

The straight-line relationships shown in Figs. 4 and 5 are taken as ample evidence that the reaction proposed in equation (1) represents the precipitation reaction at 60°.

Table I shows, for three runs, the differences between the concentrations of aluminate ion as calculated from the carbon dioxide absorbed and from the analysis of the solutions for total alu-

TABLE I
DIFFERENCES BETWEEN CONCENTRATIONS OF ALUMINATE ION AS CALCULATED FROM TOTAL ALUMINA AND FROM CARBON DIOXIDE ABSORBED

Time, hr.	Excess of AlO_2^- as calculated from total Al_2O_3 concentration over that calculated from CO_2 absorption, moles/liter		
	pH 11.20	pH 11.30	pH 11.45
1	0.006	0.007	0.002
2	.008	.013	.008
3	.013	.022	.007
4013	...
5	.012	.017	.005
6	.015	.010	.004
7012	...
8012	...
Av.	.011	.013	.005

mina. The differences suggest, as a rough approximation, that the solubility of gibbsite is about 5×10^{-3} mole per liter in sodium aluminate solutions of pH 11.20 to 11.45 and ionic strength 0.6 to 0.7.

Acknowledgment.—The investigation was made at the suggestion of R. L. Copson, Chief of Chemical Research and Engineering. Gray Lucas and E. R. Rushton assisted in the experimental work.

Summary

1. A method was developed for measurement of the pH of alkaline solutions containing carbon dioxide without their contamination by silica.
2. The equation $2\text{AlO}_2^- + 2\text{H}_3\text{O}^+ \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was found to represent the mechanism of the precipitation of alumina from sodium aluminate solutions by carbon dioxide at 60°.
3. The solubility of gibbsite in sodium aluminate solutions of ionic strength 0.6 to 0.7 and pH 11.20 to 11.45 was estimated to be about 5×10^{-3} mole per liter.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

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

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In previous papers of this series, the need of considering both polar and steric factors in theorizing has been pointed out. For example, if only the polar effect of the methyl group (+I) is considered, it would be predicted that the strength of ammonia and the methylamines as bases should increase regularly with the number of methyl groups. However, this order, $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$ (Fig. 1, curve A), is not observed. Instead, operation of the steric factor causes B-strain,¹ which slightly reduces the strength of dimethylamine and markedly reduces that of trimethylamine. As a consequence, the order of base strength observed with the aid of acids with relatively low F-strain factors, such as hydrogen chloride and trimethylboron, is $\text{NH}_3 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$ (Fig. 1, curve B). Reference acids with higher F-strain factors should cause the observed order to change successively to C, D, E, and, finally, to F (Fig. 1). Actually, the order $(\text{CH}_3)_3\text{N} < (\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{CH}_3\text{NH}_2$ (curve E) is obtained with the highly hindered reference acid, tri-*t*-butylboron.²

It should be possible to obtain order F, a decrease in base strength with increasing number of

alkyl groups, by slightly increasing the F-strain between the amines and the reference acid. This increase might be accomplished in either of two ways: (1) use of more highly hindered reference acids than tri-*t*-butylboron, or (2) use of larger, bulkier alkyl groups than methyl on the amines.

The first alternative is now being studied at this University; the second forms the subject of the present paper. In it are described the results of an investigation of the relative strengths of ammonia and the ethylamines with three reference acids: hydrogen chloride, trimethylboron, and tri-*t*-butylboron.

Experimental

The preparation and purification of trimethylboron and tri-*t*-butylboron and the experimental techniques are described in previous publications in this series.³

The amines used were Eastman Kodak Company products which had been distilled over sodium and fractionated through a 15-plate column before use.

The comparisons of the relative strengths of the amines with a given reference acid were carried out by the competition method.^{3b} In the case of trimethylboron and tri-*t*-butylboron the results thus obtained were checked by comparisons of the saturation pressure of the individual addition compounds which these acids form with the amines. (There is now considerable evidence to support

(1) Brown, Bartholomew and Taylor, *THIS JOURNAL*, **66**, 435 (1944).

(2) Brown, *ibid.*, **67**, 378 (1945).

(3) See particularly (a) Brown, Taylor and Gerstein, *ibid.*, **66**, 431 (1944), and (b) Brown, *ibid.*, **67**, 374 (1945).

the hypothesis previously advanced that the less stable of two addition compounds of closely similar structure and molecular weight exhibits the higher saturation pressure.^{3b}

Results

A. Hydrogen Chloride as the Reference Acid

Individual values for the base dissociation constants of the ethylamines reported by different investigators vary considerably. However, the variations are not sufficiently large to cast doubt upon the conclusion that the base strength rises from ammonia to ethylamine, rises further with diethylamine, and then drops sharply with triethylamine.⁴

The order of strength of these amines in aqueous solution is therefore very similar to that exhibited by the methylamines, namely, $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} > \text{R}_3\text{N}$ (Fig. 1, curve B). However, as

TABLE I
SUMMARY OF COMPETITION EXPERIMENTS

Reaction mixture, cc.	Recovered amine Amount, cc.	Mol. wt.	Composition, %
55.6 NH_3	55.6	25.2	71 NH_3
55.6 $\text{C}_2\text{H}_5\text{NH}_2$			29 $\text{C}_2\text{H}_5\text{NH}_2$
55.6 HCl			
55.6 $\text{C}_2\text{H}_5\text{NH}_2$	55.6	54.3	67 $\text{C}_2\text{H}_5\text{NH}_2$
55.6 $(\text{C}_2\text{H}_5)_2\text{NH}$			33 $(\text{C}_2\text{H}_5)_2\text{NH}$
55.6 HCl			
55.6 $(\text{C}_2\text{H}_5)_2\text{NH}$	55.6	98.0	10 $(\text{C}_2\text{H}_5)_2\text{NH}$
55.6 $(\text{C}_2\text{H}_5)_3\text{N}$			90 $(\text{C}_2\text{H}_5)_3\text{N}$
55.6 HCl			
28.8 NH_3	28.8	56.5	53 NH_3
28.8 $(\text{C}_2\text{H}_5)_2\text{NH}$			47 $(\text{C}_2\text{H}_5)_2\text{NH}$
28.8 HCl			
26.8 $\text{C}_2\text{H}_5\text{NH}_2$	26.8	84.0	30 $\text{C}_2\text{H}_5\text{NH}_2$
26.8 $(\text{C}_2\text{H}_5)_3\text{N}$			70 $(\text{C}_2\text{H}_5)_3\text{N}$
26.8 HCl			
24.2 NH_3	24.1	19.0	93 NH_3
24.3 $\text{C}_2\text{H}_5\text{NH}_2$			7 $\text{C}_2\text{H}_5\text{NH}_2$
24.3 $\text{B}(\text{CH}_3)_3$			
21.7 $\text{C}_2\text{H}_5\text{NH}_2$	21.6	65.7	26 $\text{C}_2\text{H}_5\text{NH}_2$
21.9 $(\text{C}_2\text{H}_5)_2\text{NH}$			74 $(\text{C}_2\text{H}_5)_2\text{NH}$
21.8 $\text{B}(\text{CH}_3)_3$			
29.2 $(\text{C}_2\text{H}_5)_2\text{NH}$	29.3	99.8	4 $(\text{C}_2\text{H}_5)_2\text{NH}$
29.2 $(\text{C}_2\text{H}_5)_3\text{N}$			96 $(\text{C}_2\text{H}_5)_3\text{N}$
29.2 $\text{B}(\text{CH}_3)_3$			
25.2 NH_3	25.1	25.2	85 NH_3
25.4 $(\text{C}_2\text{H}_5)_2\text{NH}$			15 $(\text{C}_2\text{H}_5)_2\text{NH}$
25.2 $\text{B}(\text{CH}_3)_3$			
25.0 NH_3	23.9	100.4	1 NH_3
25.1 $(\text{C}_2\text{H}_5)_3\text{N}$			99 $(\text{C}_2\text{H}_5)_3\text{N}$
25.1 $\text{B}(\text{CH}_3)_3$			
50.0 NH_3	46.0	31.6	48 NH_3
49.8 $\text{C}_2\text{H}_5\text{NH}_2$			52 $\text{C}_2\text{H}_5\text{NH}_2$
49.5 $\text{B}[\text{C}(\text{CH}_3)_3]_3$			

(4) Thus Bredig, *Z. physik. Chem.*, **13**, 295 (1888), reports 5.6×10^{-4} , 1.26×10^{-3} and 6.4×10^{-4} for the dissociation constants for mono-, di- and triethylamine, respectively; while Moore and Winmill, *J. Chem. Soc.*, **101**, 1651 (1912), report the values 5.2×10^{-4} , 1.14×10^{-3} , and 5.9×10^{-4} for the same three amines.

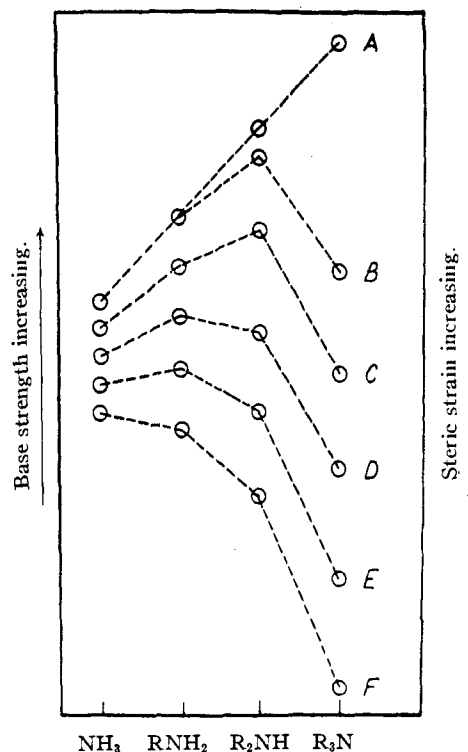


Fig. 1.—Effect of steric strain on the relative base strengths of primary, secondary, and tertiary aliphatic amines.

pointed out previously,^{3a} conclusions based upon such ionization data must be accepted with considerable reserve since they must be affected by complex solvation effects the importance of which cannot yet be estimated.

Accordingly, a series of competition experiments were carried out using hydrogen chloride as the reference acid in order to determine the relative strengths of these bases in the absence of solvents.⁵ These experiments are summarized in Table I.

B. Trimethylboron as the Reference Acid

Ethylamine-trimethylboron was prepared by treating 24.3 cc. of ethylamine at room temperature with 34.2 cc. of trimethylboron. After several minutes the reaction mixture was cooled to -80° and the excess trimethylboron distilled away. The recovery of 9.6 cc. indicated that 24.6 cc. of trimethylboron had combined with 24.3 cc. of ethylamine. The addition compound, a white solid, was purified by distillation at 0° . It melted at $24.0\text{--}24.5^\circ$. The saturation pressures were measured from 0 to 60° . Representative values are listed in Table II.

(5) These experiments involve neglect of the effects of differences in the energies of crystallization of the hydrochloride salts. However, such differences are probably rather small and should not greatly affect the results. In any case it is of interest that the order of base strength thus obtained is in agreement with the order established by the data obtained in aqueous solution.

Diethylamine-trimethylboron was prepared in a similar manner by treating 29.2 cc. of diethylamine with 50.1 cc. of trimethylboron. The excess trimethylboron was removed at -30° , leaving 29.3 cc. combined with the amine. The addition compound was purified by volatilizing small fractions at 0° until the saturation pressure became constant. The product was a white solid which melted at $26-28^\circ$. Saturation pressure data from 0 to 60° are given in Table II.

Triethylamine-trimethylboron was prepared by combining 34.0 cc. of triethylamine with 34.1 cc. of trimethylboron at -80° . The product formed was a white solid which melted from -18 to -14° . The wide range is probably due to the relatively high degree of dissociation of the compound at its melting point. At room temperature the compound is almost completely dissociated. Saturation pressure data are given in Table II.

TABLE II

SATURATION PRESSURE VALUES FOR THE TRIMETHYLBORON ADDITION COMPOUNDS WITH AMMONIA AND THE ETHYLAMINES

Compound	-20°	0.0°	25.0°	40.0°	50.0°	60.0°
$\text{NH}_3 \cdot \text{B}(\text{CH}_3)_3$, ^a mm.		0.95	7.0	22.1	44.7	86.5
$\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{B}(\text{CH}_3)_3$, mm.		0.1	1.0	3.2	6.5	13.0
$(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{B}(\text{CH}_3)_3$, mm.		0.3	2.9	9.5	20.0	37.0
$(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{B}(\text{CH}_3)_3$, mm.	24	238	>700			

^a Calculated from equation given in ref. 1; included for comparison purposes.

Competition experiments were carried out by placing equimolar amounts (20–30 cc.) of each of two amines and trimethylboron in a 300 cc. reaction vessel, allowing twenty-four hours at 0° for equilibrium to be reached, and recovering the unreacted amine by distillation from the vessel maintained at 0° . Traces of the addition compound which codistilled with the amine were removed by a second distillation at -30° and the molecular weight of the recovered amine determined. The experimental data are summarized in Table I.

C. Tri-*t*-butylboron as the Reference Acid

Ethylamine-tri-*t*-butylboron was prepared by combining 47.5 cc. (0.212 millimole) of ethylamine with 0.388 g. (0.213 millimole) of tri-*t*-butylboron. The compound thus formed was a colorless liquid at 0° and solidified to a glass at -80° . The saturation pressures were considerably higher than those previously observed for the ammonia addition compound and exhibit the same dependence upon the proportion of the compound which is vaporized.^{3b} However, the reported saturation pressures (Table III) were taken under conditions such that the observed pressure accounted for less than 10% of the amine present and are therefore comparable with the values reported for the ammonia addition compound which were measured under almost identical conditions.^{3b}

Neither diethylamine nor triethylamine showed

any tendency to combine with tri-*t*-butylboron at 0° . Equimolar mixtures of each of the two amines with tri-*t*-butylboron exhibited pressures at 0° (36 mm. and 9 mm., respectively) which are to be expected from solutions consisting of 0.5 mole fraction of the amine and 0.5 mole fraction of inert solvent of negligible vapor tension.

TABLE III

SATURATION PRESSURE VALUES FOR THE TRI-*t*-BUTYLBORON ADDITION COMPOUNDS WITH AMMONIA AND THE ETHYLAMINES

Compound	0.0°	10.0°	20.0°	25.0°	30.0°
$\text{NH}_3 \cdot \text{B}(\text{C}(\text{CH}_3)_3)_3$, mm.	1.5	4.3	9.7	13.3	19.6
$\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{B}(\text{C}(\text{CH}_3)_3)_3$, mm.	5.3	9.4	14.7	19.3	25
$(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{B}(\text{C}(\text{CH}_3)_3)_3$	No compound at 0°				
$(\text{C}_2\text{H}_5)_3\text{N}$ and $\text{B}(\text{C}(\text{CH}_3)_3)_3$	No compound at 0°				

Competition experiments were run between ammonia and ethylamine using tri-*t*-butylboron as the reference acid. In these experiments the difficulty previously reported was also encountered—the unreacted amines were strongly adsorbed by the addition compound of tri-*t*-butylboron and their recovery was not entirely quantitative. A representative experiment is summarized in Table I. However, the results of these experiments in conjunction with the saturation pressure data (Table III) leave little reason to doubt that ammonia is the stronger of the two bases with this reference acid.

Competition experiments were not carried out with diethylamine nor with triethylamine and tri-*t*-butylboron. It was evident from the non-formation of addition compounds that referred to this acid both of the above amines must be much weaker than ammonia and ethylamine.

Discussion

The replacement of the methyl groups in these amines by larger bulkier alkyl groups should affect both the polar and steric factors. The increased inductive effect (+I) of the larger alkyl groups should increase the strength of each of the bases over that of the corresponding methyl derivative. However, there is considerable evidence that the inductive effect of the larger alkyl groups is only slightly greater than that ascribed to the methyl group. It would therefore be anticipated that the increase in strength exhibited by these higher amines should be relatively small and should not markedly alter the relative strengths of ammonia and its primary, secondary and tertiary derivatives. Any marked changes in the relative strengths of these bases must therefore be largely due to changes in the steric factor.

The experimental results are summarized in Table IV. It is apparent that a reference acid with a very low F-strain factor, hydrogen chloride, does not alter the order from that observed in the methylamine series. However, trimethylboron, a reference acid with a moderate F-strain factor, changes the observed order from $\text{NH}_3 < (\text{C}_2\text{H}_5)_3\text{N} < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$ (Fig. 1, curve B) to

$(C_2H_5)_3N < NH_3 < (C_2H_5)_2NH < C_2H_5NH_2$ (curve D); and tri-*t*-butylboron, a reference acid with a high F-strain factor, yields the order $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2 < NH_3$ (curve F).⁶

TABLE IV

SUMMARY OF DATA ON RELATIVE STRENGTHS OF AMMONIA AND THE METHYL- AND THE ETHYLAMINES

Series	Reference acid	Order (Fig. 1)
Ammonia and methylamines	H ⁺ (aqueous)	B
	HCl (no solvent)	No data
	B(CH ₃) ₃	B
	B[C(CH ₃) ₃] ₃	E
Ammonia and ethylamines	H ⁺ (aqueous)	B
	HCl (no solvent)	B
	B(CH ₃) ₃	D
	B[C(CH ₃) ₃] ₃	F

These changes in the orders produced by a given reference acid in the ethylamine series as compared to the methylamine series are in complete agreement with the effect of the predicted increase in F-strain resulting from the replacement of the methyl by the larger ethyl group. The results thus offer strong support for the F-strain hypothesis.

Finally, it is noteworthy that the order yielded by tri-*t*-butylboron in the ethylamine series, $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2 < NH_3$, is the exact opposite of the order which would be pre-

(6) It should be pointed out that the present study merely establishes the order as $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2 < NH_3$ with tri-*t*-butylboron as the reference acid. However, in view of the results obtained with hydrogen chloride and trimethylboron, there is little reason to doubt that triethylamine lies below diethylamine, as indicated above.

dicted if only the polar factor were considered, $NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$. The importance of considering both factors, polar and steric, is apparent.

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, $NH_3 < (C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$, observed with hydrogen chloride as the reference acid is altered to $(C_2H_5)_3N < NH_3 < (C_2H_5)_2NH < C_2H_5NH_2$ with trimethylboron as the reference acid. Tri-*t*-butylboron causes a further change in the order of the amines to $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2 < NH_3$.

2. These changes in orders are in accord with the predicted effect of F-strain on the relative strengths of these bases. In particular, the relatively greater changes in the orders brought about by a given reference acid in the ethylamine series as compared with the methylamine series, strongly support the F-strain hypothesis.

3. In the course of this investigation, the addition compounds ethylamine-trimethylboron, diethylamine-trimethylboron, triethylamine-trimethylboron, and ethylamine-tri-*t*-butylboron were prepared and characterized. Diethylamine and triethylamine do not combine with tri-*t*-butylboron at 0°.

DETROIT, MICHIGAN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, AND MELLON INSTITUTE]

The Cyclic Dimerization of Isobutylene¹

By JOSEPH B. MCKINLEY,² DONALD R. STEVENS AND WILMER E. BALDWIN

The authors had previously found that isobutylene polymerized at high temperatures and pressures to give a cyclic dimer as the main product. This fact was never noticed before, although Ipatieff³ recognized that isobutylene reacted at 380–390° and 70 atmospheres pressure to give an unresolved complex of paraffins, naphthenes and olefins. The hydrocarbon was isolated, and, from a study of its properties and possible modes of formation, it was concluded that it might be 1,1,3-trimethylcyclopentane. The present study had as its main aims, therefore, the confirmation of the structure postulated for the dimer, and the

determination of the effect of reaction variables on its formation.

Identification of the Cyclic Dimer.—The cyclic dimer was identified by synthesizing it in a conventional manner. For the synthesis, 1,3-dimethylcyclopentanol was treated with hydrogen chloride to form 1-chloro-1,3-dimethylcyclopentane, a new substance.⁴ The chlorocyclopentane was converted to 1,1,3-trimethylcyclopentane by methylation with both zinc dimethyl and methylmagnesium iodide. The comparison of the properties of the cyclic dimer with those of the conventionally synthesized 1,1,3-trimethylcyclopentane given in Table I establishes the two as identical.

(1) An abstract of a thesis presented by Joseph B. McKinley to the graduate school of the University of Pittsburgh in August, 1943, in partial fulfillment of requirements for the degree of Doctor of Philosophy. Contribution No. 545 from the University of Pittsburgh.

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(3) Ipatieff, *Ber.*, **44**, 2978 (1911).

(4) The synthesis involved optically inactive substances. The formation of inadequately characterized optically active 1-chloro-1,3-dimethylcyclopentane is reported by Zelinsky and Rjachina, *Ber.*, **57**, 1931 (1924).