

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 solution¹³ 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(13) Similar attenuation effects have been noted in substituted pyridines: D. H. Aue, H. M. Webb, and M. T. Bowers, unpublished work.

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Methyl Substituent Effects in Protonated Aliphatic Amines and Their Radical Cations¹

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 (≤ 0.2 kcal/mol) of the standard free-energy change for the general gaseous proton-transfer reaction.²



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

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

(2) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, *J. Amer. Chem. Soc.*, **93**, 4313 (1971).

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 $\delta_R \Delta G^\circ$ 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 .

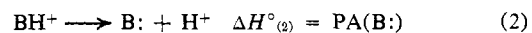
Values of $\delta_R \Delta G^\circ_{(1)}$ may be converted (at least approximately) to the corresponding enthalpies, $\delta_R \Delta H^\circ_{(1)}$, with the use of the assumption that entropy effects are limited to rotational symmetry number effects.³ Kebarle has obtained evidence supporting this assumption.⁴ Table I lists values of $-\delta_R \Delta G^\circ_{(1)}$ and $-\delta_R \Delta H^\circ_{(1)}$. 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 $\delta_R \Delta H^\circ$ and $PA_{(NH_3)} = 207$ kcal,⁵ one obtains the values of PA included in Table I, *i.e.*,

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

Base	$-\delta_R \Delta G^\circ_{(1)}$	$-\delta_R \Delta H^\circ_{(1)}$	$\delta_R HA$	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 ₂ NH	15.8	15.4	-29.6	222.4	190.0	98.8
I Me ₃ N	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>i</i> -PrNH ₂	4.9	4.9	-0.8	221.2	201.1	108.7
II <i>t</i> -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.*, $\delta_R \Delta H^\circ_{(1)}$, 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.

$PA = 207 - \delta_R \Delta H^\circ_{(1)}$ (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 combination⁶ of literature photoionization (adiabatic) potentials⁷ and the PA results.



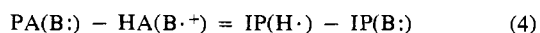
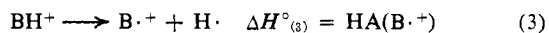
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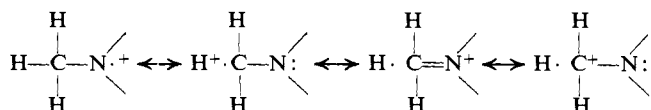
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The values of HA and literature IP are included in Table I (columns 6 and 5, respectively).

Methyl substituent effects in both series I and II are dramatically different between heterolytic (PA) and homolytic (HA) dissociations. In reaction 2, series I bases show increased stability of BH⁺ relative to dissociated B: with increased Me substitution. These Me effects are large and distinctly nonadditive (columns 1 and 2, Table I). In reaction 3 series I bases show even larger and less additive effects of Me substitution, but here, in contrast, it is the dissociated cation radical B·⁺ which is stabilized relative to BH⁺ (column 3, Table I). Series II bases show little or no effect of Me substitution on α-C in reaction 3 but a nearly additive BH⁺ stabilizing effect of ~2.5 kcal in reaction 2.

The results for series I and II bases in reaction 2 may be ascribed to predominant inductive and polarization stabilizing effects⁸ of Me on cationic BH⁺ compared to neutral B. In series I bases, stabilization of B·⁺ relative to BH⁺ may be expressed in terms of delocalization of charge and spin into Me.



The inductive, polarization, and hybridization effects probably make only minor contributions to relative HA's, since BH⁺ and B·⁺ are of the same charge type. This interpretation is consistent with the fact that series II bases show nearly additive effects on PA (reaction 2) but little or no effect of Me substitution on HA (reaction 3). The latter result is expected as a consequence of nearly equal delocalizations into C-H and C-C bonds.⁹ It is also of interest to note that Me substituent effects for series I in reaction 3 are about 2.5 times greater than for the corresponding isoelectronic (homolytic) C-H bond dissociation energy.¹⁰

Our quantitative values of $\delta_R \Delta G^\circ_{(1)}$, which are in accord with Munson's earlier qualitative results,¹¹ may be combined with solution thermodynamic properties to obtain a complete analysis for the transfer of the ammonium ions from the gas phase to aqueous solution. The results and a preliminary discussion are given in a companion paper.¹² Tests of molecular orbital theories are also provided by present results. Thus, for example, the preliminary *ab initio* calculations of proton affinities for series I amines are on the order of 50 kcal larger than the experimental results.¹³ It should also be noted that the nearly constant HA values for series II amines (as well as other series involving

similar structural changes) are of important practical utility in experimental determination of PA values.¹⁴

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(15) Contribution No. 4377.

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Nonlinear Brønsted Relationships for General Acid-Base Catalysis of Aminolysis Reactions¹

Sir:

We wish to report that the Brønsted plots for general acid-base catalysis of several acyl aminolysis reactions with nitrogen or oxygen leaving groups are nonlinear. We interpret this as evidence that there is a change in rate-determining step and an intermediate in the reactions and that the reactions are not at equilibrium with respect to transport processes involving proton transfer.²⁻⁶

Experimental studies of general acid-base catalysis of aminolysis have usually been limited to catalysis by a second molecule of the attacking or leaving groups (or their conjugate acids) in order to avoid interference by a nucleophilic reaction with the catalyst. We have avoided this problem by the use of reactive "α effect" nucleophiles and have examined the reactions of hydrazine with acetylimidazole and of methoxyamine with 1-acetyl-1,2,4-triazole in the presence of a series of relatively unreactive catalyst molecules, using previously described spectrophotometric techniques.⁷ We have also examined the partitioning of *p*-tolyl *N,N*-dimethylacetimidate to ester and amide; formation of ester from this imidate is thought to involve the breakdown of a tetrahedral addition intermediate with amine expulsion, the reverse of the first step of ester aminolysis,⁸ and is subject to catalysis by general acids whose conjugate bases are not effective nucleophiles toward the imidate.

The claim for nonlinearity of the Brønsted plot for general base catalysis of the hydrazinolysis of free

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