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## Polar Substituent Effects in Gas-Phase Lewis Acid–Base Equilibria. I. Intrinsic Basicity of Amines[1]

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**Abstract:** The polar effects on base strength of fluorine, methoxy, and alkyl substituents have been determined for $\beta$-substituted ethylamines toward trimethylboron in the gas phase. The corresponding polar effects on base strength in aqueous protonation equilibria have also been determined. The standard changes in free energy, enthalpy, and entropy have been obtained for both reactions. A linear free-energy (lfe) relationship between the solution and gas-phase basicities is demonstrated, showing that the polar substituent parameters from the condensed phase apply in the gas phase. This lfe relation holds even though the gas-phase equilibria do not involve entropy effects, whereas substantial entropy effects are found in the aqueous protonation equilibria. Accordingly, strong support is provided for the idea that effects on solvation of the base and ammonium ion functional centers appear in the solution entropy and enthalpy but are very substantially compensated in the solution free energies. Internal hydrogen bonding with methoxy substituent in the gaseous primary amine Lewis acid adducts produces anomalous stability. This interaction gives rise to substituent effects which are more complex in the gas phase than in aqueous solution.

Gas-phase Lewis acid–base equilibria studied with systems appropriate to the elimination of steric factors provide a means for quantitative determination of intrinsic base strength. Such a determination is a matter of much importance, for in even the most suitable condensed-phase equilibria the measurement of intrinsic base strength has been frustrated by the uncertainty of the role of the solvent (a) in the modification of the polarity of the substituent and functional groups,[2] (b) in the introduction of entropy effects,[3] and (c) in the transmission of polar effects,[4] including the "saturation effect."

Gas-phase Lewis acid–base equilibria were utilized by Brown and his students in their classical definitive studies of steric effects.[5] Application to studies of the secondary hydrogen isotope effect has also been made.[6] The present investigation appears to be the first application to a systematic study of the polar effect in the gas phase.

Series of fluoro, methoxy, and alkyl $\beta$-substituted ethylamines and N,N-dimethylethylamines have been selected to maintain a constant steric factor within each series in the dissociation of the boron trimethyl adduct. The method of measurement employed was that described by Brown[7] with minor modifications (Experi-

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[6] P. Love, R. W. Taft, and T. Wartik, *Tetrahedron*, **5**, 116 (1959).

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$$X_nCH_{3-n}CH_2NH_2B(CH_3)_3(g) \rightleftarrows X_nCH_{3-n}CH_2NH_2(g) + B(CH_3)_3(g) \quad (1)$$

$$X_nCH_{3-n}CH_2N(CH_3)_2B(CH_3)_3(g) \rightleftarrows X_nCH_{3-n}CH_2\text{-}N(CH_3)_2(g) + B(CH_3)_3(g) \quad (1')$$

mental Section). The thermodynamic properties which have been obtained for reaction 1 are $K_{(p)}$, $\Delta F°$, $\Delta H°$, and $\Delta S°$.

Aqueous protonation equilibria provide a great wealth of data on base strength[8] and have served as a primary standard for polar substituent parameters,[9] *e.g.*, $\sigma$ and $\sigma_I$. Nevertheless, entropy effects in such equilibria are the rule.[3,10] We have determined for comparison with the gas-phase results all of the thermodynamic properties for the corresponding aqueous ionization reactions, *i.e.*

$$X_nCH_{3-n}CH_2NH_3^+(aq) \rightleftarrows H^+(aq) + X_nCH_{3-n}CH_2NH_2(aq) \quad (2)$$

$$X_nCH_{3-n}CH_2N(CH_3)_2H^+(aq) \rightleftarrows H^+ + X_nCH_{3-n}CH_2N(CH_3)_2(aq) \quad (2')$$

The p$K_a$ determination was made by conventional methods at 25°. The entropy of ionization was obtained from the corresponding standard free energy of ionization and the standard enthalpy of ionization. The latter was obtained calometrically using the method of Arnett.[11]

## Experimental Section

Materials. **Trimethylboron** was either prepared from the reaction of methylmagnesium bromide with boron trifluoride or purchased from K and K Laboratories. Samples were purified by repeated passes from a −45° bath through a −112° bath (carbon disulfide) into a −130° (*n*-pentane) bath. The sample retained in the −130° bath was refractionated three times, discarding fore and after cuts. The final samples had a saturation pressure of 242.1–243.0 mm (corrected to the density at 0°) at −45° (chlorobenzene), independent of vapor volume. One calculates from the work of Stock and Zeidler[12] a saturation pressure of 245.3 mm (−45.2°) and from that of Furukawa and Park[13] 247.2 mm (−45.2°). The infrared spectrum was identical with that obtained by Lehmann, *et al.*[14] No impurities could be detected by a mass spectrum analysis.

**2,2,2-Trifluoroethylamine.** A sample of this amine was liberated from its hydrochloride (Penn Salt Co.) by reaction with excess potassium hydroxide. The amine was dried at room temperature over metallic sodium in a transfer ampoule. It was then fractionated several times from a −45.2° bath into a −112° bath. A sample having a saturation pressure of 150.3 mm (0°) was obtained. The vapor density molecular weight was found to be 99.3 compared to the theoretical value of 99.1.

**2,2-Difluoroethylamine** was generously supplied by Dr. J. B. Dickey of the Tennessee Eastman Research Laboratories. The sample was dried for an extended period over BaO at room temperature. The BaO was previously dried at 200° under high vacuum. The amine was fractionated several times from a −45.2 to −80° bath giving a sample with a saturation pressure of 36.6 ± 0.3 mm (0°) (independent of vapor volume). The vapor density molecular weight was found to be 81.7 compared to the theoretical value of 81.07.

**2-Fluoroethylamine hydrochloride** was prepared by the hydroboration of either fluoroacetamide or fluoroacetonitrile, which gave identical products. The procedure used was similar to that reported by Papanastassiou and Bruni[15] and by Brown and Heim.[16] The salt was recrystallized from $(C_2H_5)_2O$–$C_2H_5OH$ and dried with pumping in an Abderhalden apparatus at 65° for 24 hr, giving a sample of mp 98–100°. A sample kindly donated by Dr. P. J. Levins which was dried under the same conditions gave no depression of a mixture melting point. The F nmr spectrum consists of nine lines with coupling constants identical with those obtained from the nmr by Levins and Papanastassiou.[17]

**2-Fluoroethylamine.** This amine was liberated from its hydrochloride by reaction with NaH in diglyme. The reaction was carried out in a small one-piece distilling column to which was attached a U trap with Fisher-Porter greaseless valves and sealed with Vitron O rings. To 1 g of hydrochloride stirred with 2 ml of diglyme, 0.4 g of 50% NaH dispersion was slowly added. Immediate evolution of $H_2$ was evident. After all of the NaH was added, the system was pumped at 0.1 mm to transfer the amine and the diglyme to the trap which was immersed in liquid nitrogen. The amine was isolated from diglyme and $NH_3$ by repeated passes through traps at −30, −45, and −96°. The first trap removes diglyme and the last trap allows the $NH_3$ to pass. The amine sample was fractionated until its saturation pressure was independent of volume, 46 ± 1 mm at 0°. Saturation pressures of 12 mm (−22.9°) and 118 mm (20°) were also obtained, from which the boiling point at 760 mm is estimated to be 60–63° (lit.[4] 63.4–64.5°). The vapor density molecular weight was 61 ± 2 compared with the theoretical value of 63.09. After the determination of $\Delta H_D$ with $B(CH_3)_3$ a portion of $FCH_2NH_2$ was condensed into 0.5 cc of $D_2O$ and 0.1 cc of $D_2SO_4$. The F nmr and pmr spectra of this sample were identical with those of the original amine hydrochloride.

**3-Methoxypropylamine.** Aldrich Chemical Co. material was fractionated at atmospheric pressure to obtain a fraction, bp 115.5–115.8° (737.7 mm). This sample was dried for an extended period under high vacuum over a sodium mirror, and then fractionated four times from a −22.9° bath into one at −80°. A sample having a saturation pressure of 2.7 ± 0.3 mm (0°) was obtained. A molecular weight of 89.3 by the vapor density method compared to 89.14 (theoretical) was obtained. Final purification was made by collecting the major portion of the main peak fraction in a gas chromatographic distillation.

**3-Methoxyethylamine.** Eastman Kodak Co. practical grade (60–70% aqueous) material was distilled from a saturated solution of KOH. The fraction with bp 90–91° (733 mm) was retained, dried, and fractionated as described above for 3 methoxypropylamine. A sample having a saturation pressure of 12.7 ± 3 mm (0°) and a vapor density molecular weight of 75.6 (theoretical 75.11) was obtained. Final purification was made by collecting the major portion of the main peak fraction in a gas chromatographic distillation.

**Tertiary N,N-Dimethylamines.** The amines were prepared from the corresponding primary amine by a modified Luechhart reaction.[18] The main fraction was collected and dried over KOH and Drierite. Fractionation through a Nester-Faust spinning-band column at 28 theoretical plates was carried out.

The following boiling points were obtained: *n*-propyl-N,N-dimethylamine, 64–66° (755 mm); 3-methoxypropyl-N,N-dimethylamine, 129–130° (753 mm); 2-methoxyethyl-N,N-dimethylamine, 101–103° (748 mm). In order to remove trace amounts of primary and secondary amines, the following manipulations were carried out on a high-vacuum line. The amine (25 ml) was condensed into a bulb containing a magnetic stirrer, float valve, and 0.5 g of $LiAlH_4$. The sample was stirred at room temperature until there was no further evolution of $H_2$ and then transferred to a similar bulb containing $P_2O_5$. A final test of purity was analysis by vpc using Gas Chrom A impregnated with KOH and coated with Carbowax 20M. This

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[17] P. L. Levins and Z. B. Papanastassiou, *ibid.*, **87**, 826 (1965).

[18] *Cf.* H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

column resolves mixtures of primary, secondary, and tertiary ($RNH_2$, $RN(CH_3)H$, $RN(CH_3)_2$) amines into three well-separated peaks.[19] The observation of a single peak was taken as an indication that a given tertiary amine was pure. The following literature boiling points have been reported: *n*-propyl-N,N-dimethylamine,[20] 65–67° (760 mm); 3-methoxypropyl-N,N-dimethylamine,[21a] 129–130° (765 mm); 2-methoxyethyl-N,N-dimethylamine,[21b] 101° (757 mm).

**$B(CH_3)_3$ Addition Complexes.** All operations were performed in a high-vacuum system at $10^{-5}$ mm. The line was equipped with Hg float valves to avoid any contact with stop-cock grease. The techniques followed were those given by Sanderson.[22] The complexes were prepared by condensing approximately 20% excess of $B(CH_3)_3$ with the amine. The mixture was then fractionated three to four times with pumping from a trap at an appropriate higher temperature (*e.g.*, 25°) to one at a lower temperature (*e.g.*, −80°), the excess $(CH_3)_3B$ passing through. The pure addition compound was then transferred to the tensimeter and a saturation pressure was recorded (*cf.* Table I).

**Table I.** Saturation Pressures of Trimethylboron–Amine Adducts

|  | Base | Saturation pressure of adduct, mm[a] | Temp, °C |
|---|---|---|---|
| 1 | $FCH_2CH_2NH_2$ | 0.13 | 0.0 |
| 2 | $F_2CHCH_2NH_2$ | 1.48 | 0.0 |
| 3 | $F_3CCH_2NH_2$ | Dissociated | 0.0 |
| 4 | $CH_3O(CH_2)_3NH_2$ | <0.01 | 0.0 |
|  |  | 0.16 | 30.0 |
|  |  | 0.86 | 49.9 |
| 5 | $CH_3O(CH_2)_2NH_2$ | <0.01 | 0.0 |
|  |  | 0.62 | 36.0 |
|  |  | 2.70 | 56.0 |
| 6 | $CH_3O(CH_2)_3N(CH_3)_2$ | 0.25 | 0.0 |
| 7 | $CH_3O(CH_2)_2N(CH_3)_2$ | 0.40 | 0.0 |

[a] Experimental error is ±0.03 mm.

**Procedure. Gas-Phase Dissociation Equilibria.** A constant-volume Hg manometer or tensimeter was employed. Except for an increase from *ca.* 260 to 550 ml and minor geometrical changes to obtain improved Hg meniscus readings, the tensimeter was equivalent to that described by Brown and students.[7]

The tensimeter was thermostated in a double-walled fiber-glass-insulated tank filled with either dioctyl phthalate, Dow-Corning Silicon Fluid-200, or water, depending upon the temperature range involved. The temperature was controlled to ±0.05°. Three hours of standing at each new temperature was used to assure complete temperature equilibration. Temperatures were taken with NBS calibrated thermometers.

Pressure measurements were made with a Griffin and George, Ltd., Model S31-950 cathetometer by viewing the Hg meniscus of the tensimeter through insulating dual Pyrex plate-glass windows in the thermostated tank. A machined telescope extension permitted readings at a telescope objective-to-tensimeter distance of 46 cm. A clear field view of the illuminating background and of the horizontal straight-edge silhouette aided accuracy of the pressure measurements. The cathetometer was mounted on a 70-lb welded steel base with three point floor suspension. Readings with a vernier scale were to 0.01 mm. The experimental error of pressure readings was ±0.02 mm.

The dissociation pressure was measured as a function of temperature following essentially the procedure described by Brown, *et al.*[7] In order to assure that reversible equilibria were involved, pressures were recorded as the temperature was both increased and decreased. None of the complexes gave any evidence of irreversible decomposition. In most instances, after the completion of a set of readings with a given addition compound, a few per cent of the addition complex was pumped off and a new set of readings was taken. The agreement between successive values of $\Delta H°$ obtained in this way provided a further check on the purity of the addition complex.

The observed pressure values were corrected to the density of Hg. The pressure values corrected to 0° were then plotted *vs.* temperature on 1-mm graph paper graduated to 0.01 mm and 0.1°. Smoothed curves were obtained and pressure values were taken from the curve at constant-temperature increments to calculate the dissociation constant. Table II lists typical raw data for each complex.

**Table II.** Data Observed in Typical Experiments in Gas-Phase Dissociation Equilibria

| Temp, °C | *P*, mm | Temp, °C | *P*, mm |
|---|---|---|---|
| $CH_3O(CH_2)_3N(CH_3)_2–B(CH_3)_3$ |  | $(CH_3)_3B–NH_2(CH_2)_2OCH_3$ |  |
| 51.35 | 18.61 | 93.6 | 26.21 |
| 52.43 | 18.71 | 99.2 | 27.66 |
| 53.88 | 18.79 | 106.3 | 29.14 |
| 55.14 | 18.89 | 109.1 | 30.05 |
| 56.17 | 18.95 | 115.0 | 31.28 |
| 60.20 | 19.21 | 120.9 | 32.35 |
| 61.51 | 19.34 | 124.8 | 33.04 |
| 62.79 | 19.40 | 129.5 | 33.79 |
| 66.61 | 19.65 | 131.6 | 34.11 |
| 71.51 | 19.99 |  |  |
| $CH_3O(CH_2)_2N(CH_3)_2–B(CH_3)_3$ |  | $(CH_3)_3B–NH_2(CH_2)_3OCH_3$ |  |
| 46.57 | 21.24 | 106.28 | 25.73 |
| 48.00 | 21.35 | 110.23 | 26.71 |
| 49.57 | 21.44 | 114.43 | 27.70 |
| 50.83 | 21.61 | 118.49 | 28.65 |
| 51.41 | 21.69 | 122.88 | 29.62 |
| 52.86 | 21.80 | 125.77 | 30.21 |
| 54.01 | 21.92 | 130.26 | 31.09 |
| 55.04 | 22.01 |  |  |
| 57.78 | 22.04 |  |  |
| 68.03 | 23.03 |  |  |
| $(CH_3)_3B–NH_2CH_2CHF_2$ |  | $(CH_3)_3B–NH_2CH_2CH_2F$ |  |
| 64.32 | 59.68 | 66.09 | 21.77 |
| 68.39 | 61.12 | 75.18 | 30.39 |
| 72.43 | 62.47 | 81.53 | 31.89 |
| 76.15 | 63.60 | 87.31 | 33.04 |
| 79.75 | 64.60 | 92.88 | 34.15 |
| 83.07 | 65.51 | 97.13 | 34.88 |
| 87.03 | 66.54 | 100.54 | 35.35 |
| 91.12 | 67.58 | 106.35 | 36.32 |
| 93.87 | 68.25 | 118.35 | 37.92 |
| 98.19 | 69.24 |  |  |
| 102.29 | 70.20 |  |  |
| $(CH_3)_3B–NH_2CH_2CF_3$ |  |  |  |
| 39.28 | 60.88 |  |  |
| 43.26 | 62.42 |  |  |
| 46.99 | 63.73 |  |  |
| 51.31 | 65.14 |  |  |
| 55.25 | 66.37 |  |  |
| 59.31 | 67.56 |  |  |
| 64.47 | 68.95 |  |  |
| 68.60 | 69.98 |  |  |
| 72.39 | 70.96 |  |  |
| 76.26 | 71.93 |  |  |
| 80.43 | 72.95 |  |  |

**Determination of p*K*.** The pH meter used for the determination of p*K* was the Delta-Matic Model 145, with an expandable scale reading 0.01 pH unit and an automatic sloping calibration. The accuracy of the instrument was checked with Coleman buffers at pH's of 4.00, 9.00, and 10.00 before and after each titration curve. The result was not included in the average if the difference between the measured and buffer pH was greater than ±0.02 pH unit.

The techniques and procedures used essentially followed those outlined by Albert and Serjeant.[23] Reagent grade 0.1 *M* KOH and 0.1 *M* HCl were standardized against potassium acid phthalate. Carbon dioxide free water was prepared by boiling distilled water for 20 min and then bubbling $N_2$ through it until the water reached room temperature. The usual precautions were taken to run the

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(22) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(23) A. Albert and E. P. Serjeant, "Ionization Constants," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapters 2 and 3.

titration under $N_2$ atmosphere. At pH 11.0 the drift was less than 0.05 pH unit over 15 min. A pair of titration curves were made for each sample, adding acid and then back titrating with base. Four to six samples of each amine were studied (in ~0.05 *M* solutions); approximately 15 points were taken for each titration curve.

**Determination of Enthalpy of Ionization.** The calorimetric apparatus and procedures used have been described by Arnett, *et al.*[11] Details of the apparatus used are described elsewhere.[24] The thermistor was calibrated using KCl as a standard.[11] In typical runs, the reproducibility of the deflection factor, *A* (cal/cm), and the ratio of moles of compound added to the total deflection was within ±1%. The measurements were carried out at 25°. Depending upon the reaction vessel, full-scale deflection was equivalent to either 17 or 8 cal. Sample sizes were adjusted to give at least three-fourths full-scale deflection.

The heats of ionization were determined for either the free amines or the amine hydrochloride salt, depending upon the volatility of the amine. The heat of solution in water was determined and then the heat of reaction in 0.3 *M* HCl or KOH. The acid or base was in at least tenfold excess. No correction was made for the heat of dilution during the reaction. The estimated error is between ±0.05 and ±0.10 kcal/mole. Typical data for the measurement of the heat of solution and heat of reaction for methoxyamine hydrochloride in KOH are given in Table III.

**Table III.** Enthalpy of Ionization of Methoxyamine Hydrochloride

| Volts | Time, sec | Displacement,[a] arbitrary units | Wt of sample, g | *A*, displacement/cal[b] | Heat, kcal/mole |
|---|---|---|---|---|---|
| Heat of Solution in Water | | | | | |
| 1.12573 | 36.89 | −45.6 | | $0.245\underline{0}$ | |
| 1.12561 | 39.00 | −48.3 | | $0.244\underline{5}$ | |
| 1.12558 | 39.36 | −49.0 | | $0.243\underline{2}$ | |
| | | 38.1 | 0.2599 | | 2.74 |
| | | 29.6 | 0.2011 | | 2.76 |
| | | 24.4 | 0.1715 | | 2.66 |
| | | | | Av | 2.71 ± 0.04 |
| Heat of Reaction with KOH | | | | | |
| 1.12242 | 40.13 | −50.0 | | 0.2416 | |
| 1.12242 | 36.30 | −45.3 | | 0.2413 | |
| 1.12240 | 34.70 | −42.8 | | 0.2413 | |
| | | −13.5 | 0.0962 | | −2.83 |
| | | −37.2 | 0.2570 | | −2.92 |
| | | −33.0 | 0.2359 | | −2.82 |
| | | | | Av | −2.86 ± 0.04 |

[a] The sign indicates the direction of displacement, positive for heat adsorbed. [b] *Cf.* text.

**Data Analysis for Gaseous Dissociation Equilibria.** The dissociation equilibrium constant (in pressure units) corresponding to the homogeneous gas phase reaction $AB \rightleftarrows A + B$ is given by the relationship

$$K = \frac{\alpha^2}{1 - \alpha^2}P \qquad (3)$$

where the degree of dissociation of the addition complex at temperature *T* (°K) is given by $\alpha = (P - P_0)/P_0$; *P* is the total pressure of the equilibrium system and $P_0$ is the pressure of the undissociated adduct. Two methods of determination of $P_0$ (corrected to 0°) have been employed in this work: (a) the method of successive approximation[10a] and (b) the graphical extrapolation of the pressure *vs.* temperature curve. A direct weighing of the complex (typically ~50 mg) was subject to appreciable error resulting from the distillation of a very small amount of Hg with the sample. Method a was employed with amines 1–5 listed in Table I. Method b was used with amines 6 and 7. A method given by Mangelsdorf[25] also proved to be useful with amines 2 and 3. The Mangelsdorf method, when applicable, gives equivalent results to method a.[26] Methods a and b are discussed below in sequence.

By method a successive approximations of $P_0$ are performed until a $P_0$ value is obtained which gives a linear plot of log *K vs.* 1/*T*. Since in this method it is implicity assumed that $\Delta H°$, the heat of dissociation, is independent of temperature over the temperature interval studied, the validity of this assumption was investigated. One can estimate the approximate temperature dependence of $\Delta H°$ for the type of equilibria studied using the trimethylboron–ammonia complex as a model. A 50° interval was considered, since calculations for a given equilibrium system usually spanned 40° or less.

The heat capacity of ammonia as a function of temperature is known.[27] The geometry and the vibrational spectra of trimethylboron[14,28,29] and of the addition adduct[30] are quite well established. Using the usual statistical mechanical formulation of the gaseous heat capacity, and assuming free internal rotation of the methyl groups, one obtains from $\Delta C_p$, changes in $\Delta H°$ of 301, 312, and 363 cal/mole for 50° intervals centering about 0, 75, and 150°, respectively. Assuming hindered rotation, and considering the torsion frequencies indicated in the literature, one finds that the above changes in $\Delta H°$ may be lower by as much as 100 cal/mole.

Since a change of 0.02 mm in $P_0$ (when $P_0$ is on the order of 10 mm) alters the value of $\Delta H°$ by approximately 300 cal/mole, the experimental error in $\Delta H°$ is near 300 cal/mole. Thus the assumption that $\Delta H°$ is independent of temperature is a reasonable one, at least to this order of approximation.

Method b is applicable if $\alpha$ approaches unity within the experimental temperature range (about 140° was an upper temperature limit with the systems used in this study). When $K \geqslant 0.5$ atm at 100°, the method is practical. The asymptote to the plot of *P vs.* temperature is equal to $2P_0$. For smaller values of *K*, the method lacks sufficient accuracy, but the result serves as a useful initial estimator of $P_0$ for applying method a. Amines 6 and 7 are highly dissociated in the range 50–60° (the total change in *P* was about 0.2 mm), and their adducts are not volatile enough to permit study at lower temperatures. Consequently, method b was used to obtain the $P_0$ value from which approximate *K* values in the range 52–56° were obtained ($\Delta H°$ and $\Delta S°$ were unobtainable). For six runs made with each of the amines, consistent values of *K* were obtained with $P_0$ values which were within ±0.02 mm of the extrapolated value. Since *K* values were obtained for both tertiary amine complexes in the temperature range 52–56°, a temperature of 54° was chosen for comparison of *K* values for all of the Lewis acid–base adducts.

**Data Analysis for Enthalpy of Ionization.** The deflection factor, *A*, is the deflection in centimeters on the recorder caused by adding a known number of calories from an immersion heater in a known time interval

$$A = \frac{IRt}{4.1840d}$$

where *I* = volts, *R* = ohms, *t* = seconds, and *d* = centimeters.

The heat evolved on addition of a known weight of compound to the calorimeter is calculated as follows: heat/mole = *A* (cal/cm) × deflection (cm) × 1/moles of compound added.

The enthalpy of ionization, $\Delta H_i°$, obtained from measurements with the free amine is given by eq 4. The enthalpy of ionization obtained from measurements with the amine hydrochloride is given by eq 5.

$$\Delta H_i° = \Delta H°(\mathrm{HCl}) - \Delta H°(\mathrm{soln}) \qquad (4)$$

$$\Delta H_i° = \Delta H°(\mathrm{H^+ + OH^-}) - [\Delta H°(\mathrm{KOH}) - \Delta H°(\mathrm{soln})] \qquad (5)$$

where $\Delta H_i°$ = enthalpy of ionization, $RNH_3^+ = RNH_2 + H^+$, $\Delta H°(\mathrm{HCl})$ = enthalpy of reaction in HCl solutions, $\Delta H°(\mathrm{KOH})$ = enthalpy of reaction in KOH solutions, $\Delta H°(\mathrm{soln})$ = enthalpy of solution in water, $\Delta H°(\mathrm{H^+ + OH^-})$ = enthalpy of ionization of water. In Table IV are given the enthalpies of ionization obtained in the present work.

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(24) C. S. Giam and R. W. Taft, *J. Am. Chem. Soc.*, **89**, 2397 (1967).

(25) P. C. Mangelsdorf, *J. Appl. Phys.*, 30, 442 (1959).

(26) For a discussion of the application of the Mangelsdorf method, *cf.* Ph.D. Thesis of P. Love, Pennsylvania State University, Jan 1961.

(27) R. F. Haupt and E. Teller, *J. Chem. Phys.*, 7, 925 (1939).

(28) H. Seibert, *Z. Anorg. Allgem. Chem.*, **268**, 13 (1952).

(29) S. E. Stewart, *J. Res. Natl. Bur. Std.*, **56**, 337 (1956).

(30) J. Goubean and H. J. Becker, *Z. Anorg. Allgem. Chem.*, **268**, 1 (1952).

**Table IV.** Enthalpies of Ionization of Amines in Water at 25° ($\Delta H_i°_{25°}$)

| Amine | $\Delta H°_{soln}$[a] | $\Delta H°_{reaction}$[b] | $\Delta$[c] | $\Delta H_i°_{25°}$[d] |
|---|---|---|---|---|
| $CF_3CH_2NH_3^+Cl^-$ | 0.50 | −4.6 | 5.10 | 8.3 |
| $CH_2HCH_2NH_3^+Cl^-$ | 3.81 | 0.18 | 3.63 | 9.77 |
| $CFH_2CH_2NH_3^+Cl^-$ | 3.43 | 1.99 | 1.44 | 11.96 |
| c-$C_3H_6NH_3^+Cl^-$ | 1.00 | −0.44 | 1.44 | 11.96 |
| $CH_3ONH_3^+Cl^-$ | 2.71 | −2.86 | 5.77 | 7.63 |
| $CH_3CH_2NH_3^+Cl^-$ | 2.44 | 2.55 | −0.11 | 13.51 (13.58)[e] |
| Pyridine | −2.35 | | | |
| $CH_3O(CH_2)_3NH_3^+Cl^-$ | −7.26 | | | |
| $HO(CH_2)_3NH_2$ | −3.77 | −16.88 | 13.11 | 13.11 |
| n-$C_3H_7NH_2$ | −7.63 | | | |

[a] Heat of solution of the amine or amine hydrochloride in water. [b] Heat of reaction with KOH or HCl. [c] The sum of the heat of solution and reaction. [d] The value for the enthalpy of ionization of water used is 13.40 kcal/mole: J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67**, 2605 (1963); C. E. Vanderzee and J. A. Swanson, *ibid.*, **67**, 2608 (1963). [e] A. G. Evans and G. D. Hamann, *Trans. Faraday Soc.*, **47**, 34 (1951).

**Table V.** Dissociation Constants for Gaseous Trimethylboron–Amine Complexes

| Temp, °C | K, atm | | | | |
|---|---|---|---|---|---|
| | $H_2NCH_2CF_3$ | $H_2NCH_2CHF_2$ | $H_2NCH_2CH_2F$ | $H_2N(CH_2)_2OCH_3$ | $H_2N(CH_2)_3OCH_3$ |
| 40.0 | 0.330 | | | | |
| 45.0 | 0.470 | | | | |
| 50.0 | 0.676 | | | | |
| 55.0 | 0.960 | | | | |
| 60.0 | 1.32 | | | | |
| 65.0 | 1.76 | 0.315 | | | |
| 70.0 | 2.50 | 0.444 | | | |
| 75.0 | 3.31 | 0.608 | | | |
| 80.0 | 4.49 | 0.833 | 0.102 | | |
| 85.0 | | 1.13 | 0.141 | | |
| 90.0 | | 1.53 | 0.195 | | |
| 95.0 | | 2.05 | 0.273 | | |
| 100.0 | | 2.71 | 0.364 | 0.0391 | |
| 105.0 | | | 0.493 | 0.0595 | |
| 110.0 | | | 0.681 | 0.0779 | 0.0300 |
| 115.0 | | | 0.890 | 0.107 | 0.0419 |
| 120.0 | | | 1.17 | 0.146 | 0.0576 |
| 125.0 | | | | 0.201 | 0.0795 |
| $P_0$ range, mm | 28–36 | 24–29 | 13–18 | 10–13 | 10–12 |
| $\alpha$ range | 0.90–0.99 | 0.89–0.98 | 0.79–0.98 | 0.68–0.92 | 0.66–0.84 |

**Table VI.** Thermodynamic Quantities for Gas-Phase Dissociation of Trimethylboron–Amine Complexes

| Amine | $\Delta F°(54°)$, kcal | $\Delta F°(100°)$, kcal | $\Delta H°$, kcal | $\Delta S°$ (eu) |
|---|---|---|---|---|
| | Primary Amines | | | |
| $CF_3CH_2NH_2$[a] | +0.07 | −1.93 | 14.1 | 42.9 |
| $HCF_2CH_2NH_2$[a] | +1.24 | −0.74 | 15.3 | 43.0 |
| $FCH_2CH_2NH_2$[a] | +2.78 | +0.75 | 16.8 | 42.9 |
| $CH_3OCH_2CH_2NH_2$[a] | +4.48 | +2.40 | 19.4 | 45.5 |
| $CH_3O(CH_2)_3NH_2$[a] | +5.16 | +3.11 | 19.9 | 45.1 |
| $C_2H_5NH_2$[b] | +3.94 | +1.97 | 18.0 | 43.0 |
| n-$C_3H_7NH_2$[b] | +4.07 | +2.09 | 18.1 | 43.0 |
| n-$C_4H_9NH_2$[b] | +4.28 | +2.27 | 18.4 | 43.2 |
| | Tertiary Amines | | | |
| n-$C_4H_9NMe_2$[c] | +0.39 | −1.72 | 15.3 | 45.6 |
| $CH_3O(CH_2)_3NMe_2$[a] | −0.1 ± 0.2 | ... | ... | ... |
| $CH_3O(CH_2)_2NMe_2$[a] | −0.6 ± 0.1 | ... | ... | ... |

[a] From the present work. [b] From H. C. Brown, M. D. Taylor, and S. Sujishi, *J. Am. Chem. Soc.*, **73**, 2464 (1951). [c] From H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953).

**Table VII.** Substituent Effects on Thermodynamic Quantities for Dissociation of Gaseous Trimethylboron Adducts of $RNH_2$ and $RN(CH_3)_2$

| R | $\delta_R\Delta F°(54°)$, kcal | $\delta_R\Delta H°$, kcal | $\delta_R\Delta S°$, eu |
|---|---|---|---|
| | Primary Amines | | |
| n-$C_3H_7$ | (0.00) | (0.0) | (0.0) |
| n-$C_2H_5$ | −0.07 | −0.1 | 0.0 |
| n-$C_4H_9$ | +0.21 | +0.3 | 0.2 |
| $CH_3O(CH_2)_3$– | +1.09 | +1.8 | +2.5 |
| $CH_3O(CH_2)_2$– | +0.41 | +1.3 | +2.1 |
| $F(CH_2)_2$– | −1.29 | −1.3 | −0.1 |
| $F_2CHCH_2$ | −2.83 | −2.8 | 0.0 |
| $F_3CCH_2$ | −4.00 | −4.0 | −0.1 |
| | Tertiary Amines | | |
| n-$C_4H_9$ | (0.00) | (0.0) | (0.0) |
| $CH_3O(CH_2)_3$ | −0.5 | ... | ... |
| $CH_3O(CH_2)_2$ | −1.0 | ... | ... |

## Results

Table V lists the mean value of the dissociation constants for the gas-phase dissociation reaction 1 at 5° temperature intervals. The average deviation from the mean values was 3%. The ranges of $P_0$ values and $\alpha$ values (the fractional dissociation) employed in the several experiments with each base are also listed in Table V.

Table VI summarizes the thermodynamic quantities $\Delta F°(54°)$, $\Delta F°(100°)$, $\Delta H°$, and $\Delta S°$ for dissociation reactions 1 and 1′. The results for the alkylamines are taken from Brown and coworkers (*cf.* Table V). The estimated errors in $\Delta H°$ and $\Delta S°$ are 200–300 cal/mole and 0.7–1.0 eu, respectively. As discussed in the Experimental Section, $\Delta H°$ and $\Delta S°$ to this level of precision may be taken as temperature independent for the interval, say, 65–115°. The mean temperature employed with each amine falls within the range 65–115°.

Table VII gives the substituent effects on the thermodynamic quantities for the gas-phase dissociation reactions 1 and 1′. For primary amines, the reference amine has been taken to be n-propylamine, and the quantities $\delta_R\Delta F°(54°)$, $\delta_R\Delta H°$, and $\delta_R\Delta S°$ refer to the corresponding thermodynamic properties for the following reaction

$$X_nCH_{3-n}CH_2NH_2\text{-}B(CH_3)_3(g) + n\text{-}C_3H_7NH_2(g) = n\text{-}C_3H_7NH_2\text{-}B(CH_3)_3(g) + X_nCH_{3-n}CH_2NH_2(g) \quad (6)$$

For tertiary amines, $n$-$C_4H_9N(CH_3)_2$ is taken as the reference amine and the thermodynamic quantities in Table VI correspond to the reaction

$$X_nCH_{3-n}CH_2N(CH_3)_2\text{-}B(CH_3)_3(g) + n\text{-}C_4H_9N(CH_3)_2(g) = n\text{-}C_4H_9N(CH_3)_2\text{-}B(CH_3)_3(g) + X_nCH_{3-n}CH_2N(CH_3)_2(g) \quad (6')$$

Table VIII lists the thermodynamic quantities for the aqueous ionization reactions 2 and 2′. Values given are from this work and the literature. In the present work the estimated error in $pK_A$ is ±0.02, in $\Delta H°$ ±150 cal/mole, and in $\Delta S°$ ±0.5 eu. Table IX gives the substituent effects on the thermodynamic quantities for the aqueous ionization reactions which are analogous to those of reactions 6 and 6′, *i.e.*

$$X_nCH_{3-n}CH_2NH^+_3(aq) + n\text{-}C_3H_7NH_2(aq) = n\text{-}C_3H_7NH_3^+(aq) + X_nCH_{3-n}CH_2NH_2(aq) \quad (7)$$

$$X_nCH_{3-n}CH_2N(CH_3)_2H^+(aq) + n\text{-}C_4H_9N(CH_3)_2(aq) = n\text{-}C_4H_9N(CH_3)_2H^+(aq) + X_nCH_{3-n}CH_2N(CH_3)_2(aq) \quad (7')$$

**Table VIII.** Thermodynamic Quantities for Ionization of Aqueous Substituted Ammonium Ions[a]

| Amine | $pK_A$ | $\Delta F°(25°)$, kcal | $\Delta H°$, kcal | $\Delta S°$, eu |
|---|---|---|---|---|
| | | Primary Amines | | |
| $CH_3ONH_2$ | 4.60[d] | 6.27[d] | 7.63 | +4.6 |
| $F_3CCH_2NH_2$ | 5.59 | 7.65 | 8.30 | +2.2 |
| $HCF_2CH_2NH_2$ | 7.09 | 9.67 | 9.77 | +0.3 |
| $F(CH_2)_2NH_2$ | 8.79 | 11.99 | 11.96 | 0.0 |
| $c$-$C_3H_5NH_2$ | 9.10[e] | 12.41[e] | 11.96[j] | −0.2 |
| $C_6H_5CH_2NH_2$ | 9.35[f] | 12.75[f] | 13.09[g,j] | +0.1 |
| $CH_3O(CH_2)_2NH_2$ | 9.40 | 12.82 | ... | ... |
| $HO(CH_2)_2NH_2$ | 9.50[b] | 12.96[b] | 12.08[b,j] | −2.9 |
| $CH_3O(CH_2)_3NH_2$ | 9.92 | 13.53 | ... | ... |
| $HO(CH_2)_3NH_2$ | 9.96[h] | 13.59[h] | 13.11[j] | −2.3 |
| $C_2H_5NH_2$ | 10.63[c] | 14.50[c] | 13.58[c,j] | −3.1 |
| $n$-$C_3H_7NH_2$ | 10.53[c] | 14.41[c] | 13.67[c,j] | −2.5 |
| $n$-$C_4H_9NH_2$ | 10.60[c] | 14.51[c] | 13.88[c,j] | −2.1 |
| | | Tertiary Amines | | |
| $CH_3O(CH_2)_2NMe_2$ | 8.96 | 12.21 | ... | ... |
| $CH_3O(CH_2)_3NMe_2$ | 9.36 | 12.75 | ... | ... |
| $n$-$C_4H_9NMe_4$ | 10.00[i] | 13.63[i] | ... | ... |

[a] Results are from the present study unless otherwise indicated. [b] R. G. Bates and G. K. Pinching, *J. Res. Natl. Bur. Std.*, **46**, 349 (1951). [c] A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 34 (1951). [d] T. C. Bissott, R. W. Parry, and D. H. Campbell, *J. Am. Chem. Soc.*, **79**, 796 (1957). [e] Private communication from Professor R. M. Izatt. [f] R. A. Robinson and A. K. Kiang, *Trans. Faraday Soc.*, **52**, 327 (1956). [g] D. L. Levi, W. S. McEwan, and J. H. Wolfenden, *J. Chem. Soc.*, 760 (1949). [h] K. Schwabe, W. Graichen, and D. Spiethoff, *Z. Physik. Chem.* (Frankfort), **20**, 68 (1959). [i] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 544 (1957). [j] J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen have obtained values which differ from those listed by 0.04 to 0.37 kcal, with a mean deviation of 0.17 kcal. We are indebted to Professor Izatt for making available these results in advance of publication.

## Discussion

Hall has reported[31] the correlation of polar effects on the aqueous ionization of substituted alkylammonium ions by the polar substituent parameter, $\sigma_I$.

**Table IX.** Substituent Effects on Thermodynamic Quantities for Ionization of Aqueous Ammonium Ions, $RNH_3^+$, and $RN(CH_3)_2H^+$

| R | $\delta_R\Delta F°$, kcal | $\delta_R\Delta H°$, kcal | $\delta_R\Delta S°$, eu |
|---|---|---|---|
| | Primary Amines | | |
| $n$-$C_3H_7$ | (0.00) | (0.00) | (0.0) |
| $n$-$C_2H_5$ | +0.09 | −0.09 | −0.6 |
| $n$-$C_4H_9$ | +0.10 | 0.21 | 0.4 |
| $HO(CH_2)_3$ | −0.82 | −0.56 | 0.2 |
| $CH_3O(CH_2)_3$ | −0.88 | ... | ... |
| $HO(CH_2)_2$ | −1.45 | −1.59 | −0.4 |
| $CH_3O(CH_2)_2$ | −1.59 | ... | ... |
| $C_6H_5CH_2$ | −1.66 | −0.58 | 2.6 |
| $c$-$C_3H_5$ | −2.00 | −1.71 | 2.3 |
| $F(CH_2)_2$ | −2.42 | −1.71 | 2.5 |
| $HCF_2CH_2$ | −4.74 | −3.90 | 2.8 |
| $F_3CCH_2$ | −6.76 | −5.37 | 4.7 |
| $CH_3O$ | −8.14 | −6.04 | 7.1 |
| | Tertiary Amines | | |
| $n$-$C_4H_9$ | (0.00) | (0.00) | (0.0) |
| $CH_3O(CH_2)_3$ | −0.88 | ... | ... |
| $CH_3O(CH_2)_2$ | −1.42 | ... | ... |

Tables VII and IX disclose a substantially different pattern of entropy effects for the gaseous reaction (6) than for the aqueous ionization (7). For the same amines for which data are available for reaction 6, reaction 7 covers a $\delta_R\Delta S°$ range of 5 eu. The over-all range of $\delta_R\Delta S°$ in Table IX is 8 eu. On the other hand, for the gaseous reaction (6), $\delta_R\Delta S°$ is zero within the experimental error. The two exceptional cases with the methoxy substituents (Table VII) appear to be special and are discussed separately below.

The approximate identity, $\delta_R\Delta F° = \delta_R\Delta H°$ for the gaseous reaction (6) may be taken as evidence of "intrinsic" polar effect behavior,[32] *i.e.*, $\delta_R\Delta F° \cong \delta_R\Delta H° \cong \delta_R\Delta E°$.

Because of the similarity between $B(CH_3)_3$ and $H^+$ adducts, it seems very probable in view of the result obtained with reaction 6 that reaction 7 when measured *in the gas phase* will also give $\delta_R\Delta F° \cong \delta_R\Delta H°$. Consequently, it may be argued that the entropy effects associated with reaction 7 in aqueous solution arise through the polar substituent effect on the hydration of the functional centers, *i.e.*, $>N:$ and $>N\text{-}H^+$. In accord with this conclusion is the fact that one of the important mechanisms of hydration of these two centers is that of hydrogen bonding ($H_2O$ acting as a proton donor and acceptor, respectively). Entropy effects are probably substantial in the polar substituent effect on hydrogen-bond formation.[33]

In terms of Hepler's treatment,[10b] the effects arising from solvation of the reaction centers correspond to substantial "external" contributions to both $\delta_R\Delta H°$ and $\delta_R\Delta S°$. If one further invokes Hepler's $\beta \cong T$ condition (as he applied to the ionization of phenols), there will be a strong compensation at 25° of the "external" $\delta_R\Delta H°$ by "external" $\delta_R\Delta S°$. By this approach, in spite of the variable entropy effects, $\delta_R\Delta F°$ for reaction 7 in aqueous solution may also be taken as a good estimator of "intrinsic" behavior. Confirmation of these conclusions is provided by the relatively precise linear energy (lfe) relationship which exists between reactions 6 and 7. Figure 1, in which the $\delta_R\Delta F°(25°)$ values from Table VIII are plotted *vs.* corresponding $\delta_R\Delta F°(54°)$ values from Table VI, illustrates this lfe relationship. The relationship of Figure 1 offers confirmation that polar substituent parameters, *e.g.*, $\sigma_I$,

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(31) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441, 5444 (1957).

(32) Reference 3, pp 77–78.

(33) E. M. Arnett, private communication.

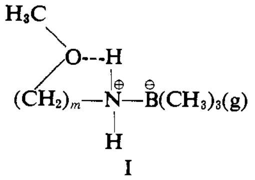
describe "intrinsic" behavior, even though these parameters have been defined by (appropriately restricted) equilibria measured in the condensed phase.

Corresponding $\delta_R\Delta F°(25°)$ and $\delta_R\Delta H°$ values from Table VIII for the aqueous reaction (7) generate a moderately precise linear free-energy–enthalpy relationship (of slope 1.18, $\Delta F°/\Delta H°$). Biggs has obtained a similar relationship for the effects of *ortho*, *meta*, and *para* substituents in the aqueous ionization of anilines.[34] The linear free-energy–enthalpy relationship for reaction 7 and the lfe relationship of Figure 1, of course, mean that there is a linear enthalpy relationship between reactions 6 and 7 which is comparable to Figure 1. Also, the linear free-energy–enthalpy relationship for reaction 7 is intimately involved with solvation entropy effects as pictured in the above discussion. A more detailed discussion will be presented in a subsequent publication.

Although volatility and stability restrictions of the adducts rather severely limit the number and variety of polar substituents which could be investigated in the gaseous reaction (6), the magnitude and nature of the effects which are accommodated by the lfe relationship of Figure 1 imply further generality. However, there is an interesting and instructive deviation for methoxy substituents found in Figure 1. This substituent follows the lfe relationship only in the tertiary amine series (the reasonable assumption is made that the slopes for the primary and tertiary amine series will be approximately the same).

In the primary amine series, the Lewis acid adducts of the methoxyamines are anomalously stronger than the alkylamines (*cf.* positive values of $\delta_R\Delta F°(54°)$ in Table VI). However, as expected from the electron-withdrawing effects of the methoxy substituent, there is greater dissociation of the methoxy- than alkyl-substituted amines for the aqueous reactions 7 and 7′ and for the tertiary amine gaseous reaction 6′. Indeed the effects on $\delta_R\Delta F°(25°)$ are essentially equivalent for the aqueous primary and tertiary amine reactions 7 and 7′. In view of this evidence, it is clear that the anomaly in Figure 1 belongs with the behavior of the primary methoxy-substituted amines in the gaseous dissociation equilibria.

This deviant behavior may be explained on the basis of the formation of a weak internal H bond in the gaseous coordination complexes of the primary methoxy substituted amines (I).



I

The dissociation of I would require more energy than the simple breaking of the N–B bond and explains the relatively great stability observed in only the primary gaseous amine series. Further, because of the constrained motions imposed by the internal H bond, the dissociation of I would be expected to be accompanied by more positive than normal values of $\delta_R\Delta S°$. Indeed, as Table VI shows, the primary methoxy-substituted amines have $\delta_R\Delta S°$ values of 2–3 eu greater than normal.

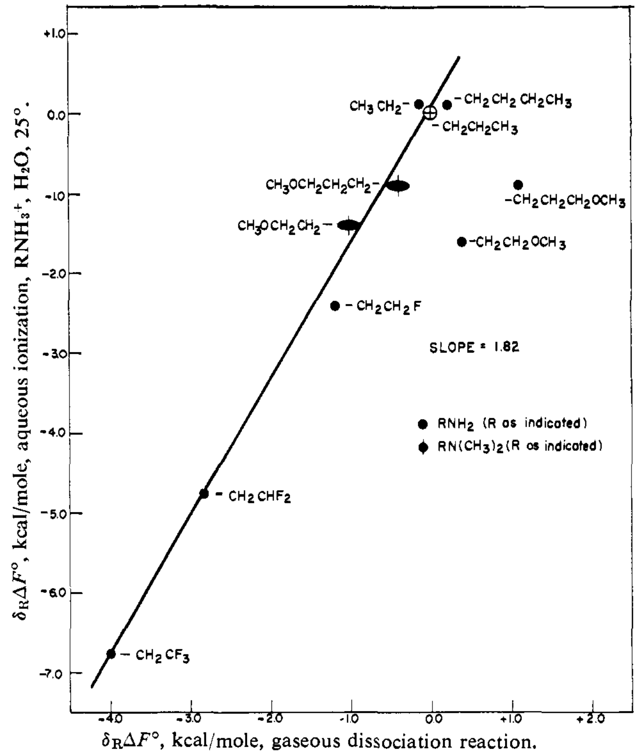


Figure 1. Linear free-energy relationship for β-substituted ethylamines between dissociation of aqueous ammonium ions and gaseous trimethylboron adducts.

The infrared spectra of 2-methoxyethylamine and its trimethylboron adduct were obtained in $CCl_4$ solution. The asymmetric N–H stretching frequency in the amine occurs at 3300 $cm^{-1}$, whereas the corresponding vibration in the complex is at 3240 $cm^{-1}$. The shift of 60 $cm^{-1}$ to lower wave members may be taken as indicative of hydrogen bonding in the adduct,[35] although this evidence is probably not conclusive. The deviation of the observed values of $\delta_R\Delta H°$ (Table VI) from the values expected by the lfe relationship of Figure 1 is 2.2–2.3 kcal and may be taken as an estimate of the strength of the internal H bond in I ($m$ = 2 and 3). Considering the acid strength of the $\gg$N–H proton donor, the relatively weak base strength of the methoxy group, and the fact that the H atom in I would not be linear between O and N, this figure of 2.3 kcal for the H-bond strength seems quite reasonable. The minor deviation of the point for $FCH_2CH_2NH_2$ in Figure 1 is in the direction which may be explained by the formation of a very weak internal F···H–N bond in its $B(CH_3)_3$ adduct.[36] On the other hand, the $CF_3$ (and presumably the $HCF_2$) substituent is too weakly basic[2b] to engage in a similar H-bonding interaction.

The internal H bonding pictured in I is not expected to occur in the aqueous reaction (7) because the $\gg N^+$–H reaction center of the proton adducts will interact instead with the more basic and more abundant water molecules. Consequently, the behavior displayed in Figure 1 shows that gas-phase equilibria (like those in

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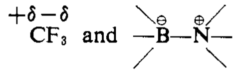
(34) A. I. Biggs, *J. Chem. Soc.*, 2572 (1961).

(35) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958, pp 248–255.

(36) H bonding to alkyl fluorides is known; *cf.* R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

aprotic solvents) by no means necessarily assures "isolated molecule-isolated substituent" behavior. In the present instance, the aqueous ionization equilibria for the primary methoxyamines provides a better measure of "intrinsic" base strength than does the corresponding gaseous dissociation equilibria.

In the gaseous reaction (6) with X = F and $n = 3$, $\delta_R\Delta F°(54°) = \delta_R\Delta H° = -4.0$ kcal. The spontaneity of the reaction may be considered from the standpoint of an electrostatic model as primarily due to the electrical work released upon relief of the dipole–dipole repulsion between the



groups. Polarizability effects and dipolar interactions in $n$-$C_3H_7NH_2$ and its adduct and in $CF_3CH_2CH_2NH_2$ may be considered to be of second-order importance (these effects will in part tend to cancel between the right- and left-hand sides of eq 6).

In order to estimate the electrical work by the electrostatic model, we have made the following simplified calculation. The $^+$N–B$^-$ bond of the adduct is taken as 1.65 Å in length, and unit electronic charges on both atoms are assumed. The $CF_3$ group is taken as a "united" diatomic $^{+\delta}$C–F$^{-\delta}$ substituent with a bond distance of 1.39 Å and with 1.15 esu of charge on each atom.[37] All bond angles in the complex were taken as tetrahedral.

Using the approximation that the distance between dipoles is large compared to the dipolar distances,[38] these assumptions give $\Delta E = -11.5$ kcal/mole if the dielectric constant of a vacuum is used, or $\Delta E = -5.2$ kcal/mole if the apparently more realistic effective dielectric constant of 2.2 is used.[39] This latter figure may be taken as being in satisfactory accord with the experimental result.

Our electrostatic model calculation has many shortcomings. First, the effective dielectric constant does not appear to be a definitive quantity even for a gaseous reaction such as (6). Secondly, some electrostatic interactions (as indicated above) have been neglected, and the relationship used is over-simplified. Thirdly, the accuracy of the atomic charges assumed is in doubt. The unit electronic charge assumed for B and N is surely too large. The measured dipole moment[40] of $F_3B$–$N(CH_3)_3$ (in benzene) is 5.76 D, which suggests about 4.0 esu of charge at B and N.

It is of interest to note that the slope of Figure 1 is 1.82. A value of $1.56 = 1.00/[1.00 - 1.00(1/2.8)]$ is expected by the formal charge method of Branch and Calvin.[41] However, the difference in these two figures may not be used to obtain the actual charges on B and N because the hydration of the reaction centers, $\geqslant\underset{\cdot\cdot}{N}$ and $\geqslant N{-}H^+$, reduces by an unknown amount the effect of a change from the uncharged amine to a unit charge on the ammonium ions.[42,43]

It is also worthy of note that the $\delta_R\Delta F°$ and $\delta_R\Delta H°$ values in Tables VI and VIII which involve the effects of successive substitution of H by F (*i.e.*, $-CH_2CH_2F$, $-CH_2CHF_3$, and $-CH_2CF_3$) are very close to additive. Although a relatively small "saturation effect" seems to be involved, the results definitely do not correspond to the ratio 1:1.16:2.23 which Jenkins has pointed out should be the ratio of the relative effect of multiple substitution from a consideration of the orientation of dipoles.[4d]

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[37] This corresponds to the experimental dipole moment of $HCF_3$(g) of 1.59 D; *cf.* L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

[38] *Cf.* W. Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957, pp 505–507.

[39] Professor C. F. Wilcox has kindly provided the authors with the results of a preliminary but more complete calculation which indicates that an effective dielectric constant of 2–3 is realistic for this system.

[40] From L. G. Wesson; *cf.* ref 35.

[41] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1941, Chapter VI.

[42] A very crude estimate of 10–20% reduction from a change of unit charge is suggested by the results of an F nmr method of measuring the extent of proton transfer in hydrogen-bonded complexes; *cf.* D. Gurka, R. W. Taft, L. Joris, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 5957 (1967).

[43] It is interesting in this connection that J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967), have found the relative electron affinities for a series of aromatic hydrocarbons to be essentially the same in the gas phase and in tetrahydrofuran solution. Also, A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 187–193, has presented a summary of literature data which indicates that the relative ionization potentials for a series of aromatic hydrocarbons is on the order of 20% greater in the gas phase than in acetonitrile solution.