-18 cal. per deg. mole,[22] giving the heat of vaporization at 25° as 16.14 kcal. per mole. Subtraction of RT leaves the energy of vaporization, 15.55 kcal. per mole. It must be emphasized at the outset, however, that the uncertainty in ΔC_p leaves a margin of about 1.5 kcal. per mole in ΔE, which will be reflected in the calculation based on equation (2).

From the density of solid aluminum bromide at 25°, 3.01, and the coefficient of cubical expansion, 2.83×10^{-4},[11] the molal volume at 100° is calculated as 181 cc. At that temperature, the molal volume of the liquid is 203 cc.[23] Assuming the same percentage increase in volumes on melting the solid at 25 and 100°, we find the molal volume of molten aluminum bromide at 25° to be 198 cc. The possible error in this value can be at most 10 cc. and will not affect the conclusions to be drawn.

Hildebrand lists the required constants for *n*-butane,[24] the energy of vaporization and molal volume at 25° being 4.44 kcal. per mole and 102.0 cc., respectively.

The value of $\ln \gamma$ calculated from equation (2) on the above bases is 1.4, which is to be compared with the observed value of 1.3, taken as the ratio of the ideal to the observed (extrapolated 3°) solubility. The agreement is quite good and could be made perfect by a slight lowering of $-\Delta C_p$ of vaporization of aluminum bromide. We conclude that solutions of aluminum bromide in *n*-butane are quite regular in the Hildebrand sense.[25]

The system Al_2Br_6–$AsBr_3$ is apparently normal. There is good evidence for the lack of compound formation.[26]

We have throughout written aluminum bromide as the dimer Al_2Br_6. It seems to us that this is logical in view of our knowledge of its molecular state when no chemical reaction has occurred. To write it as $AlBr_3$ would be analogous to using the formula I for liquid iodine or iodine in solution. The fact that in both cases a reaction with certain solvents may occur renders it even more important to compare such solutions with others on the basis of the ideal solution, in which Al_2Br_6 (or I_2) is certainly the true molecular formula.

Summary

The solubility of aluminum bromide in *n*-butane has been measured from 28.3° to the melting point of the salt, 97.5°.

There appears to be no convincing evidence for a phase transformation in aluminum bromide near 70°, as has been reported by other workers.

The difference between the actual and ideal solubility of aluminum bromide in *n*-butane is predicted by Hildebrand's equation relating solubility to internal pressure differences. The system is regular in the Hildebrand sense.

The solubility relationships of aluminum bromide in other solvents have been briefly discussed.

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[22] Fischer and Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 1 (1932). The value of $-\Delta C_p$ is surprisingly large.

[23] Biltz and Voight, *ibid.*, **126**, 39 (1923).

[24] Hildebrand, ref. 7, p. 104.

[25] Other effects, such as deviations from random mixing in solution [Rushbrooke, *Proc. Roy. Soc.* (London), **166A**, 294 (1938); Kirkwood, *J. Phys. Chem.*, **43**, 97 (1939)], and a size effect due to dimerization of the solute, which can be applied in this case [Fowler and Rushbrooke, *Trans. Faraday Soc.*, **33**, 1272 (1937)], are quite small in comparison to the Hildebrand term for regular solutions.

[26] Yankelewich and Sheka, *Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R.*, **5**, 81 (in English) (1938).

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Acid-Base Studies in Gaseous Systems. I. Precise Dissociation Measurements

BY HERBERT C. BROWN,[1] MODDIE D. TAYLOR AND MELVIN GERSTEIN

The rarity of simple reversible organic reactions has always been a major difficulty in the development of rational chemical theories. Because of this scarcity, the effects of structure and of substituents upon chemical behavior have been investigated largely by means of competitive reactions and reaction rate studies. Work with irreversible systems and the interpretation of the results thus obtained, however, involve great difficulties and uncertainties. Although much ingenuity has been displayed in overcoming such obstacles, and although modern physical methods for examining molecular structure have been of great service, simple reversible reactions, were they available, would still play an important role in the further development of organic chemical theory.

The reversible dissociation of addition compounds in the vapor phase has been the object of several studies in recent years.[2] These dissociations of the type $B{:}A$[3] $\rightarrow B{:} + A$ are simple reversible reactions are representative of a large class, the study of which should yield much valuable information. In studies of such dissociations, it is possible to make quantitative measurements from

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[2] (a) Schlesinger, Flodin and Burg, THIS JOURNAL, **61**, 1078 (1939); (b) Davidson and Brown, *ibid.*, **64**, 316 (1942); (c) Brown and Adams, *ibid.*, **64**, 2557 (1942); (d) Laubengayer and Finlay, *ibid.*, **65**, 887 (1943).

[3] The formula of the addition compound is frequently written $B^+{:}^-A$ in order to indicate the formal charges on the bonding atoms. Since there is no evident advantage in this more complex symbolism, the simpler version will be here employed.

which the thermodynamic quantities ΔF, ΔH and ΔS readily may be determined. The substituents in A and in B may be widely varied, and the effects of such variations on ΔF, ΔH and ΔS may then be compared. Thus it is possible to compare a particular change of the substituents in A with a similar change of the substituents in B. Moreover, the substituents in both A and B may be kept constant while the bonding atoms are varied. By comparisons of the results thus obtained, the "electrical" effects of substituent groups and the dependence of these effects on the nature of the bonding atoms may be distinguished from the "steric" effects. It is evident that the quantitative data secured from an investigation of the dissociative characteristics of a selected series of compounds offer important possibilities for broadening our understanding of the specific influences of substituent groups in organic chemistry.

The interest of such studies is considerably heightened by Lewis' suggestion that such dissociations are typical acid–base reactions.[4] The ionization of organic acids and bases in suitable solvents has hitherto been one of the few simple reversible reactions available to workers in theoretical organic chemistry. The conclusions drawn from the study of such ionizations have, however, always been open to the objection that the results may be greatly affected by complex solvent effects, the importance of which cannot yet be estimated. If Lewis' interpretations of the dissociation reaction, $B:A \rightarrow B: + A$, can be shown to be correct, the effect of structure on acid and base strength may be determined by observations made on the vapor phase, where the complexities inherent in solution work are absent. The accumulated data from solution studies may then be reëxamined in order to determine whether the customary neglect of the solvent has led to serious errors.

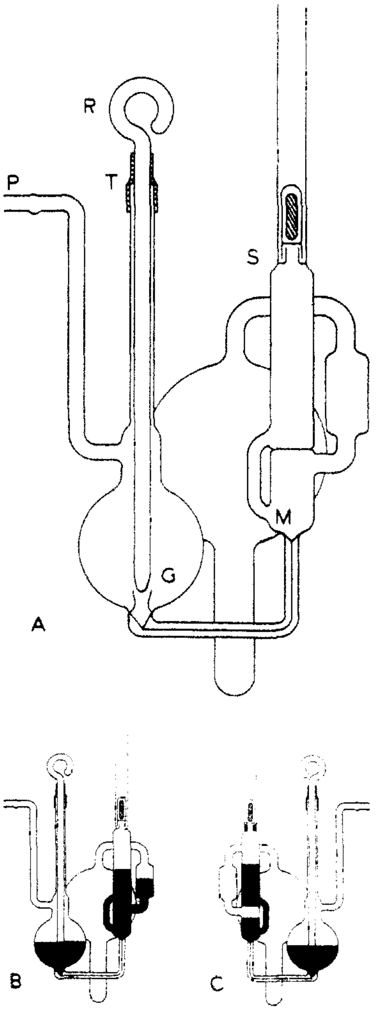

Fig. 1.—Dissociation tensimeter: A, diagram illustrating construction; B, mercury in position to read low pressures (below 20 mm.); C, mercury in position to read dissociation pressures (20–100 mm.).

For these reasons, it has seemed desirable to initiate a series of studies on the dissociation of selected addition compounds in the gas phase. It was decided early that in order to derive the maximum value from the experimental data, the limits of accuracy of the measurements should be set as high as practical. The following limits were tentatively fixed: the dissociation constants should be accurate to 1–2%; the heat of dissociation should be correct to 0.1% (0.1–0.2 kcal.). The technique finally developed, and described in the present paper, is both simple and accurate—it is easily reliable to these limits. The results obtained by the application of this technique to specific problems will be discussed in later papers of this series.

The Apparatus

The apparatus used for studying the dissociations (the "dissociation tensimeter") is shown in Fig. 1.

The volumes of the two dissociation tensimeters (*ca.* 260 ml.) were matched to within 1 part in 2000. This was accomplished by comparing the pressure exerted by a given volume of gas transferred from one tensimeter to the other. Minor changes in the volumes of the tensimeter were made by adjusting the zero marks to which the mercury in the manometer was raised.

The mercury manometer was constructed of 25-mm. tubing and designed as shown to bring the upper mercury meniscus directly above the lower (Fig. 1-C). In this way the height of the mercury column could be accurately measured as a single vertical distance to within 0.01 to 0.02 mm. with the aid of a Gaertner micrometer slide (range, 100 mm.) carrying a short focus telescope. Pressures below 20 mm. could not be measured in this way. By allowing the mercury to rise in the manometer until the two menisci were side by side (Fig. 1-B), pressures below 20 mm. (*e. g.*, saturation pressure) could be read with an ordinary cathetometer with somewhat poorer precision (±0.04 mm.).

Mercury was brought into the evacuated manometer M by raising the rod R (Fig. 1-A), thus opening the ground glass closure G between the reservoir and the manometer. The mercury was lowered by connecting the mercury reservoir to a pump at the point P while the rod was lifted. The necessary vertical movement of the rod was obtained by using thin gum rubber tubing for the closure at the point T. The mercury vapor seal S was introduced to

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

TABLE I

SUMMARY OF DISSOCIATION DATA FOR TRIMETHYLAMINE–TRIMETHYLBORON[a]

Detn. no.	Inital pressure,[b] mm.	Temp., °C.	Pressure, mm.		Degree of dissociation	Dissociation constant, K (atm.)	Log K_p = $-A/T + B$		ΔH	ΔS	$\Delta F_{80°}$
			Observed	Calcd.[c]			A	B			
1	23.39	70.4	49.77	29.42	0.692	0.0601	3852	9.9978	17619	45.7	1472
		80.0	54.35	30.24	.797	.125					
		90.6	58.48	31.15	.877	.257					
		99.0	61.18	31.87	.920	.441					
		111.3	64.47	32.92	.960	.956					
2	26.12	70.4	55.14	32.85	.678	.0619	3831	9.9392	17523	45.5	1470
		83.9	61.99	34.14	.816	.162					
		88.7	64.07	34.60	.852	.223					
		96.3	67.08	35.33	.899	.371					
3	23,01	74.6	51.18	29.30	.747	.0850	3849	9.9829	17605	45.7	1482
		78.4	52.75	29.62	.781	.108					
		85.9	55.85	30.25	.846	.185					
		93.6	58.59	30.90	.896	.314					
							Average values		*17582 ± 40*	*45.6 ± 0.1*	*1475 ± 3*
4	28.13	75.7	62.25	35.93	.732	.0948	3807	9.8903	17413	45.3	1439
		85.3	67.37	36.93	.824	.188					
		91.3	70.01	37.53	.865	.275					
		95.2	71.64	37.94	.888	.352					
5	10.04	54.1	19.66	12.03	.634	.0174	3885	10.1138	17770	46.2	1440
		65.9	22.16	12.46	.778	.0449					
		71.1	23.15	12.69	.830	.0674					
		80.7	24.71	13.01	.899	.137					
5′	10.07	54.1	19.66	12.06	.630	.0170	3809	9.8738	17422	45.2	1475
		65.9	22.16	12.50	.773	.0432					
		71.1	23.15	12.69	.824	.0646					
		80.7	24.71	13.03	.893	.129					

[a] To reduce the amount of material tabulated, only every other measurement from each determination has been reported. The corresponding dissociation constants are plotted in Fig. 2. [b] Calculated to 0°. [c] Calculated from the initial pressure to the temperature, T, assuming no dissociation.

eliminate errors resulting from the evaporation of mercury into the vacuum above the upper meniscus. In operation, the plug rested in the mercury well (Fig. 1-C), beneath the surface of the oil-bath. Thus, at equilibrium, both the bulb of the tensimeter and the space above the upper meniscus were saturated with mercury vapor. Whenever materials were introduced or removed from the tensimeter, the plug was lifted with magnets to break the seal. The tensimeter was surrounded by a thermostat maintained at a temperature constant to ±0.1° for one-hour intervals, charged with clear mineral oil and provided with a plate glass window sealed with Glyptal cement to permit observation of the manometer, this cement being resistant to the bath liquid up to 160°. Its temperature was measured by means of a mercury thermometer calibrated by the U. S. Bureau of Standards.

Procedure

A sample of component A, the amount of which had been previously measured roughly in the vacuum apparatus (±0.5%), was condensed with liquid nitrogen in one of the dissociation tensimeters. The mercury was then raised into the manometer, shutting off the tensimeter from the rest of the apparatus while component B was similarly brought into the other tensimeter. The samples used were of such a size that within the tensimeter they exerted a pressure of 20–30 mm., low enough to minimize deviations from the ideal gas laws, yet high enough to maintain the desired precision of measurement.

TABLE II

CALCULATED DISSOCIATION CONSTANTS

Detn. no.	Temperatures, °C. 70.0	80.0	90.0	100.0
1	0.0590	0.123	0.245	0.472
2	.0593	.123	.245	.469
3	.0582	.121	.241	.464
Av. values	*.0588 ± 0.0004*	*.122 ± 0.001*	*.244 ± 0.002*	*.468 ± 0.003*
4	.0623	.128	.254	.468
5	.0617	.129	.259	.509
5′	.0592	.122	.242	.462

The sizes of the two samples were adjusted until the two pressures agreed within 0.02 mm. The adjustment was conveniently made in the following manner. The ratio between the volume of the tensimeter to the bottom of the manometer (point M) and the volume from that point to the mercury seal S was known. Calculations based upon the measured excess pressure and the known vapor pressure of the compound at low temperatures permitted an accurate fraction of the total sample to be removed by simply cooling the flask to the calculated temperature and momentarily withdrawing the mercury from the manometer. After the manometer was closed, the small plug was lifted from the mercury seal and the material trapped in the space beneath it was distilled away. In working with a series of addition compounds in which one component was maintained constant (*e. g.*, the addition compounds of trimethylboron with aliphatic amines), it proved convenient always to have the constant component (trimethylboron) present in slight excess so that the adjustment could be made to the same component.

The two matched samples were then quantitatively brought together into one tensimeter by means of liquid nitrogen. To transfer the substances quantitatively (loss

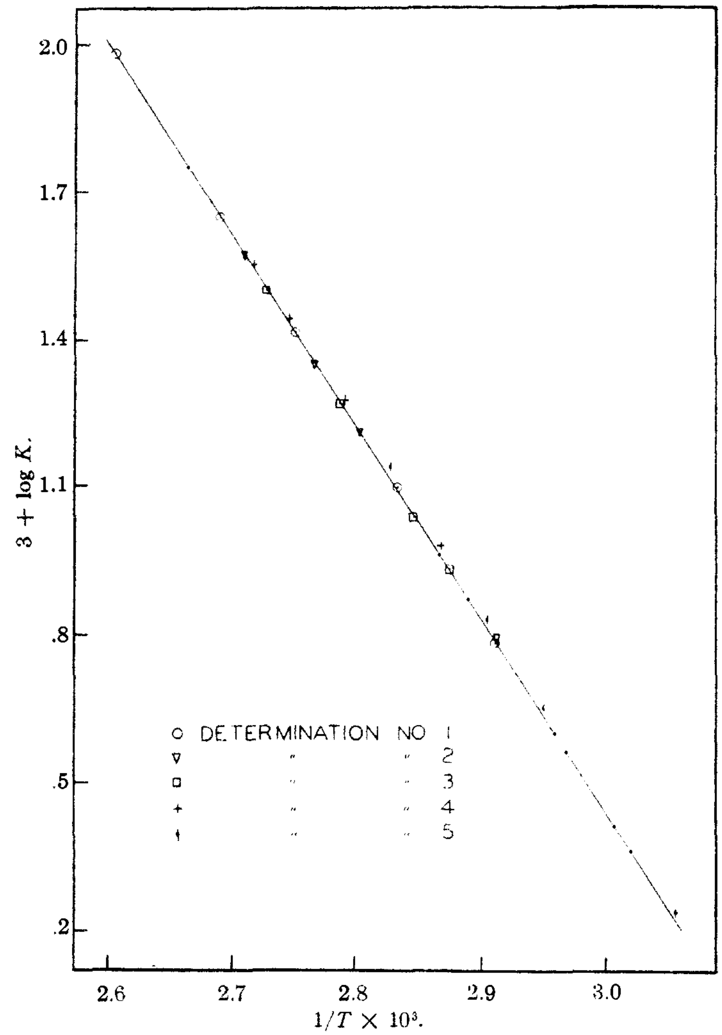

Fig. 2.—Composite graph of trimethylamine–trimethylboron dissociation data.

less than 1 part in 2000) test experiments indicated that a condensation time of close to ten minutes was necessary. Usually twenty to thirty minutes were assigned to this operation. Ordinarily the more volatile of the two components was the one transferred.

The vapor pressure of the addition compound thus synthesized from its components was measured at 0°. If this pressure agreed with that obtained for the previously prepared and purified sample of the addition compound, the heating bath was placed in position and the heating begun. The point of complete vaporization could be determined by comparison of the observed pressure with the previously measured saturation pressure. (This point could also be detected by observing the instant the glass walls of the tensimeter lost their foggy appearance and became perfectly transparent.) Usually no dissociation measurements were made for approximately 10° above this point, for the values of the dissociation constant determined near the saturation point tended to be low. The measurement of at least 8 to 10 dissociation pressures (roughly every 5°) allowed the importance of random errors in the determination of individual values to be minimized. Several check readings were also made as the bath cooled and compared with readings taken during the temperature rise in order to insure that equilibrium had been reached and to establish that no irreversible changes had occurred in the course of the experiment.

Test of Method

The reliability of the procedure described was tested by a number of studies on the dissociation of trimethylamine–trimethylboron.[5] These series of measurements were made by three different investigators who used different pairs of dissociation tensimeters and individual preparations of the components. The results are summarized in Table I (determinations 1, 2 and 3) and represented graphically in Fig. 2. To facilitate comparison between these runs, individual values of the dissociation constants for four temperatures were calculated (Table II) by means of the equation which best represented each series of measurements.[6] The agreement is excellent. The heats of dissociation calculated from these three runs agree within 0.1 kcal.; the dissociation constants agree to within 1%.

It can be shown that the value of the dissociation constant is very sensitive to small quantities of inert impurities in the components A and B used in the preparation of the addition compound. Fortunately, the nature of the addition compound and the method of its preparation offers a simple but sensitive check on the purity of the individual components and the compounds they produce. In practically all cases to which the method described is applicable, the components A and B are very volatile substances with vapor pressures of the order of 0.1 to 4 atmospheres to 0°. These components may easily be individually purified to the point where the absence of any impurities of markedly different volatility is assured. On the other hand, the addition compound B:A is, ordinarily, only slightly volatile; in most cases its saturation pressure is below 0.3 mm. at 0°. An inert impurity present to the extent of 0.2% in A would leave uncombined an equal quantity of B. If 25-mm. samples of A and B each are used, the saturation pressure of the addition compound B:A would be 0.1 mm. above the true value. A discrepancy of this magnitude is detected easily. Reactive impurities, that is, those which react with the other component to form addition compounds, are less easy to detect; their absence may be demonstrated by the constancy of the saturation pressure of the complex. That the requisite purity can be attained is indicated by the agreement between determinations 1, 2 and 3.

The effect of deviations from the perfect gas laws on the accuracy of the results remains to be considered. To obtain experimental evidence on the importance of such deviations, a run was made at a considerably lower pressure than in the three determinations already mentioned. At this low pressure the specially designed manometer and the slide cathetometer could not be used. Accordingly, the two-limb manometer and an ordinary cathetometer were used. As a check, a run was made with the same appa-

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[5] Previous work on this compound and its physical properties will be described in the second paper of this series. This addition compound was selected for testing the experimental method because from its previous study, it was known that its degree of dissociation was in a moderately difficult region, α = 0.70 to 0.95. Its study, therefore, furnished a relatively severe test of the reliability of the experimental method.

[6] The dissociation data from a number of runs were studied both by standard statistical methods and by graphical methods; the results obtained by both procedures agreed very closely. The agreement was much better than the limits of accuracy set for the results. It was, therefore, decided that the simpler graphical method should be adopted as the standard procedure for working up the experimental data.

ratus at the usual pressure. The results are given in Tables I and II, determinations 4 and 5. It is apparent that within the lower precision of these results, there is no significant difference between the constants thus obtained and those observed in runs 1, 2 and 3. It may be concluded that the accuracy of the constants is not seriously affected by deviations from the perfect gas laws. Although errors due to this factor might be reduced by using an extrapolation procedure, the sensitivity of the dissociation data obtained in the lower pressure range to variations in the initial pressures[7] suggests that very little would be gained by recourse to such a method.

Summing up, then, it appears that the method described in this paper for measuring the dissociation of addition compounds yields dissociation data with the desired accuracy: the dissociation constants are estimated to be reliable to 2% and the heat of dissociation to 0.1%. The optimum pressure range (initial pressure of each component) is 20–30 mm. Operating below this range (*e. g.*, 10 mm.) does not noticeably affect the experimental values of the constants, but it greatly increases the probable error.

There is little doubt that the precision of the measurements could be further improved by additional refinements. However, the uncertainty introduced by neglect of the gas law deviations suggests that higher precision is of uncertain value. Certainly, the field is so new and the questions to be answered are so many that it appears more important now to concentrate on the more urgent problems and to leave further refinements to such a time as the need for even more accurate data becomes apparent.

Summary

Accurate dissociation data of addition compounds in gaseous systems are of considerable interest and value for theoretical organic chemistry. A simple technique for precise measurement of such dissociations has been developed and tested by a series of studies on the dissociation of trimethylamine–trimethylboron. The tests indicate that by this method the dissociation constants can be determined to 2% and the heat of dissociation to 0.1%.

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[7] Comparison of the calculated values in runs 5 and 5' illustrates this sensitivity. In the 5' series of calculations, 10.07 mm. was used for the initial pressure instead of the 10.04 (±0.04) actually observed.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Acid–Base Studies in Gaseous Systems. II. The Anomalous Base Strength of the Methylamines; A New Manifestation of Steric Strain[1,2]

BY HERBERT C. BROWN,[3] HERMAN BARTHOLOMAY, JR., AND MODDIE D. TAYLOR

Organic acids and bases have played a significant role in the development of modern physical theories.[4] The influences which structure and substituents exert on the relative strengths of acids and bases are an important part of the foundations upon which such present-day theories as those of the "inductive effect" and the "resonance effect" are constructed. Although much research has been devoted to this subject, a number of interesting phenomena have not yet received satisfactory explanations.

One such phenomenon is the well-known anomalous behavior of the methylamines. The introduction of a methyl group into the ammonia molecule produces an increase in base strength which is ascribed to the positive inductive effect (+I) of the methyl group. The introduction of a second methyl group causes a further increase which is ascribed to the same effect. Introduction of a third methyl group, however, markedly reduces the strength of the tertiary amine formed[5] (Table I).

TABLE I

BASE DISSOCIATION CONSTANTS FOR AMMONIA AND THE METHYLAMINES AT 25°

Amine	$K_b \times 10^5$
NH_3	1.79
$CH_3 \rightarrow NH_2$	42.5
$\begin{matrix} CH_3 \searrow & \\ & NH \\ CH_3 \nearrow & \end{matrix}$	59.9
$\begin{matrix} CH_3 \searrow & \\ CH_3 \rightarrow & N \\ CH_3 \nearrow & \end{matrix}$	6.31

The behavior of the normal aliphatic acids and amines furnishes other puzzling problems. Acetic acid is considerably weaker than formic acid, a result which might be expected in view of the inductive (+I) effect postulated for the methyl group. Propionic acid is still weaker, a fact which is also in accord with the theory. Butyric acid, however, is stronger than propionic.[6]

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[1] This publication is also paper IV in the series, Studies in Stereochemistry; for paper no. III in this series, see THIS JOURNAL, **64**, 2563 (1942).

[2] Presented before the Division of Physical and Inorganic Chemistry at the Detroit Meeting of the American Chemical Society. A preliminary communication was published in *J. Chem. Phys.*, **11**, 43 (1943).

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[4] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940; Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, Oxford, 1941.

[5] Everett and Wynne-Jones, *Proc. Roy. Soc.* (London), **177A**, 449 (1941). Earlier values for the dissociation constants of the methylamines are summarized in this paper.

[6] Dippy, *Chem. Rev.*, **25**, 151 (1939). Particular attention is called to the graph on page 189 of this review. The increase in the acid strength of butyric acid has been ascribed to hydrogen bond formation between the end methyl group and the carboxyl group. Since we have observed similar phenomena in compounds where such hydrogen bond formation is impossible, this explanation is no longer satisfactory. The subject will be discussed in subsequent papers of this series.