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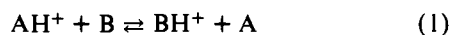
Quantitative Proton Affinities, Ionization Potentials, and Hydrogen Affinities of Alkylamines

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Abstract: Quantitative proton affinities of a series of alkylamines and related alicyclic and saturated heterocyclic amines have been measured by equilibrium ion cyclotron resonance techniques. Adiabatic and vertical photoelectron ionization potentials have been measured for these amines and a set of adiabatic and vertical hydrogen affinities derived from these proton affinities and ionization potentials. The proton affinity changes have been interpreted in terms of a charge-induced dipole model for interaction of the charged nitrogen and the alkyl groups. The proton affinities have also been correlated with ab initio and CNDO/2 molecular orbital calculations. Changes in the hydrogen affinities have been attributed to charge-induced dipole and hyperconjugation interactions in the amine radical cations.

The effect of alkyl substituents on basicity and related molecular properties has long been a source of confusion in physical organic chemistry.¹ Until very recently the vast bulk of these studies had been carried out in solution. With the advent of mass spectrometers capable of studying ion-molecule reactions, however, the determination of relative gas-phase basicities was possible. In one of the first such studies, Munson^{2a} was able to show that the basicities of methyl-substituted amines increased regularly with increasing methyl substitution in the gas phase. The solution basicities, on the other hand, fall in an irregular order.¹ Similar results were obtained by Brauman and Blair^{2b} on the basicities of alkylamines and the acidities of aliphatic alcohols. These early gas-phase studies used reaction bracketing techniques,³ which are suitable for determining relative orders of basicity or acidity. Recently, however, we have developed quantitative ion cyclotron resonance techniques for the measurement of proton transfer equilibrium constants for reactions of type 1, where GB(A) is the gas-phase basic-



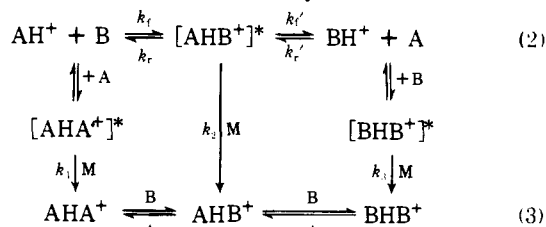
$$\Delta G^0 = \text{GB}(\text{A}) - \text{GB}(\text{B})$$

$$\Delta H^0 = \text{PA}(\text{A}) - \text{PA}(\text{B})$$

ity of A and PA(A) is the proton affinity of A.⁴ A number of such equilibrium studies have now been carried out on a variety of compounds.⁴⁻⁹ These studies allow the relative proton affinities of bases to be determined to an accuracy better than ± 0.2 kcal/mol. Absolute proton affinities are much more difficult to obtain. Promising methods currently being developed include appearance potentials using photoionization,¹⁰ onsets of endothermic reactions using tandem mass spectrometers,¹¹ and empirical correlations of excess kinetic energies of reaction.¹² Accurate relative PA's, how-

ever, are usually as satisfactory as exact absolute values for most interpretational purposes. In this paper we apply the equilibrium proton transfer technique to investigate alkyl substituent effects in a series of alkylamines. The results are used to quantitatively elucidate the nature of alkyl group effects on intrinsic basicities. In addition, a consistent set of ionization potentials (IP's) of these amines has been measured using photoelectron spectroscopy. These IP's, in conjunction with the experimental PA's, allow the accurate determination of the hydrogen atom affinities (HA's) of the amine radical cations. The accurate thermodynamic quantities determined here will be shown to be useful diagnostic parameters in elucidating structure and bonding in ammonium ions and amine radical cations.

The Equilibrium Technique. Equation 1 presents a somewhat simplified picture of the proton transfer equilibrium between a pair of amines. A more realistic picture is given by eq 2 and 3, where M is a third body that stabilizes the vi-



brationally excited proton bound dimer. The proton bound dimers of most alkylamines are long lived (10^{-4} to 10^{-7} sec) and can be readily stabilized in the ICR spectrometer at pressures as low as 1×10^{-4} Torr. Large amounts of proton bound dimers are then observed at the high pressures used to attain the proton transfer equilibrium 1 or 2. In fact, it is possible to measure ligand transfer equilibria 3

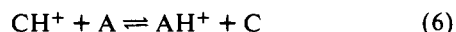
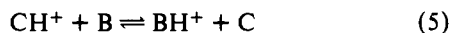
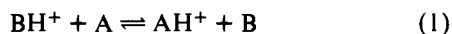
under these conditions.^{4a,13a} The occurrence of such dimerization reactions (or other condensation reactions of AH⁺ or BH⁺) in competition with proton transfer can, potentially, interfere with the attainment of the proton transfer equilibrium in eq 1 or 2. To attain equilibrium, the rate of proton transfer must be greater than the total rate of proton bound dimer formation, especially if

$$k_1[\text{AHA}^+]* \gg k_3[\text{BHB}^+]* \quad (4)$$

The values of the proton transfer and dimerization rates are then required to be sure that equilibrium can be achieved under a given set of experimental conditions. Preliminary calculations based on the kinetic scheme in eq 2 and 3 indicate that difficulties in the attainment of proton transfer equilibria can arise if the dimerization rate terms $k_1[\text{AHA}^+]*$, $k_2[\text{AHB}^+]*$, and $k_3[\text{BHB}^+]*$ become much larger than 5×10^{-24} cm⁶/sec and the proton transfer rate constants become smaller than 2×10^{-10} cm³/sec. For the amines studied here, however, the proton transfer rates appear to all be large enough relative to the dimerization rates to attain equilibrium.^{13b,c} The measurements were limited to equilibrium constants less than ca. 50 ($\Delta G^0 = 2.3$ kcal/mol) though, in order to avoid the problem of a slow reverse rate constant k_r for large K 's.

When the masses of the two ions AH⁺ and BH⁺ are much different, the occurrence of dimerization can cause another complication in the measurement of proton transfer equilibrium constants at high pressures. Since the drift time in the ICR cell is proportional to the magnetic field strength, the reaction times for ions AH⁺ and BH⁺ can be significantly different in the usual ICR experiment, where the magnetic field is scanned at constant observing frequency. Thus, the extent of dimerization is different for the two ions when they are at resonance, and an error may appear in the resulting relative intensity measurements. Errors of this type can be eliminated by operating the spectrometer at constant magnetic field and varying the frequency to obtain resonance. This procedure requires the marginal oscillator detector be calibrated at the two frequencies. Recent development of "Q-Spoiler" devices make this calibration possible.^{13d} All of the data presented in this manuscript have been measured at constant magnetic field with the marginal oscillator detector calibrated in this way. In several instances these equilibrium constants have been measured here on a McIver trapped ion cell^{4a} that operates at low pressures and long reaction times. In all cases these data were consistent with the high-pressure measurements. The PA data quoted here also agree reasonably well with that measured elsewhere by trapped ion^{6a} and high-pressure mass spectral^{7c} techniques.

An important test for the attainment of equilibrium is the consistency of the results of overlapping equilibrium measurements within thermodynamic cycles. Consider, for example, three molecules with relative proton affinities $A > B > C$:



If reactions 1, 5, and 6 represent true equilibria, then eq 7 and 8 should hold. Checks for such consistency have been

$$\Delta G_6^0 = \Delta G_1^0 + \Delta G_5^0 \quad (7)$$

$$K_6 = K_1 K_5 \quad (8)$$

made for all measurements in this study. A more complete

discussion of the approach to and attainment of equilibrium in gaseous ionic systems will be given elsewhere.^{13c}

Experimental Section

All the alkylamines were obtained in the highest purity possible from commercial sources. They were distilled freshly before use and a center cut used for the photoelectron spectra and ICR equilibrium measurements. The samples were degassed by freeze-pump-thaw cycles and checked for impurities by mass spectrometry or low-pressure ICR spectra.

The experiments were performed at 30° on a laboratory built drift cell ion cyclotron resonance mass spectrometer that has been previously described.¹⁴ The ions are formed by electron impact and modulated with a square wave on a grid positioned between the filament and the cell. Electron trap currents were maintained at low levels ($<1 \times 10^{-9}$ A) to minimize differential ion loss at the highest pressures. The absolute pressure is measured on a Baratron capacitance manometer connected directly to the cell vacuum chamber. Ionization energies are kept near threshold to minimize ion chemistry resulting from fragment ions. In a few cases the parent ion is unreactive, and it is necessary to use either fragment ions or a third molecule to protonate the parent neutral.

Each pure component gas is introduced at low pressures (10^{-5} – 10^{-4} Torr) and the mass spectrum scanned to be sure that the parent and fragment ions disappear as the pressure is raised. The spectrum of each amine is scanned separately at higher pressure, ca. 4×10^{-4} Torr, over the relevant mass range to ensure that one compound does not produce ions of masses that might interfere with the ion produced by protonation of the second compound. If each amine is found to be free of interfering peaks, the two amines are introduced into the spectrometer to a total pressure usually in the range of 2 – 8×10^{-4} Torr. These pressures were found to be sufficient to achieve equilibrium between two compounds if the difference in their GB's is 2.3 kcal/mol or less. An important and necessary test to indicate that equilibrium is attained is that K remain constant over widely varying neutral mixes. Each of the ΔG^0 's quoted in this paper represents an average of several neutral gas ratios. Ratios in excess of 10:1 are found to yield inconsistent results under our operating conditions due to the lack of a sufficient number of collisions of the minor component. All results here have been determined on mixes of 10:1 or less and almost all results on mixtures of 4:1 or less. All experiments were performed at constant magnetic field using Q-spoiler calibration of the marginal oscillator.^{13d}

Ionization potentials were measured on a Perkin-Elmer PS-18 photoelectron spectrometer. The resolution was approximately 30–40 mV at 12 eV. The vertical IP's (vIP's) were taken as the maximum of the first band except where vibrational structure is well resolved. In those instances the maximum of the most intense vibrational component was used. The adiabatic IP's (aIP's) were measured by two methods. In one case, the IP's were obtained by straight line extrapolations tangent to the peak at half-height to the baseline. In the second case, the onset of the first band was used. The precision obtained by either method was within ca. ± 2 kcal/mol. The aIP's determined by extrapolated tangents averaged 14 ± 2 kcal/mol lower than the corresponding vIP's, and those determined at onset averaged 18 ± 2 kcal/mol lower than the respective vIP's. Although assignment of the onset is subject to a ± 2 kcal/mol error, these values were used in Table I in view of their relative consistency with the extrapolated tangent and the similarity in peak shape and width for alkylamines.¹⁵ The difference between onset and extrapolated aIP's (4 kcal/mol) is greater than the thermal energy spread of the photoelectrons analyzed (0.05 max eV \equiv 1.2 kcal/mol), and consequently the onset values probably correspond more closely to the true aIP's.

Each spectrum was individually calibrated with xenon and argon mixed with the alkylamine sample and measured together. The estimated accuracy of these determinations is ca. ± 0.02 eV (0.5 kcal/mol) for the vIP's and ca. ± 0.1 eV (2 kcal/mol) for the aIP's. The error in the vIP's is the result of the usually broad peaks of unresolved vibrational structure. Only a few of the amines studied have shown any observable fine structure. The amines showing vibrational structure are ammonia (970 cm⁻¹), methylamine (890 cm⁻¹), ethylamine (820 cm⁻¹), 2,2,2-trifluoroethylamine (830 cm⁻¹), and quinuclidine (800 cm⁻¹).

Table I. Proton Affinities, Adiabatic and Vertical Ionization Potentials, and Hydrogen Affinities of Aliphatic Amines at 25°C^a

Amine	GB ^{b,i}	PA ^{c,i}	aIP	aHA ⁱ	vIP	vHA ⁱ
NH ₃	198 ± 3	207 ± 3	234.3 ^d	127 ± 3	250.2	143 ± 3
MeNH ₂	210.0	218.4	205	109	222.8	127.6
EtNH ₂	213.0	221.4	202	109	218.4	126.2
<i>n</i> -PrNH ₂	214.4	222.8	197	106	216.8	126.0
<i>i</i> -PrNH ₂	215.3	223.7	199	109	214.9	125.0
<i>n</i> -BuNH ₂	214.9	223.3				
<i>i</i> -BuNH ₂	215.4	223.8	196	106	214.5	124.7
<i>s</i> -BuNH ₂	216.4	224.8	195	106	214.5	125.7
<i>t</i> -BuNH ₂	217.3	225.7	195	107	213.4	125.5
Neopentylamine	216.1	224.5	197	108	213.3	124.2
<i>tert</i> -Amylamine	218.2	226.6	195	108	212.2	125.2
Me ₂ NH	216.6	224.8	188	99	205.9	116.9
MeNH ₂ Et	219.1	227.3				
Et ₂ NH	221.2	229.4	181	96	199.0	114.8
<i>n</i> -Pr ₂ NH	223.2	231.4	179	96	196.9	114.7
<i>i</i> -Pr ₂ NH	225.0	233.2	175	94	193.7	113.3
<i>n</i> -Bu ₂ NH	224.3	232.5				
<i>i</i> -Bu ₂ NH	224.8	233.0				
<i>s</i> -Bu ₂ NH	227.0	235.2				
<i>tert</i> -Amyl- <i>tert</i> -butylamine	229.0	237.2	180	103	185.6	109.2
Me ₃ N	220.8	228.6	179	94	196.7	111.7
Et ₃ N	227.7	235.5	164	86	186.3	108.2
<i>n</i> -Pr ₃ N	229.9	237.7	162	86	182.6	106.7
<i>n</i> -Bu ₃ N	231.3	239.1	161	86	182.2	107.7
Me ₂ NEt	223.1	230.9				
MeNEt ₂	225.5	233.3	171	90	189.6	109.3
<i>n</i> -PrNEt ₂	228.4	236.2				
Pyrrolidine	220.4	228.6			202.2 ^f	117.2
Piperidine	221.5	229.7	181	97	199.7	115.8
<i>N</i> -Methylpyrrolidine	224.4	232.2			193.9 ^f	112.5
<i>N</i> -Methylpiperidine	225.4	233.2			191.2 ^f	110.8
1,4-Diazabicyclo[2.2.2]octane	225 ^e	233 ^e			198.0 ^g	117
Quinuclidine	227.9	235.7	173	95	173.4 ^h	92
Cyclohexylamine	217.2	225.6	193	105	185.6	107.7
					211.2	123.2

^a All values in kcal/mol. ^b GB's measured relative to methylamine (210.0 kcal/mol). ^c PA's calculated from GB's by correction for symmetry (see text). ^d See ref 26. ^e Semiquantitative value by double resonance. ^f See ref 27b. ^g Average value of the vIP's of the first two bands caused by splitting of the two nitrogen lone pairs. ^h Maximum of the first band. ⁱ Recent results indicate that PA(NH₃) = 202 kcal/mol and that the values for GB, PA, and HA of all the other amines should be lower by ca. 7 kcal/mol; see ref 12.

Results

The gas-phase basicities of a large number of alkylamines have been determined relative to methylamine. These results are listed in Table I. The data were obtained from a large number of equilibrium measurements between pairs of alkylamines. The data were all checked for self-consistency, and numerous multiple overlaps were obtained. Figure 1 summarizes some of the overlap data within the alkylamines. Overlap data with numerous other compounds were used also. The maximum deviation of the multiple overlap data is ±0.2 kcal/mol with the usual deviations less than 0.1 kcal/mol. The accuracy of the assigned relative GB's is expected to be better than ±0.2 kcal/mol. The proton affinities were calculated from the experimental GB's by assuming all entropy effects were negligible¹⁶ except for the entropy of the free proton and the entropy due to symmetry differences in the amines and ammonium ions. The free proton entropy is determined to be 26.01 eu from the Sackur-Tetrode equation. The difference in entropy due to symmetry is calculated¹⁷ from eq 9, where σ is the symmetry number for the ion or molecule and R is the ideal gas constant.

$$\Delta S_{\text{sym}}^0 = R \ln (\sigma_{\text{BH}^+} / \sigma_{\text{B}}) \quad (9)$$

The assignment of absolute values of PA's is somewhat arbitrary, since none of the alkylamines has a precisely determined experimental value. We have chosen to make our data relative to a PA for ammonia of 207 kcal/mol, in line with a semiempirical determination of Haney and Franklin and from crystal lattice energy calculations.¹² Preliminary

results from these laboratories and others^{6a,7e} establish the ammonia-methylamine gap to be 9–11 kcal/mol. This region of the proton affinity scale is particularly difficult to study experimentally, however, due to a paucity of convenient bridging compounds. We have also estimated the ammonia-methylamine gap using an empirical method. In Figure 2, PA's are plotted vs. vertical IP's for the methylamines. Straight line extrapolations of the primary, secondary, and tertiary methyl-, ethyl-, and *n*-propylamines yield a value of ca. 11 kcal/mol for the difference between the ammonia and methylamine PA's. A recent absolute PA of 222.5 ± 2.0 kcal/mol for aziridine has been established from the appearance potential of the aziridinium ion.¹⁸ This value suggests an assignment of ca. 13.7 ± 2.0 kcal/mol difference between ammonia and methylamine, since we have accurately found the PA of aziridine to be 1.9 kcal/mol higher than methylamine. We have chosen a value of 210.0 kcal/mol for the GB of methylamine and 218.4 kcal/mol for the PA as a compromise between these various experimental data and empirical correlations. Further support for this assignment comes from theoretical calculations. In Figure 3 experimental PA's are plotted vs. ab initio theoretical values^{19,20} and CNDO/2 values. An excellent straight line is obtained in the ab initio comparison indicating the 11.4 kcal/mol value assigned for the ammonia-methylamine PA difference is probably close to correct (vide infra). A similar straight line fit is obtained with CNDO/2 calculations although more scatter is apparent. A better assignment of the absolute and relative values of ammonia and methylamine will require further experiments.¹²

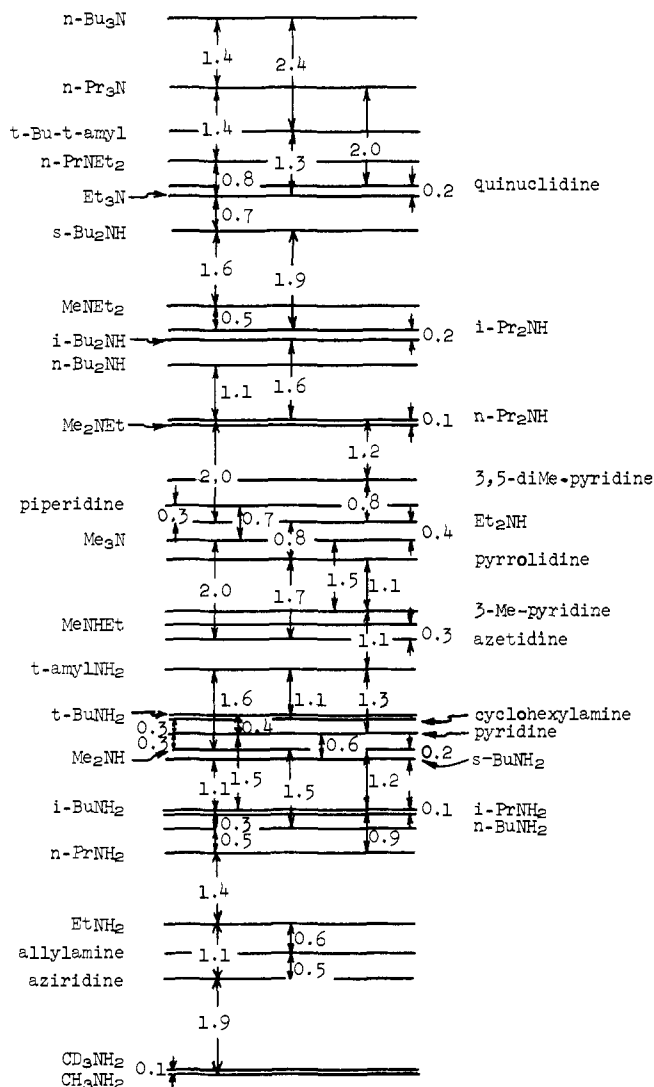


Figure 1. Experimental ΔG^0 's (ΔG_B 's) between alkylamines at 25°, showing internal consistency of overlapping.

A complete set of vertical and adiabatic IP's has been measured by photoelectron spectroscopy, and these data are summarized in Table I together with the respective PA's and other derived thermodynamic data.

Discussion

Alkyl Substituent Effects. The effect of alkyl substituents in the solution phase has been the subject of a variety of explanations.¹ The intrinsic effect of methyl substituents can be evaluated from gas-phase proton affinity data to eliminate complicating solvation effects. Qualitative proton affinities of methyl amines have shown that the anomalous order of their basicities in solution ($\text{NH}_3 \approx \text{Me}_3\text{N} < \text{MeNH}_2 \approx \text{Me}_2\text{NH}$) becomes quite regular in the gas phase ($\text{NH}_3 < \text{MeNH}_2 < \text{Me}_2\text{NH} < \text{Me}_3\text{N}$).^{2a} This intrinsic order is in accord with the electron-releasing "inductive effect" often attributed to alkyl groups. That methyl groups are electron releasing inductively is not generally supported, however.^{2b,c} From the qualitative order of alcohol and amine acidities measured in the gas phase,^{2b,c} it becomes clear that alkyl groups can stabilize negative ions as well as positive ions. Thus the intrinsic acidities of alcohols is $t\text{-BuOH} > \text{EtOH} > \text{MeOH} > \text{H}_2\text{O}$, although the order is the opposite of this in solution.^{2b} Brauman and Blair have suggested that a polarizability effect could explain these intrinsic basicities and acidities in a way that accounts for the

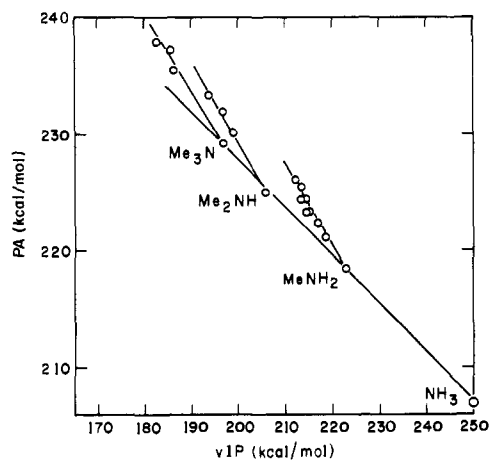


Figure 2. Plot of PA vs. vIP for alkylamines.

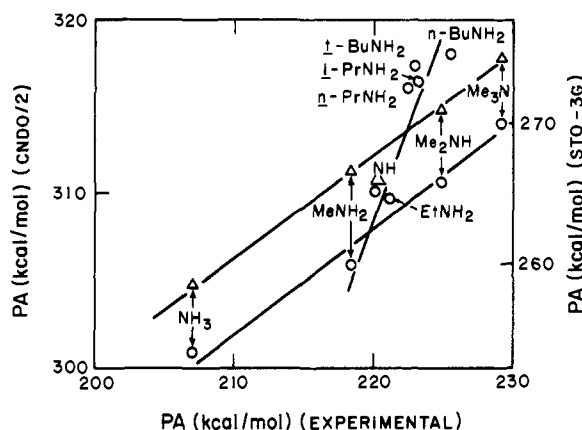


Figure 3. Plot of experimental PA vs. ab initio calculated PA (Δ) and CNDO/2 calculated PA (O).

ability of an alkyl group to stabilize both positively and negatively charged centers.²¹

A mechanism by which a polarizable alkyl group can stabilize a charge involves a charge-induced dipole interaction. The energy of interaction, U , between a neutral polarizable group and a point charge, q , depends on the polarizability, α , of the group and the distance of separation, r (eq 10), but

$$U = -\alpha q^2 / 2\epsilon r^4 \quad (10)$$

is independent of the sign of the charge, where ϵ is the effective dielectric constant of the medium. The proton affinities reported in Table I now provide the basis for a quantitative test of this model for alkyl group stabilization effects.²¹ Methyl substitution at successively greater distances from nitrogen results in a rapid attenuation in ΔPA (see Table II) as expected from a $1/r^4$ dependence of ΔPA on the distance between the charged nitrogen and each additional methyl substituent. The conformation of the hydrocarbon chain used was an extended one in each case.

The charge stabilization calculated from eq 10 is roughly in accord with the observed differences in proton affinities resulting from methyl substitution. These comparisons then show that a polarizability effect is of the proper magnitude to explain the observed proton affinities of higher alkylamines. The effective dielectric constant which best fits these experimental data is between 1 and 2. That only extended conformations and no gauche conformations were used in these calculations may explain the fact that the experimental ΔPA 's in Table II fall off less rapidly than predicted from these calculations.²²

As another test of the model, the effect of adding methyl

Table II. Comparison of Experimental ΔPA 's for Some Primary Alkylamines with Values Calculated from Electrostatics (eq 10)^a

Amine	$r, \text{\AA}^b$	$\Delta E_{\epsilon=1}^c$	$\Delta E_{\epsilon=2}^c$	ΔPA_{exptl}
CH_3NH_2	1.47	19.2 ^d	9.6 ^d	11
$\text{CH}_3\text{CH}_2\text{NH}_2$	2.49	5.8	2.9	3.0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	3.80	1.2	0.6	1.4
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	4.95	0.5	0.2	0.5

^a All energies in kcal/mol. ^b Distance from a point charge at nitrogen to the methyl carbon atom as measured from Dreiding models in a staggered, extended conformation. ^c These values are the differences in the interaction energy calculated from eq 10 for replacement of a hydrogen with a methyl group at appropriate distances, r , from nitrogen. The polarizability of the methyl group used was $2.2 \times 10^{-24} \text{ cm}^3$ and that used for the hydrogen atom was $0.4 \times 10^{-24} \text{ cm}^3$. These group polarizabilities are consistent with the polarizabilities in Table III. They were derived from the polarizabilities of methane ($2.6 \times 10^{-24} \text{ cm}^3$) and hydrogen ($0.8 \times 10^{-24} \text{ cm}^3$); see G. W. Castellan, "Physical Chemistry", Addison-Wesley, Reading, Mass., 1964, p 481-483. ^d These values are very sensitive to r and are not quantitatively very meaningful.

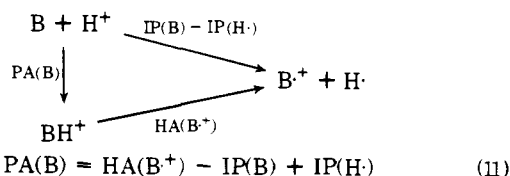
Table III. Additivity of ΔPA 's for Methyl Substitution at the α and β Positions in Alkylamines

Amine	PA ^a	ΔPA	$\alpha \times 10^{24}, \text{ cm}^3/\text{mol}$ ^b	$\Delta \alpha \times 10^{24}, \text{ cm}^3/\text{mol}$
MeNH_2	218.4		3.8	
EtNH_2	221.4	3.0	5.8	2.0
<i>i</i> -PrNH ₂	223.7	2.3	7.8	2.0
<i>t</i> -BuNH ₂	225.7	2.0	9.6	1.8
EtNH_2	221.4		5.8	
<i>n</i> -PrNH ₂	223.8	1.4	7.7	1.9
<i>i</i> -BuNH ₂	223.8	1.0		1.8
Neopentylamine	224.5	0.7	11.3	1.8

^a All PA's in kcal/mol. ^b Calculated from the Clausius-Mosotti equation and refractive indices.

substituents to α and β carbon atoms is summarized in Table III. As expected from a polarizability model, successive additions of methyl substituents at a fixed distance from the charge at nitrogen results in nearly equal stabilizing effects in the proton affinities. This group additivity makes it possible to estimate with good accuracy the PA of virtually any alkylamine simply by treating the overall PA as a sum of contributions due to each carbon atom at various positions in the chain. From examination of all of the data on hand, we have assigned approximate PA contributions, or substituent factors, to the α , β , and γ carbon atoms in an alkyl chain. Substitution of a methyl group on the carbon α to nitrogen increases the PA by ca. 2.1 kcal/mol, while at the β and γ positions methyl groups increase the PA by 0.9 and 0.5 kcal/mol, respectively. Quantitatively similar, but smaller, methyl stabilizing effects have been observed in gas-phase measurements of alcohol acidities.^{6d}

Quantitative Hydrogen Affinities. The PA's of alkylamines have been interpreted above in terms of changes in polarizabilities as a function of alkyl substitution. An alternative analysis of such substituent effects involves the study of ionization potentials (IP's) of the nitrogen lone pair. The PA and IP are related to each other as shown in the thermodynamic cycle below and in eq 11.²³ When the IP(B) and



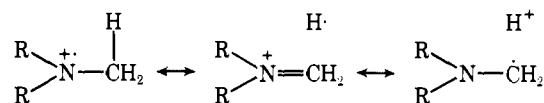
PA(B) are known, then the hydrogen atom affinity, HA-

(B⁺), can be calculated. The hydrogen affinity is equal to the homolytic bond dissociation energy of the $\equiv \text{N}^+ - \text{H}$ bond in the protonated amine. For alkylamines, the neutral amine and the ammonium ion should have nearly identical hybridization and geometry at nitrogen (sp^3 tetrahedral). The most readily interpretable HA's are, then, the vertical HA's (vHA's) derived from measured vertical ionization potentials (vIP's) since in this case there is no change in geometry between B, BH^+ , and B^+ . The most favorable ground state geometry, however, for the radical cations of alkylamines is not tetrahedral but planar.^{15,24} Adiabatic ionization potentials (aIP's) and derived aHA's represent ground state values of these properties and are useful thermodynamic quantities. When studying substituent effects, however, they may be less useful than vIP's and vHA's because of the geometry changes noted above.²⁵

Only a limited number of vIP's of alkylamines have been reported in the literature.²⁶ Of these, only two or three amines have been studied by more than one investigator, and discrepancies of up to 1.4 kcal/mol (0.06 eV) are encountered. Consequently, we have measured a set of accurate and self-consistent IP's to yield accurate HA's. Our vIP's agree well with those in the literature.²⁶ The determination of aIP's, on the other hand, presents difficulties.^{27,28} The aIP's determined in this work for the alkylamines are consistently ca. 18 ± 2 kcal/mol lower than the corresponding vIP's in contrast to certain of the aIP's reported by Watanabe.²⁸ This internal consistency suggests that our photoelectron aIP's may be more accurate than those reported by Watanabe.

Alkyl substitution affects PA, IP, and HA values differently. These differences can be seen graphically in Figure 2 where PA is plotted vs. vIP. Three very nearly parallel lines of slope ca. -0.6 result for the primary, secondary, and tertiary amines. If the PA and vIP are equally affected by alkyl substitution, the slope of the lines in Figure 2 would be unity and the vHA would be constant within a particular primary, secondary, or tertiary series. Instead the vHA decreases slightly with alkyl substitution within each series.

The strongest substitution effects operate when substitution occurs directly at nitrogen. The methyl-substituted amines are found to fall on a straight line of slope ca. -0.42 . Larger HA changes then occur with methyl substitution at nitrogen than with substitution at more remote sites. These changes can be conveniently rationalized in terms of hyperconjugative stabilization of the alkyl-substituted radical cations.



The decrease in HA between methylamine and ethylamine might be explained by assuming that C-C hyperconjugation is more effective than C-H hyperconjugation, but the HA's unexpectedly continue to decrease with more remote methyl substitution. The linear PA vs. IP plots in Figure 1 indicate that methyl stabilization of the radical cations is greater than for the ammonium ions and shows the same trends within a series of primary, secondary, or tertiary amines. Thus, to the extent that the radical and cationic sites can be treated separately, they appear to be stabilized in a quantitatively similar fashion by all alkyl substituents within a series. In comparisons between primary, secondary, and tertiary amines, however, there is additional stabilization of the radical cation site by the hyperconjugation mechanism above.

Since the difference in energy between vIP's and aIP's is virtually constant for the alkylamines, the aHA's behave in

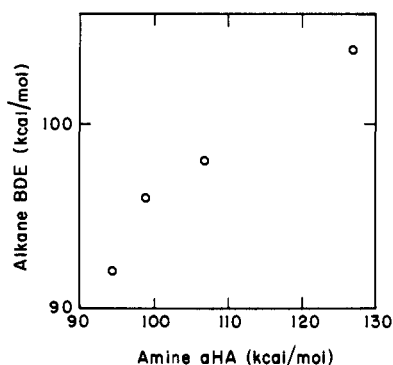


Figure 4. Plot of BDE (R_3C-H) vs. aHA of amine radical cations [$BDE(R_3N-H^+)$].

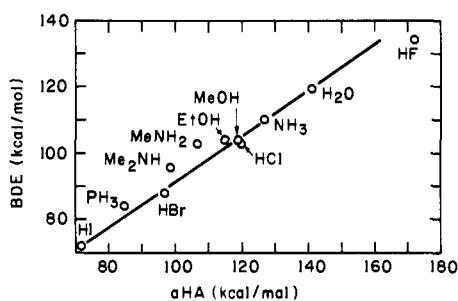


Figure 5. Plot of BDE($H-X$) vs. aHA of $HX\cdot^+$ [$BDE(HX-H^+)$].

a manner very much like the vHA's. Apparently, the relaxation energies of all of these amine radical cations from the tetrahedral to planar geometries are similar.¹⁵ A comparison of aHA's of the amine radical cations with the bond dissociation energies (BDE) of isolectronic alkanes is given in Figure 4.²⁹ The near linearity of the aHA vs. BDE plot indicates that a similar hyperconjugative stabilization mechanism is operative for the amine radical cations and for the alkane radicals, although the aHA's are all higher than the BDE's.³⁰ The nearly linear relationship between amine HA and isolectronic alkane BDE may be useful in estimating BDE's for hydrocarbons that do not lend themselves to direct experimental measurement. Such linear plots of BDE's are also observed for pairs of compounds of the type $H-X$ and $H-X-H^+$, where again the charged species has the higher dissociation energy (see Figure 5).^{23,30}

Molecular Orbital Calculations. These accurate proton affinity data should be useful in testing present quantum mechanical methods. We have carried out a number of semiempirical quantum mechanical calculations on the simpler alkylamines using the CNDO/2 approximation.³¹ Previous work has shown that the CNDO/2 method is qualitatively successful in correlating relative gas-phase acidities^{32,33} of alcohols and basicities of amines.³³

Using standard geometries, Lewis³³ calculated the PA's of ammonia and the methylamines using a CNDO/2 program. We have calculated PA's of some primary amines and the methylamines by varying some C-N, C-C, C-H, and N-H distances to find a set of geometry parameters that would give the minimum energy structures.³⁴ The results of these PA calculations are plotted against experimental PA's in Figure 3. Interestingly, the primary amines appear to correlate on a different line than the methylamines. Hehre and Pople¹⁹ have done ab initio STO-3G calculations on ammonia and the methylamines, and their calculated PA's correlate well with our experimental PA's (Figure 3). The slope of that line (0.77) is close to that from our CNDO/2 calculations (0.6) for the methylamines, but the STO-3G calculations are closer to the correct absolute PA's.

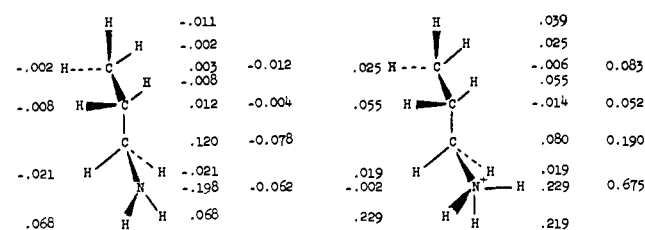
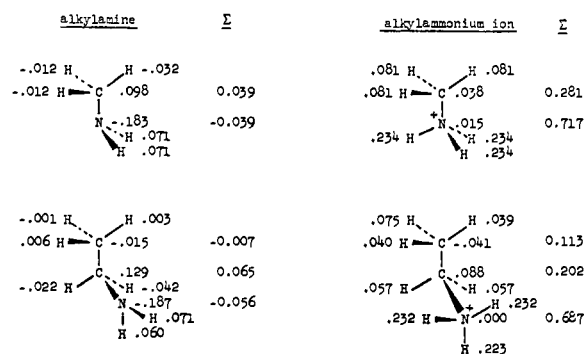


Figure 6. Charge densities from CNDO/2 calculations on alkylamines and alkylammonium ions. Sums (Σ) indicate the total charge on the C or N and the attached H's.

Table IV. Charge Densities from CNDO/2 Calculations on Alkylammonium Ions

Ion	Total charge on $-NH_x^+$	Ion	Total charge on $-NH_x^+$
NH_4^+	1.00	<i>i</i> - $BuNH_3^+$	0.67
$MeNH_3^+$	0.72	<i>i</i> - $PrNH_3^+$	0.65
$EtNH_3^+$	0.69	<i>t</i> - $BuNH_3^+$	0.63
n - $PrNH_3^+$	0.68	$Me_2NH_3^+$	0.49
n - $BuNH_3^+$	0.67	Me_3NH^+	0.30

The CNDO/2 energies of the highest occupied molecular orbitals of these amines have also been found to correlate linearly with the experimental IP's in Table II. For $MeNH_2$, Me_2NH , and Me_3N , the slope of this correlation is near 1.0, but the IP calculated for ammonia is too high. The IP's of the primary amines are somewhat low (slope = 2). The absolute values of the IP's, like the PA's, are all calculated to be about 50% too high. The core-level binding energies of amines have also been correlated with proton affinities and explained in terms of polarization effects on the relaxation energies.³⁵

In the series NH_3 , $MeNH_2$, Me_2NH , Me_3N , the charge on nitrogen and its attached hydrogens decreases in a nearly linear fashion with PA, while the series of primary amines show smaller, but still linear, changes in charge density with PA (Table IV). Charge densities in some representative ammonium ions are shown in Figure 6.³⁶ It can be seen that a large fraction (19–28%) of the positive charge is delocalized onto each adjacent CH_2 or CH_3 group. Methyl or methylene groups further away from the nitrogen assume less positive charge as expected. The individual atomic charge densities of the carbons and hydrogens reveal a general trend in which the C-M bonds become polarized on charging the nitrogen such that the carbons actually become more negative.³⁷ The amount of positive charge on the hydrogens is much larger, however, than the increase in negative charge at carbon. This may result from large C-C bond polarizations which, in effect, shift electron density to the nitrogen via delocalized molecular orbitals. Thus, the mechanism of the charge stabilization appears from these calculations to be a combination of C-H and C-C bond po-

larization, in accord with the classical theoretical approach based on the polarization interaction in eq 10.

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