series. However, the corresponding term $\delta_R(T\Delta S°)_s(B)$ for the free bases is very sensitive to the size and number of alkyl groups and dominates the structural effect on entropy of ionization in solution, $\delta_R(T\Delta S°)_i(w)$. Thus, contrary to Trotman-Dickenson's proposal, the decreasing entropy of ionization in going down the series NH_3, primary, secondary, tertiary, is caused primarily by an overwhelmingly large decreasing entropy of solution of the amines rather than to an increasing entropy of solution for their ions.

(c) The heats of solution of the amines become increasingly exothermic, as the carbon content is increased, and are apparently much more dependent on hydrophobic structure-making effects[15–17] than on hydrogen bonding to or from the amino group.[7] Hydrophobic effects assert themselves less strongly in the corresponding $\delta_R\Delta H_s°(BH^+)$ for the primary ions. However, the same increasingly endothermic progression of NH_3 (0) < primary (~9) < secondary (~15) < tertiary (~21) is found for the methyl and ethyl series. The decreasing increments 9 > 7 = 7 kcal/mol are of the correct magnitude to be attributed to hydrogen bonding.[8,18] Some contribution from Born charging energy due to changing ion size must be involved, but the effect of changing alkyl groups within a primary, secondary, or tertiary series is so small compared to differences between series that we feel safe in attributing the effect primarily to hydrogen bonding.

(d) Finally, we note that a complete analysis of these ionization data still does not lead to a simple interpretation of the anomalous order. Most of the contributing thermodynamic properties change in a reasonable and orderly way. The inverted order of aqueous base strength arises from slight differences in the rate of change of the thermodynamic properties in response to progressive alkyl substitution.

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* Address correspondence to this author at the University of Pittsburgh.

Edward M. Arnett,* Frederick M. Jones, III
M. Taagepera, W. G. Henderson
J. L. Beauchamp, D. Holtz, R. W. Taft
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213
Mellon Institute of Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213
Department of Chemistry, University of California
Irvine, California 92664
Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109
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Quantitative Relative Gas-Phase Basicities of Alkylamines. Correlation with Solution Basicity[1]

Sir:

While many relative gas-phase basicities have been established in recent years, the inherently qualitative nature of these data make a precise evaluation of the factors governing gas-phase basicity impossible. We have described new equilibrium techniques for determining accurate quantitative relative gas-phase basicities of amines.[2,3] Gas-phase basicities of alkylamines determined by these techniques are reported here and correlated with ionization potentials to provide quantitative relative hydrogen affinities. These data provide a basis for detailed quantitative interpretation of the factors governing basicity of alkylamines in the gas phase and in solution.

We define the gas-phase basicity (GB) of B as the negative of the free energy ($\Delta G°$) for reaction 1, while the proton affinity (PA) is the negative of the enthalpy ($\Delta H°$) for reaction 1. The hydrogen affinity (HA)

$$B + H^+ \rightleftharpoons BH^+ \qquad (1)$$

$$B\cdot^+ + H\cdot \rightleftharpoons BH^+ \qquad (2)$$

$$PA(B) = -IP(B) + HA(B\cdot^+) + IP(H\cdot) \qquad (3)$$

of $B\cdot^+$ is the negative enthalpy for reaction 2 and is equivalent to the bond dissociation energy of BH^+. From these definitions eq 3 readily follows. From our PA's and from known adiabatic IP's,[4] accurate relative hydrogen affinities can be calculated for the first time (Table I).

Table I. Gas-Phase Basicities (GB) and Derived Thermodynamic Data for Alkylamines[a]

Amine	GB[a]	PA[b]	IP[d]	HA
Ammonia	[198 ± 3]	[207 ± 3][c]	234.1	127 ± 3
Methylamine	[209.8][a]	[218.4][a]	206.8	111.6
Ethylamine	212.5	221.1	204.3	111.8
n-Propylamine	213.7	222.3	202.5	111.2
n-Butylamine	214.3	222.8	200.9	110.1
Isobutylamine	214.6	223.2	200.6	110.2
Isopropylamine	214.7	223.3	201.1	110.8
sec-Butylamine	215.8	224.4	200.6	111.4
tert-Butylamine	216.8	225.4	199.2	111.0
Dimethylamine	216.6	224.9	190.0	101.3
Diethylamine	221.8	230.1	184.7	101.2
Di-*n*-propylamine	223.6	231.9	180.8	99.1
Di-*n*-butylamine	224.4	232.7	177.3	96.4
Diisopropylamine	226.0	234.3	178.3	99.0
Trimethylamine	221.3	229.1	180.3	95.8
Triethylamine	228.0	235.8	173.0	95.3
Tri-*n*-propylamine	230.3	238.2	166.7	91.3

[a] All values in kcal/mol. GB's were measured relative to methylamine (209.8 kcal/mol). Multiple overlap of $\Delta G°$'s established errors in relative GB's at 0.2 kcal/mol (see ref 3). [b] PA's calculated from GB's by correction for symmetry and the entropy of H^+ [A. P. Altshuller, *J. Amer. Chem. Soc.*, **77**, 3480 (1955)]. [c] A plot of PA *vs.* IP (Figure 1) was used to approximate ΔPA for NH_3 and CH_3NH_2. Absolute PA of NH_3 taken as 207 ± 3 kcal/mol [M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2029 (1969)]. [d] Reference 4.

Basicities of amines in solution have presented difficulties in interpretation for many years.[5] Munson

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(1) Supported by NSF Grant No. GP-1628 and ACS-PRF Grants No. 5031-AC4 and 5993-AC5.

(2) Both high pressure and trapped ion techniques provide equilibrium constants for proton-transfer reactions (ref 3).

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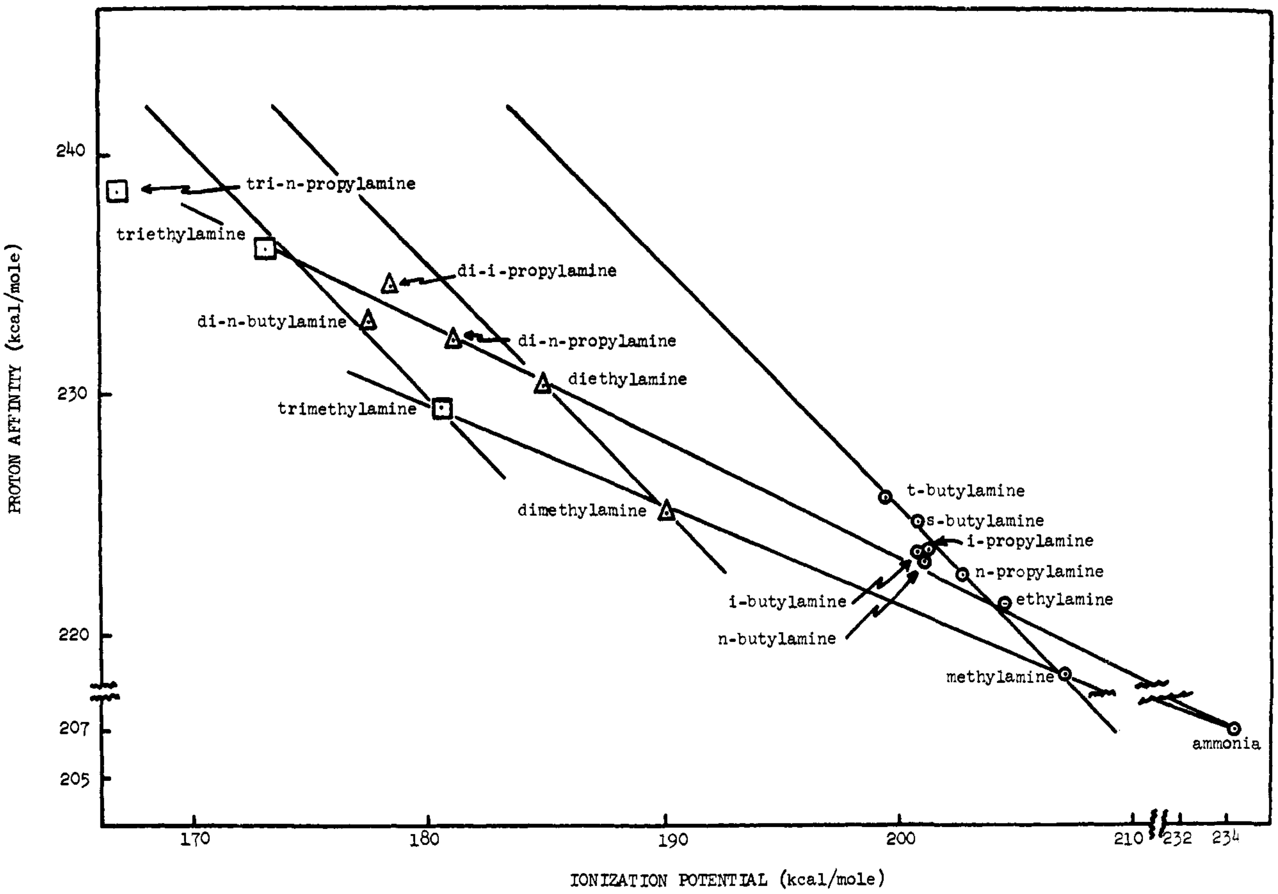

Figure 1. Plot of PA *vs.* IP for alkylamines.

clarified some of the problems in interpreting solution basicities by establishing the gas-phase basicity order of methyl-substituted amines as $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$.[6,7] This order has been confirmed by our quantitative studies. The effect of alkyl substitution on the PA's of amines can be interpreted in terms of effects on (1) the IP of the amine and (2) the HA of the amine radical cation. Within the groups of primary, secondary, and tertiary amines the HA's are approximately 111, 101, and 96 kcal/mol, respectively. The IP's decrease in larger increments than the HA's and dominate the HA changes in determining changes in PA's. The plot of proton affinities *vs.* ionization potentials in Figure 1 shows the series of primary, secondary, and tertiary amines nearly falling on the lines of slope minus one expected from eq 3 when the HA's remain constant within a series. An unexpected deviation from these lines is systematically displayed by *n*-propyl- and *n*-butylamines. The linear variation of PA with IP in thes eries CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ (slope -0.42) and $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ (slope -0.49) indicates that changes in the HA and IP are both a linear function of the number of alkyl groups on nitrogen but that the effect is only about half as large for the HA as for the IP. The PA's of all the alkylamines are closely fit by additive substituent factors. Substitution of a methyl group on the carbon α to nitrogen increases the PA by *ca.* 2.2 kcal/mol while substitution on the β carbon and γ carbon increases the PA by *ca.* 0.9 and 0.4 kcal/mol, respectively. The changes in PA with alkyl substitution are consistent with a stabilization mechanism based simply on the polarizability of the substituent.[7-9]

Differences between gas-phase basicities and solution basicities must result from entropies and enthalpies of solvation. Entropies of protonation in solution are mainly the result of solvation effects and have been partially interpreted elsewhere.[5d,10] The effect of water on enthalpies of protonation[5c] can be seen in the linear correlations in Figure 2. The large differences between primary, secondary, and tertiary amine lines are primarily the result of changes in hydration of the ammonium ions.[11] The data confirm a suggestion[5e,f]

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(6) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965).

(7) This order was confirmed and other qualitative amine GB's determined by J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

(8) Changes in IP and bond strengths closely parallel analogous figures for carbonium ion and carbon radical stabilities, but calculations on CH_3^+ and $CH_3CH_2^+$ suggest that alkyl stabilization is more complicated than suggested by a polarization model: J. E. Williams, V. Buss, and L. C. Allen, *ibid.*, **25**, 6867 (1971).

(9) We find an excellent linear correlation (slope = 0.74) of our PA's with those from *ab initio* calculations [W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970)] and from CNDO/2 calculations. Our CNDO/2 calculations indicate that larger alkyl groups support a proportionally greater amount of the positive change in alkylammonium ions.

(10) Entropies of hydration suggest that the hydrophobic interaction between alkylamines and water is also present with the ammonium ions.

(11) Heats of hydration of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ are -8.5, -11.1, -13.3, and -13.2 kcal/mol (ref 12), while the heats of hydration calculated from our PA's for the corresponding ammonium ions are -83.8, -75.7, -70.2, and -62.8 kcal/mol.

(12) D. L. King, Ph.D. Thesis, University of Nebraska, Lincoln, Neb., 1968; W. A. Felsing and P. H. Wohlford, *J. Amer. Chem. Soc.*, **54**, 1442 (1932); A. Patterson, Jr., and W. A. Felsing, *ibid.*, **60**, 2693 (1938). See F. M. Jones, Ph.D. Thesis, University of Pittsburgh, Pitts-

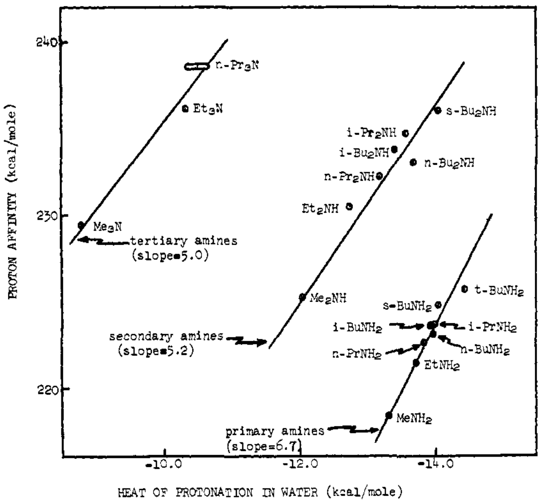

Figure 2. Plot of PA *vs.* heat of protonation in water for alkylamines.

that the heats of hydration of ammonium ions increase (by *ca.* 7 kcal/H bond) with the number of $N^{+}-H\cdots OH_2$ hydrogen bonds possible. The slopes of the lines through the alkylamines indicate that there is an approximate sixfold attenuation in the stabilizing effect of alkyl groups on the ammonium ions in solution. This attenuation may result from decreased alkyl polarizability stabilization of hydrogen bonded ammonium ions in solution[13] and from changes in ionic radius. Steric hindrance to solvation near nitrogen appears not to be a major factor since amines with branched alkyl groups (*e.g.*, *tert*-butyl) show no deviation from linearity.

burgh, Pa., 1970, for a good summary of thermochemical data on amines in solution.

[13] Similar attenuation effects have been noted in substituted pyridines: D. H. Aue, H. M. Webb, and M. T. Bowers, unpublished work.

Donald H. Aue,* Hugh M. Webb, Michael T. Bowers
Department of Chemistry, University of California
Santa Barbara, California 93106

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Methyl Substituent Effects in Protonated Aliphatic Amines and Their Radical Cations[1]

Sir:

The pronounced effects of alkyl substituents on the energetics of protonation of ammonia and amines in the gas phase have been evaluated quantitatively. Pulsed ion cyclotron resonance (icr) techniques provide for relatively precise determination ($\leqslant 0.2$ kcal/mol) of the standard free-energy change for the general gaseous proton-transfer reaction.[2]

$$NH_4^+(g) + NR_1R_2R_3(g) = HNR_1R_2R_3^+(g) + NH_3(g) \qquad (1)$$

$$\delta_R\Delta G°_{(1)} = -RT \ln K_{eq} \; (R_1,R_2,R_3 = \text{H or alkyl})$$

Stepwise increments in base strength of 0.4–2.5 kcal have been utilized to determine (and to recheck) the complete range of gas-phase base strengths from NH_3 to $(C_2H_5)_3N$. This communication reports the results for methyl substitution in two series: (I) Me for H on N, *i.e.*, NH_3, NH_2Me, $NHMe_2$, NMe_3; (II) Me for H on α-C, *i.e.*, NH_2Me, NH_2CH_2Me, NH_2CHMe_2, NH_2CMe_3. The other bases used to cover the range of $\delta_R\Delta G°$ include: $CF_3CH_2NH_2$, *i*-PrOEt, $HCF_2CH_2NH_2$, 3- and 4-cyanopyridine, $CF_3(CH_2)_2NH_2$, DMSO, DMF, $CNCH_2NMe_2$, 3- and 4-trifluoromethylpyridine, $CF_3(CH_2)_3NH_2$, MeEtNH, and Et_2NH.

Values of $\delta_R\Delta G°_{(1)}$ may be converted (at least approximately) to the corresponding enthalpies, $\delta_R\Delta H°_{(1)}$, with the use of the assumption that entropy effects are limited to rotational symmetry number effects.[3] Kebarle has obtained evidence supporting this assumption.[4] Table I lists values of $-\delta_R\Delta G°_{(1)}$ and $-\delta_R\cdot\Delta H°_{(1)}$. The standard enthalpy of heterolytic bond dissociation of the proton from the ammonium ion is taken by convention as the proton affinity (PA). Combining the values of $\delta_R\Delta H°$ and $PA_{(NH_3)} = 207$ kcal,[5] one obtains the values of PA included in Table I, *i.e.*, $PA = 207 - \delta_R\Delta H°_{(1)}$ (column 4). The results in Table I provide a basis for the prediction of gaseous base strengths. Further, the first quantitative values for the homolytic bond dissociation energies of the ammonium ions (*i.e.*, hydrogen affinities of the cation radical, HA) are obtained through combination[6] of literature photoionization (adiabatic) potentials[7] and the PA results.

Table I. Thermochemical Data (kcal/mol), 298°K

	Base	$-\delta_R\cdot\Delta G°_{(1)}$	$-\delta_R\cdot\Delta H°_{(1)}$	δ_RHA	PA[a]	IP[b]	HA[c]
I	NH_3	0.0	0.0	0.0	(207.0)	235.0	128.4
I	$MeNH_2$	9.5	9.3	−18.9	216.3	206.8	109.5
I	Me_2NH	15.8	15.4	−29.6	222.4	190.0	98.8
I	Me_3N	20.4	19.6	−35.1	226.6	180.3	93.3
II	$MeNH_2$	0.0	0.0	0.0	216.3	206.8	109.5
II	$EtNH_2$	2.5	2.5	0.0	218.8	204.3	109.5
II	*i*-$PrNH_2$	4.9	4.9	−0.8	221.2	201.1	108.7
II	*t*-$BuNH_2$	7.0	7.0	−0.6	223.3	199.2	108.9

[a] Heterolytic bond dissociation energy, reaction 2. Haney and Franklin (ref 5) list the uncertainty at ±3 kcal for NH_3. Thus, all PA values are uncertain by at least this amount. However, differences between PA values, *i.e.*, $\delta_R\Delta H°_{(1)}$, are precise to ±0.3 kcal for any pair of bases, except pairs involving NH_3, for which the precision is ±0.6 kcal. Work is in progress to obtain improved accuracy of the absolute values of PA, utilizing thermochemical data and protonated imines. The latter may be formed by either direct protonation or by fragmentation of the parent ions of appropriate amines. Preliminary results support the value of 207 kcal for NH_3. [b] Adiabatic ionization potential, ref 7. [c] Homolytic bond dissociation energy, reaction 3.

$$BH^+ \longrightarrow B\colon + H^+ \quad \Delta H°_{(2)} = PA(B\colon) \qquad (2)$$

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[1] This work was supported in part by grants from the Public Health Service, the National Science Foundation, and the Atomic Energy Commission.

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