between the addition compounds of *n*-butyl- and *n*-amylamine. It therefore appeared desirable to extend the investigation to a higher homolog in order to establish whether there was any indication that the heat of dissociation was tending toward a limit.

***n*-Hexylamine-trimethylboron.**—The addition compound was readily synthesized by treating *n*-hexylamine with an excess of trimethylboron. The excess was removed at 0°, and the product, a colorless liquid at room temperature, was purified by distillation in the high vacuum apparatus. A middle fraction was utilized for measurement of the saturation pressures, from 70.9° to 110.3°. The data, summarized in Table IV, may be represented by the equation; $\log P = -3300/T + 10.217$. The extrapolated "boiling point" is 177°.

TABLE VIII

SATURATION PRESSURES OF *n*-HEXYLAMINE-TRIMETHYLBORON

Temp., °C.	70.9	75.2	80.5	85.3	89.8	94.7	100.0	104.7	110.3
Press., mm.,	4.24	5.57	7.69	10.2	13.5	17.8	23.6	30.5	41.4

The dissociation pressures were determined by the method of approximations.[6b] Data for a typical series of measurements are given in Table IX.

TABLE IX

DISSOCIATION DATA FOR *n*-HEXYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation α	Dissociation constant K (atm.)
125.3	61.98	33.18	0.8447	0.203
129.6	63.50	33.97	.8693	.258
134.9	65.23	34.42	.8953	.349
140.6	66.98	34.90	.9194	.482
145.5	68.32	35.31	.9348	.624
149.6	69.37	35.66	.9456	.771
154.7	70.62	36.09	.9570	1.01
160.9	72.02	36.61	.9673	1.38

[a] Pressure of *n*-hexylamine and trimethylboron was approximated as 23.04 mm. (calcd. to 0°).

The change of the equilibrium constant with temperature may be represented by the equation: $\log K_p = -4042/T + 9.426$.

From these data a value for the dissociation constant at 100° of 0.0393 atm. may be calculated, with 18.49 kcal. as the heat of dissociation.

It is of particular interest that the value of the heat of dissociation is in good agreement with that obtained for *n*-butylamine-trimethylboron, and is appreciably lower than the *n*-amylamine value. It may be concluded that the heat of dissociation of the trimethylboron compounds with the normal aliphatic primary amines tends to a limit of 18.5 kcal., the *n*-amylamine derivative showing a moderately large irregularity.

Discussion

The derived constants for the dissociation of the addition compounds of trimethylboron with ammonia and the normal aliphatic primary amines are summarized in Table X.

TABLE X

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

R	K_{100} atm.	$\Delta F°_{100}$ cal.	ΔH kcal.	$\Delta S°_{100}$ e.u.
Hydrogen[b]	4.62	−1134	13.75	39.9
Methyl[b]	0.0360	2463	17.62	40.6
Ethyl[c]	.0705	1965	18.00	43.0
n-Propyl	.0598	2088	18.14	43.0
n-Butyl	.0470	2266	18.41	43.2
n-Amyl	.0415	2359	18.71	43.9
n-Hexyl	.0390	2404	18.53	43.2

[a] The values reported are averages of two duplicate determinations except for ammonia (R = hydrogen) where the values of only a single determination are reported, and for *n*-amylamine, where the values listed represent the average of six determinations (Table VI, No. 3–8). [b] Ref. 7. [c] Ref. 8.

It was pointed out earlier that lengthening of the carbon chain does not result in a smooth change either in the acid dissociation constants of the carboxylic acids or in the base dissociation constants of the primary amines. In the case of the carboxylic acids, butyric acid is unexpectedly strong; among the amines, *n*-propylamine is unexpectedly weak (Fig. 1). Examination of the dissociation data (Table X) reveals a surprising observation. The dissociation constants of the addition compounds also do not change smoothly with increase in chain length, but in this case the unexpected reversal in the trend occurs with ethylamine (Fig. 2). That is to say, in aqueous solution the irregularity is observed in *n*-propylamine; in the gas-phase dissociation studies the point of irregularity is observed in an amine with a still shorter chain, the ethyl derivative.

It is apparent that the hydrogen bonding interpretation proposed for butyric acid can be extended only with difficulty to *n*-propylamine in aqueous solution, and cannot reasonably be stretched to cover ethylamine in the gas phase. Yet the similarity in the phenomena suggest that one general explanation should be valid. It is proposed here that the point of irregularity is first observed when the length of the chain becomes such that certain configurations are denied to the molecule.

Consider ethylamine-trimethylboron. In this molecule we have a chain of five atoms other than hydrogen, namely, C–C–N–B–C. This number is identical with that in the butyric acid molecule, C–C–C–C–O. The instability of ethylamine-trimethylboron appears from the data to be primarily an entropy effect. In the free amine there is essentially free rotation of the ethyl group about the carbon–nitrogen bond. In the addition compound conflicting steric requirements of the ethyl group and the trimethylboron group prevent such free rotation. Therefore, formation of the addition compound is accompanied by an additional loss of entropy as compared to that occurring in the formation of the corresponding ammonia and methylamine derivatives. The effect would be present in all of the higher amines, so that the stability of the addition compounds formed by these amines should be similar to that of the ethylamine derivative, modified by the increased inductive effect of the larger alkyl group.

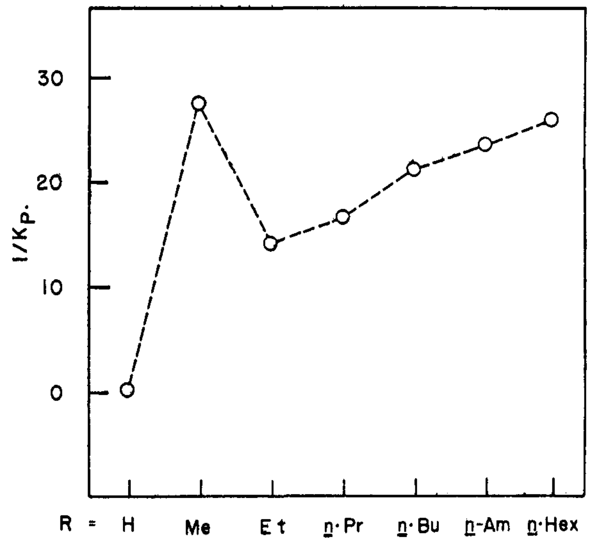

Fig. 2.—Reciprocal of the dissociation constants at 100° of the addition compounds of trimethylboron and the normal primary amines.

It is noteworthy that the heat of dissociation of ethylamine-trimethylboron is entirely regular, supporting the interpretation that the high dissociation constant is primarily an entropy effect.

Extension of this interpretation to *n*-butyric acid and *n*-propylamine in aqueous solution requires the assumption that there are appreciable differences in the steric requirements of the hydrated carboxyl and amino groups and their respective ions. There would then be an appreciable difference between the entropy of the carboxylate ion and that of the un-ionized acid, and between those of the free amine and the corresponding alkyl ammonium ion, over and above the differences observed in acids and bases with shorter chains. It would be desirable to seek independent evidence for the existence of such entropy effects, but this phase of the problem is out of the range of our present interests and will not be pursued further.

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