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Gas-Phase and Solution-Phase Homolytic Bond Dissociation Energies of H−N$^+$ Bonds in the Conjugate Acids of Nitrogen Bases

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The oxidation potentials of 19 nitrogen bases (abbreviated as B: six primary amines, five secondary amines, two tertiary amines, three anilines, pyridine, quinuclidine, and 1,4-diazabicyclo[2,2,2]-octane), i.e., E_{ox}(B) values in dimethyl sulfoxide (DMSO) and/or acetonitrile (AN), have been measured. Combination of these E_{ox}(B) values with the acidity values of the corresponding acids (pK_{HB^+}) in DMSO and/or AN using the equation: $BDE_{HB^+} = 1.37pK_{HB^+} + 23.1\,E_{ox}(B) + C$ (C equals 59.5 kcal/mol in AN and 73.3 kcal/mol in DMSO) gave estimates of solution phase homolytic bond dissociation energies of H−B$^+$ bonds. Gas-phase BDE values of H−B$^+$ bonds were estimated from updated proton affinities (PA) and adiabatic ionization potentials (aIP) using the equation, $BDE(HB^+)_g = PA + aIP - 314$ kcal/mol. The BDE_{HB^+} values estimated in AN were found to be 5−11 kcal/mol higher than the corresponding gas phase $BDE(HB^+)_g$ values. These bond-strengthening effects in solution are interpreted as being due to the greater solvation energy of the HB$^+$ cation than that of the $B^{+\bullet}$ radical cation.

Introduction

During the past ten years a simple method has been developed in our laboratory to estimate homolytic bond dissociation enthalpies (BDE_{HA}s) of the acidic H−A bonds in weak organic acids by using eq 1.[1] Even though the oxidation potentials of the conjugate anions are usually irreversible and the constant C is empirical,[1b] the BDE_{HA} values estimated by eq 1 with $C = 73.3$ kcal/mol in DMSO for the acidic C−H bonds in 10 carbon acids have been shown to be in agreement with the best available gas-phase values to ±1 kcal/mol[1d] when the oxidation potentials are referenced to the ferrocenium/ferrocene couple.[1b] ($C = 59.5$ kcal/mol in acetonitrile, AN;[2] henceforth kcal/mol will be abbreviated as kcal.)

$$BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + C \qquad (1)$$

The BDE_{HA} values obtained in this way for carbon acids can be considered to be empirically derived gas phase values. The true relationship between BDE_{HA} and $BDE(HA)_g$ should include an account of the solvation effect, however (eq 2). For carbon acids, it is understandable that good agreement between the empirically based BDEs and the gas-phase BDEs is obtained, even though solvation effects have been ignored, since the final two terms in eq 2 can be assumed to essentially cancel one another [the $\Delta H_{solv}(H^\bullet)_s$ term should also be considered, but it is small and difficult to evaluate.[2]]. For weak acids that are hydrogen-bond donors, such as phenols, however, the $\Delta H_{solv}(HA)_s$ term is much larger than the $\Delta H_{solv}(A^\bullet)_s$ term, and the empirically derived BDE_{HA} values are expected to be higher than the gas-phase BDEs. Griller *et al.* have suggested that solution BDE_{HA} values in such cases will differ to the extent to which polar species are destroyed,[3a] and Wayner *et al.* have demonstrated that a correction for the hydrogen-bond energy should be applied to estimate the BDE value for phenol in DMSO.[3b]

$$BDE_{HA} = BDE(HA)_g + \Delta H_{solv}(H^\bullet)_s + \Delta H_{solv}(A^\bullet)_s - \Delta H_{solv}(HA)_s \quad (2)$$

For nitrogen bases (B) and their conjugate acids (HB$^+$), the BDE values for H−B$^+$ bonds, such as N−H$^+$ bonds in conjugate acids of amines, can be estimated by eq 1. Replacement of A$^-$ and HA in eq 1 by B and HB$^+$ gives eq 3. Equation 3 indicates that BDE_{HB^+} values can be estimated from a combination of the solution-phase acidities of HB$^+$ (pK_{HB^+}) and the oxidation potentials E_{ox}(B) of the bases. The relationships between BDE_{HB^+} values and gas-phase BDEs for H−B$^+$ bonds, $BDE(HB^+)_g$, is similarly given by eq 4. From eq 4, we see that the relative size of the solvation energy of HB$^+$ and that of $B^{+\bullet}$ determine the size of corrections to be applied to the BDE_{HB^+} values.[4]

$$BDE_{HB^+} = 1.37pK_{HB^+} + 23.1E_{ox}(B) + C \qquad (3)$$

$$BDE_{HB^+} = BDE(HB^+)_g + \Delta H_{solv}(H^\bullet + B^{+\bullet} - HB^+)_s \qquad (4)$$

Gas phase homolytic bond dissociation energies of H−B$^+$ bonds for amine conjugate acids, $BDE(HB^+)_g$, can be estimated from proton affinities (PA) and adiabatic

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[4] A referee has pointed out that alkylamine radical cations formed by homolytic dissociation of the conjugate acids of primary or secondly amines are stronger acids than their conjugate acid precursors, e.g., $Me_2NH_2^+ \rightarrow H^\bullet + Me_2NH^{+\bullet}$. These radical cations might then hydrogen bond strongly with the DMSO solvent. Actually, the $Me_2NH^{+\bullet}$ radical cations are only moderately stronger acids. (The $Me_2NH^{+\bullet}$ is only 3.8 pK_{HA} units more acidic than $Me_2NH_2^+$. See: Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857.) Furthermore, the H-bonding capability difference between HB$^+$ and $B^{+\bullet}$ will be only about one fifth of the acidity difference in DMSO (Table 4 and Figure 1).

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Table 1. Oxidation Potentials of Amines in Acetonitrile (AN) and DMSO Compared to Literature Values

compound	E_{ox}(B) (AN)[a]	E_{ox}(B) (DMSO)[a]	E_{ox}(B) (lit.)[b]	*vs* Fc/Fc$^+$ [c]	ΔE[d]	ref
s-BuNH$_2$	1.281		1.62 (AN, NHE)	1.092	189	10
t-BuNH$_2$	1.300		1.64 (AN, NHE)	1.112	188	10
Me$_2$NH	0.707	0.614	1.03 (aq, SCE)	0.742	−35	11
Et$_2$NH	0.702	0.628	1.00 (aq, SCE)	0.712	−10	11
PhNH$_2$	0.475	0.494	0.86 (AN, SCE)	0.573	−98	12
PhNHMe	0.425	0.409	0.70 (aq, Ep1/2 SCE)	0.463	−38	13
PhNMe$_2$	0.380	0.378	0.71 (aq, Ep1/2 SCE)	0.473	−93	14
NMe$_3$	0.542	0.493	1.29 (AN, NHE)	0.762	−220	10
			0.76 (aq, SCE)	0.472	−48	11
NEt$_3$	0.450	0.436	1.19 (AN, NHE)	0.662	−212	10
			0.69 (aq, SCE)	0.402	+48	11
			0.78 (AN, SCE)	0.475	−25	15
quinuclidine	0.597	0.620	1.1 (AN, SCE)	0.795	−198	15
DABCO	0.292	0.264	0.60 (AN, SCE)	0.295	−3	15

[a] Irreversible oxidation potentials measured in 1 to 2 mM solution by cyclic voltammetry using 0.1 M $Et_4N^+BF_4$ as the electrolyte at a sweep rate of 100 mV/s vs Ag/AgI and referred to the ferrocene/ferrocenium couple. [b] Data taken from the literature and referred to Fc/Fc$^+$ by adding: −0.528 for (AN, NHE); −0.305 for (AN, SCE); +0.24 − 0.528 = −0.288 for (aq, SCE). [c] Potentials vs Fc/Fc$^+$ calculated as explained in footnote b. [d] The difference (in mV) of E_{ox}(B) values of this work and literature values.

ionization potentials (aIP) of amines by using eq 5.[5]

$$\mathrm{BDE(HB^+)_g = PA(B) + aIP(B) - 314\ kcal/mol} \quad (5)$$

Measurements of gas-phase proton affinities of amines have been made in a number of laboratories in the past two decades as part of the development of an extensive proton affinity scale.[6,7] These PA(B) values[6] can be used in eq 5 with updated aIP values[8] to obtain gas-phase homolytic bond dissociation energies of the H−N$^+$ bonds in amine conjugate acids, which have also been referred to as hydrogen atom affinities of amine radical cations.[5] It was of interest to compare the $\mathrm{BDE_{HB^+}}$ values, uncorrected for solvation effects, with gas-phase $\mathrm{BDE(HB^+)_g}$ values in order to obtain information concerning the importance of solvation effects on solution-phase BDEs.

Results and Discussion

Oxidation Potentials of Amines. Estimates of $\mathrm{BDE_{HB^+}}$ values by eq 3 require the oxidation potentials of amines, E_{ox}(B) values, and equilibrium acidities of their conjugate acid, $\mathrm{p}K_{\mathrm{HB^+}}$ values. Reliable $\mathrm{p}K_{\mathrm{HB^+}}$ values in dimethyl sulfoxide (DMSO) and acetonitrile (AN) for many amines are available in the literature.[9] Literature values for E_{ox}(B) values for many amines are also available,[10−15] but those reported from different laboratories were found to vary appreciably. For example, the values for $E_{ox}(Et_3N)$ varied by over 200 mV from two different laboratories.

Measurements of E_{ox}(B) values in our laboratory in AN and DMSO solutions using conventional cyclic voltammetry with a fixed sweep rate of 100 mV/s showed that peak potentials were independent of concentration below 5 mM (0.1−5 mM), but that positive shifts in potentials occurred for most amines at higher concentrations. The oxidation potentials were therefore measured at substrate concentrations of 1 to 2 mM, and the peak potentials were taken from an average of at least three measurements. Under these conditions the experimental error was judged to be less than 50 mV, but the values often differed from literature values (with different electrodes) by as much as 200 mV. Comparisons of our E_{ox}(B) values for 11 amines in DMSO and/or AN with literature values are shown in Table 1.

Examination of Table 1 shows that the oxidation potentials for most amines differed but little with a change in solvent from AN to DMSO. The potentials were generally slightly lower in DMSO, but were within 50 mV (1.1 kcal) in the two solvents, except for Et_2NH (74 mV) and Me_2NH (93 mV) (Measurements for the primary amines, *s*-BuNH$_2$ and *t*-BuNH$_2$, in DMSO could not be carried out because of solvent oxidation). Comparisons with literature values were made by referring all the potentials to the ferrocene−ferrocenium couple. The overall agreement between our E_{ox}(B) values in AN and the literature values is poor, as is evidenced from the ΔE values in Table 1. But there is good agreement between our values and those given in ref 11, and the really large differences (ΔE's) are primarily with those from a single reference (no. 10).

Estimates of $\mathbf{BDE_{HB^+}}$ Values. Literature $\mathrm{p}K_{\mathrm{HB^+}}$ values in DMSO and/or AN for 20 nitrogen bases are shown in Table 2 along with the corresponding E_{ox}(B) values, when available. $\mathrm{BDE_{HB^+}}$ values in DMSO and/or AN calculated by combining the $\mathrm{p}K_{\mathrm{HB^+}}$ and E_{ox}(B) values using eq 3 are given in the final two columns of Table 2.

Examination of the $\mathrm{p}K_{\mathrm{HB^+}}$ values in Table 2 shows that those in AN are, on an average, about 9 units (12 kcal) higher than those in DMSO, a difference similar to that for the acidities of the uncharged weak acids in the two solvents, which is believed to be a consequence of the smaller proton affinity of AN than DMSO.[9] As shown in Table 1, the E_{ox}(B) values between AN and DMSO usually varied by no more than 50 mV for secondary and tertiary amines. The same would probably be true for primary amines, if their oxidation potentials could be

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Table 2. Homolytic Bond Dissociation Energies (BDEs) for the HN^+ Bonds in the Conjugate Acids of Amines Estimated in Acetonitrile (AN) and/or Dimethyl Sulfoxide (DMSO)

entry	compound	pK_{HB^+} (AN)[a]	pK_{HB^+} (DMSO)[a]	E_{ox}(B) (AN)	E_{ox}(B) (DMSO)	BDE_{HB^+} (AN)[k]	BDE_{HB^+} (DMSO)[l]
1	NH_3	16.46[b]	10.5[d]				
2	$MeNH_2$	18.37[b]	11.0[e]	1.298		114.6	
3	*i*-$BuNH_2$	18.2[i]		1.250		113.3	
4	*s*-$BuNH_2$	17.92[b]		1.281[c]		113.6	
5	*t*-$BuNH_2$	18.14[b]		1.300[c]		114.3	
6	c-$C_6H_{12}NH_2$	18.0[i]		1.276		113.6	
7	$BzNH_2$	16.76[b]		1.208		110.3	
8	Me_2NH	18.73[b]	10.3[e]	0.707[j]	0.614[j]	101.5	101.6
9	Et_2NH	18.75[b]	10.5[d]	0.702[j]	0.608[j]	101.4	101.7
10	pyrrolidine	19.58[b]	10.8[f]	0.656	0.597	101.5	101.9
11	piperidine	18.92[b]	10.5[f]	0.732	0.668	102.3	103.1
12	morpholine	16.61[b]	(8.5)[i]	0.822	0.738	101.2	102.0
13	$PhNH_2$	10.56[b]	3.6[d]	0.475[j]	0.494[j]	84.9	89.6
14	PhNHMe	10.0[i]	2.76[g]	0.425[j]	0.409[j]	83.2	86.5
15	$PhNMe_2$	10.0[i]	2.51[g]	0.380[j]	0.378[j]	82.0	85.5
16	NMe_3	17.61[b]	8.4[e]	0.542[j]	0.493[j]	96.1	96.2
17	NEt_3	18.70[b]	9.0[d]	0.450[j]	0.436[j]	95.5	95.3
18	quinuclidine	19.51[c]	9.8[h]	0.597[j]	0.620[j]	100.0	101.0
19	DABCO	18.29[b]	8.6[i]	0.292[j]	0.264[j]	91.3	91.2
20	pyridine	12.3[b]	3.5[f]	2.230		127.5	

[a] From ref 9a. [b] From ref 9b. [c] From ref 9c. [d] From ref 9d. [e] From ref 9e. [f] From ref 9f. [h] From ref 9h. [i] Estimated from comparison of a series pK_{HB^+} data of amines. [j] Taken from Table 1. [k] Calculated by eq 3 ($C = 59.5$ kcal, ref 2). [l] Calculated by eq 3 ($C = 73.3$ kcal).

measured in DMSO. Secondary amines are usually more easily oxidized than primary amines, i.e., they have more positive oxidation potentials, and tertiary amines are usually more easily oxidized than secondary amines. Aniline is more easily oxidized than other primary amines, and PhNHMe and $PhNMe_2$ are in turn more easily oxidized than aniline. Comparison of the BDE_{HB^+} values in AN and DMSO shows that they agree to within 1 kcal, except for the anilines (Table 2). This good agreement gives us confidence in the validity of the E_{ox}(B) values in the two solvents.

Concerning the Error of Using Irreversible Oxidation Potentials. Reversible oxidation potentials are theoretically required for use of eq 1 and eq 3.[2] The errors in using irreversible oxidation potentials are caused by kinetic peak potential shifts according to theory.[16] These shifts have been evaluated and shown to depend on the order and rate of the chemical reactions of the radicals formed during the oxidation of the anions on the electrode.[2] Using irreversible oxidation potentials in eq 1, the kinetic peak potential shift can be estimated to be 2.6 kcal/mol since most of the unhindered radicals formed during oxidation of their anions will decay in second-order kinetics with rates around 10^9 M^{-1} s^{-1}.[17] The corrections made for these errors did not lead to improvement in the estimated BDE_{HA}s, however, when made for 9-$AnCH_2$-H, Ph_3C-H, Ph_2CH-H, c-C_5H_5-H, and Fl-H bonds.[2]

Decay kinetic studies have shown that both unhindered and hindered amine radical cations decay with “clean” second-order kinetics, and the decay rates at ambient temperature in $H_2SO_4-CH_3COOH$ media have been evaluated to be of the order of 10^7 M^{-1} s^{-1} for the unhindered dimethylamine radical cation and 10^5 M^{-1} s^{-1} for the hindered 2,2,6,6-tetramethylpiperidine radical cation.[18] The decay kinetics and the rates can be assumed to be similar in DMSO and in $H_2SO_4-CH_3COOH$ media. In fact, the decay rate of amine radical cations in DMSO must be larger than 10^6 M^{-1} s^{-1} since the oxidation potential measurements for most amines were found to be completely irreversible at 1000 V/s. The kinetic peak potential shift for unhindered amines can therefore be estimated to be about 2 kcal. This is not much different from the kinetic peak potential shift for H−A type acids, so the additional error of using irreversible oxidation potentials in eq 3 is likely to be small.

It has been reported that 1,4-diazabicyclooctane (DABCO) gives a reversible oxidation potential.[15] In our hands, its oxidation potential was found to be irreversible at a scan rate of 0.1 V/s, but reversible at scan rates of over 200 V/s in AN and in DMSO. The average of the two reversible potential peak values (0.292 V in AN, 0.263 V in DMSO vs the Fc/Fc^+ couple) were in excellent agreement with the peak value of the irreversible oxidation peak (0.292 V in AN, 0.245 V in DMSO vs the Fc/Fc^+ couple). The BDE difference between quinuclidine and DABCO obtained in solution using eq 3 (8.7 kcal) and in gas phase (9 kcal)[19] agreed well, even though an irreversible E_{ox}(B) value for quinuclidine was used in making the estimates. This result shows that the irreversible E_{ox} value of quinuclidine is not far from its $E°_{ox}$ value. This again indicates that the error for using irreversible oxidation potentials is small.

Estimates of $BDE(HB^+)_g$ Values. To estimate $BDE(HB^+)_g$ values, one needs the PAs and aIPs values of the bases. Discrepancies between the proton affinity scales obtained in different laboratories can be larger than 4 kcal since absolute proton affinities higher than NH_3 are difficult to anchor due to the lack of reliable standards,[6] and the discrepancies in aIP values may also be substantial. So, it is not surprising that the $BDE(HB^+)_g$ values obtained from different sets of PA and aIP values may have discrepancies larger than 5 kcal. For example,

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Table 3. Comparison of $BDE_{HB}{}^{+}$ Values in AN Solutions and $BDE(HB^{+})_g$ Values for Amines and Pyridine

compound	PA(g)[a]	PA(g)[c]	aIP(g)[e]	$BDE(HB^{+})_g$[f]	$BDE_{HB}{}^{+}$[g]	$BDE(HB^{+})_g$[h]
NH_3	204[b]	208.3	233.6	123.6		127.9
$MeNH_2$	214.1[b]	219.6	206.8	106.9	114.6	112.4
s-$BuNH_2$	220.5	226.5	200.6	107.1	113.6	113.1
t-$BuNH_2$	220.8[b]	229.2	199.2	106.0	114.3	114.4
Me_2NH	220.6[b]	227.8	189.8	96.4	101.5	103.6
$PhNH_2$	209.5	214.8	178.0	73.5	84.9	78.8
$PhNMe_2$	223.4	230.9	164.2	73.6	82.0	81.1
NMe_3	225.1	232.7	180.3	91.4	96.1	99.0
NEt_3	232.3	239.9[d]	172.9	91.2	95.5	98.8
quinuclidine	232.1	239.7[d]	173	91.1	100.0	98.7
DABCO	229.0	236.8[d]	167	82	91.3	89.8
pyridine	220.8	227.6	213.3	120.1	127.5	126.9

[a] Gas phase proton affinities (in kcal) from ref 7 unless otherwise indicated. [b] From ref 6a. [c] Gas phase proton affinities (in kcal) from ref 6c unless otherwise indicated. [d] Estimated from PA of NMe_3 reported in ref 6c (232.7 kcal) and the relative PA against NMe_3 reported in ref 7. [e] Adiabatic ionization potentials (in kcal) from ref 8. [f] Homolytic bond dissociation energies calculated from the PA scale listed in the first column by eq 5. [g] Values in AN taken from Table 2. [h] Homolytic bond dissociation energies calculated from the PA scale listed in the second column by eq 5.

Alder *et al.*[19] adopted a PA value of 234 kcal and an aIP value of 7.1 eV (164 kcal) to obtain a $BDE(HB^{+})_g$ value of 84 kcal for Et_3N-H^{+}, but if a PA value of 239.9 kcal (see Table 3) and an aIP value of 7.5 eV (176 kcal)[7] are applied, a $BDE(HB^{+})_g$ value of 98.8 kcal for Et_3N-H^{+} is obtained.

As indicated in Table 3, values selected from two sets of PA scales were used in the present paper. The first set uses the PAs reviewed by Lias *et al.*[7] and recently checked by Szulejko *et al.*[6a,b] The second set uses the PAs reported by Mautner et al.[6c] The aIP values were selected from a review article of Lias *et al.*[8b] The PA and aIP data together with the $BDE(HB^{+})_g$ values estimated by eq 5 are given in Table 3. The $BDE(HB^{+})_g$ values obtained from the first PA set are about 4−8 kcal lower than $BDE(HB^{+})_g$ values obtained from the second PA set.

Comparison of $BDE_{HB}{}^{+}$ Values and Gas-Phase $BDE(HB^{+})_g$ Values. Examination of Table 3 shows that $BDE_{HB}{}^{+}$ values obtained in AN are about 5∼7 kcal higher than $BDE(HB^{+})_g$ values obtained from the first PA set, but agree to within ±3 kcal with $BDE(HB^{+})_g$ values obtained from the second PA set, except for aniline. We believe the latter agreement is fortuitous because AN is a strong H-bond acceptor, and $N-H^{+}$ is expected to be a strong H-bond donor. By analogy with the results with phenol,[3] we therefore expect the $BDE_{HB}{}^{+}$ values, which are uncorrected for solvation effects, to be *higher* than the gas-phase values. Alkylammonium cations in aqueous solution are known to be strong H-bond donors toward water and are also strong H-bond donors in AN or DMSO. For alkylammonium cations in aqueous solution, each additional hydrogen bond increases the solvation energy by 5−6 kcal.[20] Examination of the literature revealed that the extent of H-bonding for oxygen acids is linearly related to their acidities (Table 4 and Figure 1).

Table 4. Acidities and Heats of Hydrogen Bond with Solvent for Oxygen Acids in DMSO

compound	pK_{HA}(DMSO)[a]	$\Delta H(OH\cdots OSMe_2)$[b]
$(CH_3)_3COH$	32.2	4.7[c]
PhOH	18.1	7.2[c]
CH_3COOH	11.93	8.3[d]
PhCOOH	11.01	8.8[d]

[a] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463. Corrected for homo-hydrogen bonding. [b] Heat of formation of $OH\cdots OSMe_2$ hydrogen bond (in kcal). [c] Reference 22. [d] Reference 21.

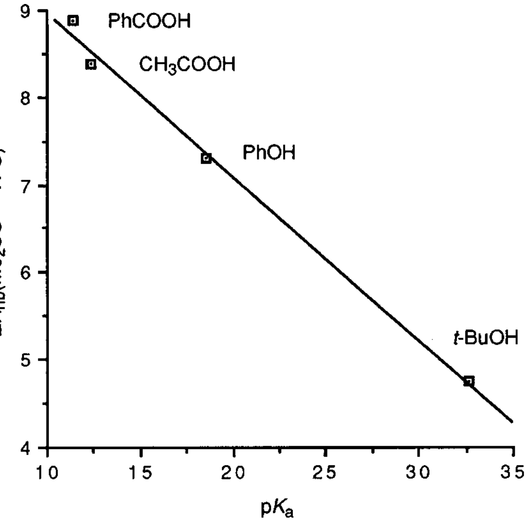

Figure 1. Plot of $\Delta H_{hb}(Me_2SO\cdots H-O)$ vs pK_a. $\Delta H_{hb}(Me_2SO\cdots H-O) = 10.69 - 0.188\ pK_a$; $R^2 = 0.994$.

The strength of the H-bonding of these hydroxylic acids to Me_2SO are seen in Figure 1 to increase with decreasing pK_{HA} values. If the $pK_{HB}{}^{+}$ values for the conjugate acids of alkylamines in DMSO (Table 2) are placed on this line, the BDEs of the H-bonds in their conjugate acids are predicted to be similar to those of carboxylic acids, i.e., about 8−9 kcal and those for conjugate acids of anilines and pyridine should be stronger. The H-bonds of the conjugate acids in AN would be expected to be weaker because their pK_{HA} values are about 9 unit higher. The 3.3−4.7 kcal higher $BDE_{HB}{}^{+}$ values for anilines in DMSO than in AN (Table 2) follows this trend. The increase in $BDE_{HB}{}^{+}$ is caused by solvation is therefore estimated to be approximately between 5−11 kcal.

Examination of the $pK_{HB}{}^{+}$ values (Table 2) and the first set of PA values for simple alkylamines in Table 3 shows that the $pK_{HB}{}^{+}$ values remain nearly constant (18 ± 1 in AN and 10 ± 1 in DMSO) whereas the PA values change by as much as 18 kcal (232.3 for Et_3N to 214.1 for $MeNH_2$). The constancy of $pK_{HB}{}^{+}$ values is apparently due to a cancelation of the effects of structural changes on proton affinities and solvation energies. For Et_3N and its isomer *n*-Pr_2NH, the proton affinity change is 4.8 kcal, which corresponds roughly to the solvation energy change

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(20) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318.

(21) Rosenberg, M. S.; Iogansen, A. V.; Mashkovsky, A. A.; Odinokov, S. E. *Spectrosc. Lett.* **1972**, *5*, 75−80.

(22) Arnett, E. M.; Jaris, L.; Mitchell, E. J.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365.

Table 5. Comparison of BDE(HB$^+$)$_g$ for the Conjugate Acids of Amines with BDE$_{HN}$ Values of Amines and BDE$_{HC}$ Value of Isoelectronic Hydrocarbons

no.	Amine	BDE(HB$^+$)$_g$^{a}	BDE(N−H)^b	BDE(C−H)^c
1	NH_3	123.6	107.5	104.9 (Me−H)
2	$MeNH_2$	106.9	100.1	101.0 (Et−H)
3	Me_2NH	96.4	91.6	98.7 (*i*-Pr−H)
4	$PhNH_2$	73.5	88.0	88.0 ($PhCH_2$−H)
5	Me_3N	91.4		96.5 (*t*-Bu−H)
6	pyridine	120.1		111 (Ph−H)

^{a} Taken from the fourth column of Table 3. ^{b} Homolytic N−H bond dissociation energies of amines from ref 8a. ^{c} Homolytic C−H bond dissociation energies of isoelectronic hydrocarbons from ref 8a.

(5.1 kcal)[20] in aqueous solution for Et_3NH^+ vs $Pr_2NH_2^+$. This proton affinity change also corresponds roughly to the estimated bond-strengthening effect for the difference between the BDE$_{HB}$$^+$ values, uncorrected for solvation effects, and the gas-phase BDE(HB$^+$)$_g$ values for simple alkylamines. It seems likely that the higher values estimated for BDE$_{HB}$$^+$ values in AN than in the gas phase are due to the greater solvation energy for HB^+ than $B^{+\bullet}$, and that the agreement between the BDE$_{HB}$$^+$ values and BDE(HB$^+$)$_g$ values obtained for the second set of PA values may be due to an error in this PA scale.[6a,b]

The BDE$_{HB}$$^+$ values in AN are about 10 kcal higher than the BDE(HB$^+$)$_g$ values for anilines and 7.5 kcal higher than for pyridine (Table 2). According to the rationale given for such differences, this would suggest that the difference between HB^+ and $B^{+\bullet}$ solvation energies is somewhat greater between these acids than for alkylamine conjugate acids. This is in line with the expected stronger H-bond solvation for the more acidic anilinium and pyridinium ions (Figure 1).

Comparison of BDEs of N$^+$−H, N−H, and C−H Bonds in Isoelectronic Molecules. Comparison of (a) the BDEs for N−H$^+$ bonds in the conjugate acids of nitrogen bases, BDE(HB$^+$)$_g$ values, (b) BDEs for N−H bonds in the corresponding nitrogen bases, BDE$_{NH}$ values, and (c) BDEs for C−H bond in isoelectronic hydrocarbons, BDE$_{CH}$ values, are shown in Table 5.

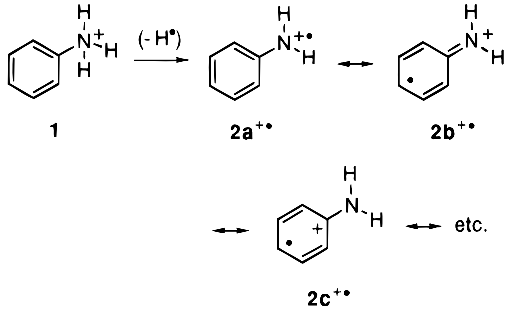
The BDE(HB$^+$)$_g$ values are seen in Table 5 to be greater than the corresponding BDE$_{NH}$ values. For example, the N−H$^+$ bond in $Me_2NH_2^+$ is 5 kcal stronger than the N−H bond in Me_2NH, the N−H$^+$ bond in $MeNH_3^+$ is about 7 kcal stronger than the N−H bond in $MeNH_2$, and the N−H$^+$ bond in NH_4^+ appears to be about 20 kcal stronger than the N−H bond in NH_3 (The first member of a series often exhibits exaggerated properties).

The N−H$^+$ bonds in the conjugate acids of amines are also stronger than the C−H bonds in their isoelectronic hydrocarbons. For example, the N−H bond in $MeNH_3^+$ is about 6 kcal stronger than the C−H bond in ethane, and the N−H bond in NH_4^+ is about 16 kcal stronger than the C−H bond in methane.

The N−H$^+$ bond in pyridinium ion is 9 kcal stronger than the C−H bond in benzene, its isoelectronic hydrocarbon. These data suggest that neither the positive charge nor odd electron in the pyridine radical cation can be stabilized by delocalization, evidently because delocalization of the positive charge or odd electron into the ring will disrupt the aromaticity.

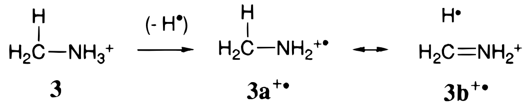
The stronger N−H$^+$ bonds in the conjugate acids of amines than the N−H bonds in the corresponding amines and the C−H bonds in their isoelectronic hydrocarbons follow the general rule that electron deficiency strengthens bonds.

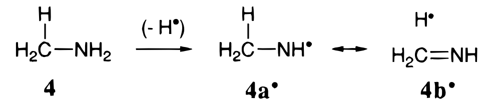
On the other hand, the N−H$^+$ bond in $PhNH_3^+$ is 14.5 kcal weaker than either the N−H bond in aniline or the C−H bond in toluene. This result suggests that the aniline radical cation is highly stabilized by delocalizing its positive charge to the phenyl ring as illustrated in the resonance contributions of **2**.



Structural Effects on BDEs of N$^+$−H Bonds. The N−H$^+$ bond in protonated DABCO is 8.7 kcal weaker than that in the quinuclidinium cation. This is because the DABCO radical cation is stabilized by a 1-spin-4-nonbonded-electron orbital interaction.[15,19] The H−N$^+$ bond in the quinuclidinium ion is 5 kcal stronger than that in protonated triethylamine since the strain energy is not relieved by the homolytic cleavage of the N−H$^+$ bond in the quinuclidinium cation due to its rigid structure.[5]

Introduction of methyl groups causes BDE decreases in the N−H$^+$ bond strengths (Table 5). The α-Me type effects are similar to those observed for the BDE$_{HN}$ and BDE$_{HC}$ bonds, e.g., aliphatic amines, H_2N−H (108 kcal) > MeNH−H (100 kcal) > Me_2N−H (92 kcal) and to those in aliphatic hydrocarbons, e.g., Me−H (105 kcal) > $MeCH_2$−H (101 kcal) > Me_2CH−H (98.7 kcal) (Table 4). The decreases in N−H bond energies in NH_4^+ and NH_3 on methyl substitution and the decrease in the C−H bond energy in CH_4 on methyl substitution can be attributed to hyperconjugation stabilization (e.g., **3** → **3a**$^{+\bullet}$ ↔ **3b**$^{+\bullet}$, **4** → **4a**$^{+\bullet}$ ↔ **4b**$^{+\bullet}$).





Summary and Conclusions

Our simple method of estimating homolytic bond dissociation energies in DMSO solution by the use of eq 1 has been extended to the N−H$^+$ bonds in the conjugated acids of amines. The BDE$_{NH}$$^+$ values in acetonitrile (AN) were estimated to be 5−11 kcal/mol stronger than those in the gas phase estimated by eq 5. These bonds are also stronger than those of the N−H bonds in amines or the C−H bonds in isoelectronic alkanes. This follows the general rule that a deficiency of electrons in a bond is bond strengthening. The strengthening of these N−H$^+$ bonds by solvation in AN or DMSO is similar to the solvation effects observed for O−H bonds in phenols.[3]

Experimental Section

Materials. The amines were commercially available, and the purity was determined to be better than 98%. Tetramethylammonium tetrafluoroborate was recrystallized from absolute alcohol and dried at 110 °C at 0.1τ for 24 h.

The oxidation potentials were measured by a conventional cyclic voltammetric instrument, as described previously.[1] The working electrode (BAS) consists of a 1.5 mm diameter platinum disk embedded in a cobalt glass seal. It was polished with 0.05-mm Fisher polishing alumina and rinsed with ethanol and dried before each run. The counter electrode was platinum wire (BAS). The reference electrode was Ag/AgI, and the reported redox potentials were referenced to the ferrocene/ferrocenium couple. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. The electrochemical experiments were carried out under an argon atmosphere.

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