Basicity of 1,8-bis(dimethylamino)naphthalene and 1,4-diazabicyclo[2.2.2]octane in water and dimethylsulfoxide

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This paper is dedicated to Professor Douglas E. Ryan on the occasion of his 65th birthday


The ionization constants of the conjugate acids BH"+ of two bases widely used in synthesis, 1,8-bis(dimethylamino)naphthalene (PS), and 1,4-diazabicyclo[2.2.2]octane (DABCO), have been obtained in Me2SO and water. The partition coefficients of both bases B and their heats of solution and protonation have also been determined. The basicity of PS is dramatically reduced when passing from water to Me2SO while the basicity of DABCO remains unchanged, thus making DABCO the stronger base in Me2SO. The solvent effect on the base strength is analyzed in terms of free energy and enthalpy of transfer for B and BH". While DABCO is abnormally low when compared to that of gaseous PSH"+, BH"+ is better solvated by Me2SO while DABCOH"+ does not show a definite preference for one solvent. The calculated enthalpy of solution of gaseous PSH"+ is abnormally low when compared to that of DABCOH"+ and of related BH"+ ions, thus indicating that the proton of PSH"+ in a strong intramolecular H-bond, does not normally H-bond to the solvent. Our results suggest that the proton sponge acid--base system could be used as a convenient reference to determine the free energy and enthalpy of transfer of H+ between solvents.


Les constantes d'ionisation des acides conjugués BH"+ du bis(dimethylamino)-1,8 naphtalène (PS) et du diaza-1,4 bicyclo[2.2.2]octane (DABCO), deux bases largement utilisées en synthèse, ont été obtenues dans le Me2SO et l'eau. Les constantes de partage des deux bases B et leurs chaleurs de solution et protonation ont aussi été déterminées. On note une diminution remarquable de la basicité du PS lorsque l'on passe de l'eau au Me2SO, alors que la basicité du DABCO n'est pas affectée, de telle sorte que le DABCO devient la base la plus forte dans le Me2SO. On analyse l'effet du solvant sur la force des bases à partir des énergies libres et enthalpies de transfert de B et H+, et de BH+, de l'eau au Me2SO. La solvatisation plus forte du PS dans le Me2SO, contrôlée par un terme entropique, est analogue à celle des composés aromatiques alors que la solvatisation accrue du DABCO dans l'eau est due à des liaisons H avec les deux azotes. PSH"+, comme H+, est mieux solvatisé par le Me2SO tandis que DABCOH"+ n'a pas de préférence nette pour l'un des solvants. L'enthalpie de solution calculée pour l'ion gazeux PSH"+ est anormalement basse si on la compare à celle du DABCOH"+ et d'ions BH"+ voisins, ceci indique que le proton de PSH"+, engagé dans une liaison-H intramoléculaire forte, ne forme pas de liaison-H normale avec le solvant. Ces résultats nous suggèrent d'utiliser le système acide--base du PS comme référence simple pour déterminer l'énergie libre et l'enthalpie de transfert de H+ entre les solvants.

Introduction

In aqueous solution 1,8-bis(dimethylamino)naphthalene (proton sponge) shows an unusually high basicity for an aromatic amine (1, 2). Since it was first proposed by Alder et al., this high basicity has generally been attributed to steric strain in the neutral base which is effectively relieved in the conjugate acid where the proton is intramolecularly H-bonded to the two nitrogen atoms (3). Proton sponge (denoted PS) is of interest not only for its high basicity but also for its weak nitrogen nucleophilicity due to steric hindrance resulting from the vicinity of the two bulky dimethylamino groups (1). In fact with strong electrophiles PS reacts preferably as a carbon nucleophile (4). The unusual rates of proton transfer between PS, and related compounds, and their conjugate acids have also attracted wide interest (5).

As a continuation of our comparative thermodynamic study of the protonation of nitrogen bases in water and Me2SO (6) we recently examined the behaviour of a series of aliphatic α,ω-diamines in both solvents (7) and searched for possible evidence in solution of the intramolecular H-bonded monoprotonated form observed in the gas phase. During this work we looked briefly at two other diamines, PS and DABCO (1,4-diazabicyclo[2.2.2]octane), and also at related quinuclidine. While we found that the basicity of DABCO is little changed when passing from water to Me2SO, the pKₐ of PSH"+ shows a dramatic decrease of some 4.5 units in Me2SO so that

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{N} \\
1,8\text{-bis(dimethylamino)napthalene} & \quad 1,4\text{-diazabicyclo[2.2.2]octane} \\
\text{Proton sponge} & \quad \text{DABCO}
\end{align*}
\]

DABCO becomes a better base than PS in Me2SO. Terrier and Hallé (8), during the course of recent preparative work, also observed the superior basicity of DABCO over PS in Me2SO.

Because of the synthetic utility of PS and DABCO and the wide use of Me2SO as reaction medium, we have further explored our preliminary findings and compared more fully the thermodynamics of protonation of PS and DABCO in water and Me2SO. In addition, we evaluated the part played by solvent effects on PS and PSH"+ in modifying the intrinsic high basicity of PS and shed some light on the interactions between the intramolecular H-bonded proton in PSH"+ and both solvents.

Experimental

Materials
Proton sponge (Aldrich) was twice recrystallized in ethanol, washed with water, and dried under vacuum at room temperature. Purity of the compound as checked by titration with trifluoromethanesulfonic acid in Me2SO was 101 ± 1%. DABCO (MCB) was purified by sublimation at
75°C then dried under vacuum at room temperature and kept in a desiccator over P2O5. Its purity was 99 ± 1% as determined by HCl titration. Tetraethylammonium perchlorate (Eastman Kodak) was recrystallized in a 4:1 water–ethanol mixture and dried under vacuum at room temperature. NaCl (McArthur), trifluoromethanesulfonic acid (Aldrich) and H2SO3 (Baker) were used as received. HCl (0.1 M) and NaOH (0.1 M) were from BDH. Buffer solutions were prepared from reagent grade chemicals. Finally, Me2SO (BDH, analytical reagent) and n-heptane (A & C American Chemicals), were used without further purification. Me2SO-d6 was from Cambridge Isotope Laboratories.

pKb determinations
Potentiometric titrations of Me2SO solutions of PS and DABCO (5 × 10^{-3} to 1 × 10^{-2} M) with standardized 0.1 M HCF3SO3 in Me2SO were carried out at 25.0 ± 0.1°C as previously described (6). The solutions were made initially 0.100 M in Me2SO to keep the ionic strength constant.

A spectrophotometric procedure was used to determine the pKb value for PSHH+ in water. The spectrum of PSHH+ (pH < 9.0) shows an absorption band with a maximum at 285 nm, two small shoulders at 275 and 295 nm, and negligible absorption above 335 nm. When the pH is increased this band decreases in intensity and a new one appears at 335 nm. The basicity constant, and of the molar absorptivity \( \varepsilon \) of PS were obtained by dilution of 10^{-2}–10^{-3} M solutions in Me2SO. Preparation of PS solutions by neutralization of PSHH+ solutions with NaOH, or extraction of n-heptane solutions of PS with NaOH proved unsatisfactory. The absorbances were measured with a PMQII Zeiss spectrophotometer using 2 cm thermostatted cells. The values of pKb, the basicity constant, and of the molar absorptivity \( \varepsilon \) of PS were obtained at 25°C from the absorbances at 335 nm by the graphical procedure used by Hibbert (2). This \( \varepsilon \) value, 6500 ± 200 M^{-1} cm^{-1}, was used to calculate \( \kappa_b \) at other temperatures from additional measurements made at 5-deg intervals up to 55°C. The solutions were more stable at higher temperatures and the absorbances increased on standing.

Solubility and partition coefficient determinations
The solubility of PS in water is very low (~1 × 10^{-5} M) and is difficult to determine directly. On the other hand, the solubility of PS in Me2SO is high (~0.8 M), and while that of DABCO is high in both water and Me2SO (>2 M), so that the saturated solutions of the bases in both solvents may not behave ideally. Thus, in order to avoid the problems inherent in determining the activities of both PS and DABCO in their saturated solutions in water and Me2SO, we determined the partition coefficient of PS and DABCO between water and Me2SO using n-heptane as the common immiscible reference solvent.

First, the partition coefficient of PS between n-heptane and Me2SO, \( P_{h/w} \), was obtained by determining potentiometrically the concentration of PS in the Me2SO phase after equilibration of three 50 mL samples of 2.2 × 10^{-2} M PS solution in n-heptane and 50 mL Me2SO, and also of two 50 mL n-heptane with 50 mL 0.7–1.0 × 10^{-2} M PS in Me2SO. The equilibrium concentration of PS in n-heptane was calculated by difference. Since it was not practical to determine directly \( P_{h/w} \), the partition coefficient of PS between n-heptane and water, \( P_{w/w} \), was obtained indirectly from experimental values of the distribution coefficient \( D = (P_{h/w}/(P_{w/w} + (PSH^+))) \) at several pH and the relation

\[
\log D = \log P_{h/w} - pK_a + pH
\]

which is valid for pH < pK_a. Then, 50 mL of 3.3–0.12 × 10^{-3} M PS solutions in n-heptane were equilibrated with 50 mL of five buffer solutions (pH 4.80, 5.74, 6.29, 6.86, 6.99). The equilibrium PS concentration in n-heptane was determined by spectrophotometry at 327 nm with \( \varepsilon = 9020 \) and that of PS (i.e. PSHH+) in water was calculated by difference.

The determination of the partition coefficients of DABCO, \( P_{h/v} \), and \( P_{w/v} \) did not present any difficulty. First, 20 mL samples of 0.172 M DABCO solution in Me2SO were equilibrated with 20 mL of n-heptane, and the Me2SO phase was analyzed potentiometrically with standard HCl at 25°C. The equilibrium DABCO concentration in n-heptane was found by difference. Second, 2 mL portions of 1.51 M DABCO solutions in water were equilibrated with 25 mL of n-heptane; then 20 mL of this n-heptane solution was analyzed for DABCO by equilibrating with 20 mL water and titrating the aqueous phase with standard acid.

Calorimetric measurements
The heats of solution of PS in Me2SO, and of DABCO in water and in Me2SO were measured at 25.0°C with a LKB Model 8725-2 isoperibol calorimeter as previously described (6), the amount of base dissolved being known from the weights of the glass ampoules. For each base, three to five separate determinations were made at different concentrations by dissolving 3–10 × 10^{-4} mole of base in 100 mL of solvent. The heats of neutralization of the solid bases were determined similarly using an excess of 0.1 M HCF3SO3 in Me2SO or 0.1 M HCl in water. For DABCO the heat of neutralization for the first protonation was subsequently determined by dissolving a known excess of DABCO in 2.4–5.2 × 10^{-3} M HCF3SO3 in Me2SO. Some difficulties were experienced in determining the heat of neutralization of PS in aqueous 0.1 M HCl because the PS particles dissolve slowly and have a tendency to float. In order to improve the accuracy, 0.35 M HCl and H2SO3 solutions were also used. The heat of solution of PS in water could only be determined indirectly from its heat of neutralization, and from its heat of protonation which, in turn, obtained from the variation of \( pK_a \) with temperature.

Nuclear magnetic resonance measurements
The second protonation of PS was studied by 13C nmr. Spectra of 0.3 M solutions of PS were recorded rapidly between 10–18 M H2SO4 because some decomposition takes place on standing. The quaternary carbons were easily singled out and other carbons were identified from literature data on aniline and dimethylaniline (9). The 13C spectra were acquired at 25°C on a Bruker WP-80 spectrometer operating at 20.2 MHz. Data acquisition and Fourier transformation were performed with 8 K data points. 13C chemical shifts were measured relative to external dioxane in D2O and converted to the Me4Si scale with \( \delta_{Me4Si} = \delta_{dioxane} + 67.40 \) ppm. 13C spectra in Me2SO were also taken on 0.2 M PS solutions to which HCF3SO3 was added to obtain molar ratios of acid-to-base equal to 0, 0.25, 0.50, 1.00, and 2.00. Similar molar ratio experiments were carried out on 0.1 M PS solutions in Me2SO-d6 for the recording of 1H spectra. A Bruker WH-90 spectrometer operating at 90.0 MHz was used and 1H chemical shifts were determined using Me4Si as internal reference. The protonation of DABCO was also studied by 13C nmr using the molar ratio method, first by adding HCF3SO3 to a 0.2 M DABCO solution in Me2SO, then by adding HClO4 to 0.1 M DABCO in water.

Results

\( pK_{a} \) and free energies of transfer
The ionization constants \( K_a \) of the protonated bases PSHH+, DABCOH+, and DABCOH2+ in Me2SO were obtained from the potentiometric neutralization data by using a program described previously (6). Our \( pK_a \) values for BH2+ are given in Table 1 together with the very accurate values of Paoletti et al. (10) for DABCOH+ and DABCOH2+ in water. No corrections were made for the effect of ionic strength, which would be small for such reactions.

The basicity constant \( K_b \) and molar absorptivity of PS in water at 25°C were determined from absorbance measurements in 10^{-3}–10^{-1} M NaOH by using the graphical procedure of Hibbert (2). The corresponding \( pK_b \) value in Table 1 was then deduced from \( pK_b = 1.8 \pm 0.1 \) and the dissociation constant of water at 0.11 ionic strength. The \( pK_b \) for PSHH+ was obtained from the 13C nmr data in 10–18 M H2SO4 by using the excess acidity method and the program developed by Cox as previously described (11).
The free energy of transfer $\Delta G^0$ (hypothetical 1 M solution as standard state) from water to Me$_2$SO for both PS and DABCO was obtained from the partition coefficient $P_{h/w}$ calculated in turn from the partition coefficient between Me$_2$SO and n-heptane, $P_{h/s}$, and the partition coefficient, $P_{h/w}$, between water and n-heptane. For PS, we determined $P_{h/w}$ from the experimental relation between the distribution coefficient $D$ and pH, log $D$ as standard state) from water to experimental relation between the distribution coefficient $D$ and 5.2

### Table 1. Ionization constants $K_a$ of BH$_n^{n+}$ ions at 25°C

<table>
<thead>
<tr>
<th>BH$_n^{n+}$</th>
<th>Me$_2$SO</th>
<th>H$_2$O</th>
<th>$\Delta pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSH$^+$</td>
<td>7.47 ± 0.04</td>
<td>12.0 ± 0.1</td>
<td>-4.5</td>
</tr>
<tr>
<td>PSH[3]+</td>
<td>-9.0 ± 0.2</td>
<td>5.2</td>
<td>-2.7</td>
</tr>
<tr>
<td>$\delta$NM$_2$H$_2$ $^{n+}$</td>
<td>2.5</td>
<td>8.4</td>
<td>-1.4</td>
</tr>
<tr>
<td>Me$_2$NH$_2$ $^{+}$</td>
<td>9.8</td>
<td>11.0</td>
<td>-1.2</td>
</tr>
<tr>
<td>Quinuclidine H$^+$</td>
<td>9.8</td>
<td>11.0</td>
<td>-1.2</td>
</tr>
<tr>
<td>DABCOH$^+$</td>
<td>8.93 ± 0.05</td>
<td>8.82 ± 0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>DABCOH$_2$$^{+}$</td>
<td>2.97 ± 0.05</td>
<td>2.97 ± 0.01</td>
<td>0.1</td>
</tr>
</tbody>
</table>

$^a$Reference 18.  
$^b$Reference 21.  
$^c$M. Fréchet, Unpublished data.  
$^d$Reference 10.

The values of the free energies of transfer $\Delta G^0$ (BH$^+$) of the conjugate acids BH$,^+$, from water to Me$_2$SO, are calculated by means of relation [2] derived from the thermodynamic cycle relating protonation processes in both solvents.

\[
\Delta G^0(BH^+) = \Delta G^0(B) + \Delta G^0(H^+) + \Delta G^0_{ps} - \Delta G^0_{pw}
\]

where $\Delta G^0_{ps}$ and $\Delta G^0_{pw}$ are the free energies of protonation in both solvents calculated from the $pK_a$ values in Table 1. The free energy of transfer of the proton, $-19$ kJ mol$^{-1}$, is based on an extrathermodynamic assumption (12).

The $\Delta G^0(BH^+)$ values are, respectively, $-21$ and $-3$ kJ mol$^{-1}$ for PSH$^+$ and DABCOH$^+$; the errors are unknown, since they depend on the validity of the extrathermodynamic assumption. All of our free energies of transfer are listed in Table 2.

**Protonation enthalpies and enthalpies of transfer**

The plots of the heats of solution of DABCO in water and of both bases in Me$_2$SO and Me$_2$SO solutions of 0.1 M HCl or H$_2$SO$_4$ against the number of moles dissolved were linear and the least-squares slopes gave $\Delta H^0_{ps}$ or $\Delta H^0_{pw}$ [3] and $\Delta H_{ns}^0$ (Me$_2$SO) or $\Delta H_{nw}^0$ (B) [4] according to

\[
\begin{align*}
\text{[3]} & \quad \Delta H^0_{ps} = B(c) = B(s) + \text{w} \\
\text{[4]} & \quad \Delta H^0_{ps} + H^+(s \text{ or w}) = BH^+(s \text{ or w}) \\
\text{[5]} & \quad \text{DABCO(c) + 2H^+(s) = DABCOH}_2^+(s) \\
\text{[6]} & \quad \text{B(s or w) + H^+(s or w) = BH^+(s or w)}
\end{align*}
\]

$\Delta H^0_{ps}$, the enthalpy for the first protonation of DABCO (eq. [6]) in Me$_2$SO was obtained by subtracting from $Q_n$, the heat change found for dissolving $n_b$ moles of DABCO in $n_a$ moles of acid ($n_b \gg n_a$), $Q_n = n_b \times \Delta H^0_{ps}$, and by taking $\Delta H^0_{ps} = (Q_n - Q_i)/n_a$. The heat of neutralization of PS (reaction [4]) in water, $\Delta H^0_{nw}$, is an average of values determined in 0.1–0.35 M HCl and H$_2$SO$_4$. The $pK_a$ values for PS were determined at 5 deg intervals between 25 and 55°C from absorbance measurements at 335 nm on three series of solutions with 2.5, 5.0, and 10.0 $\times$ 10$^{-3}$ M NaOH. The $pK_a$ values were plotted against 1/T to give by a least-squares procedure the associated enthalpy value, $-11 \pm 4$ kJ mol$^{-1}$, which, in turn, was combined with the enthalpy for the dissociation of water at 25°C and 0.11 ionic strength to give the enthalpy of protonation $\Delta H^0_{nw} = -65 \pm 4$ kJ mol$^{-1}$ according to [6].

Then $\Delta H^0_{nw}$ for PS was obtained from

\[
\Delta H^0_{nw}(B) = \Delta H^0_{nw}(B) - \Delta H^0_{pw}(B)
\]

A similar equation was used to calculate this time $\Delta H^0_{pw}$ for PS and DABCO in Me$_2$SO. The $\Delta H^0_{pw}$ values used for DABCO were from Paoletti et al. (10). The values of the enthalpy of solution and protonation of PS and DABCO are listed in Table 3.

The values of the enthalpies of transfer of PS and DABCO, $\Delta H^0_{ps}(B)$, were calculated from the enthalpies of solution of both bases in water and Me$_2$SO. $\Delta H^0_{ps}(B)$ was obtained from eq. [8] for DABCOH$^+$ and from eq. [9] for PSH$^+$ taking $\Delta H^0_{nw}(H^+) = -25.5$ kJ mol$^{-1}$ (12).

\[
\begin{align*}
\text{[8]} & \quad \Delta H^0_{ps}(BH^+) = \Delta H^0_{bs}(B) + \Delta H^0_{ps}(H^+) + \Delta H_{ps}^0 - \Delta H_{pw}^0 \\
\text{[9]} & \quad \Delta H^0_{ps}(BH^+) = \Delta H^0_{ps}(H^+) + \Delta H_{ns}^0 - \Delta H_{nw}^0
\end{align*}
\]

The enthalpies of transfer are given in Table 4.

**Enthalpies of transfer from the gas phase to Me$_2$SO and water**

The enthalpies of protonation of both PS and DABCO in the gas phase $\Delta H^0_{ps}$ according to

\[
\begin{align*}
\text{[10]} & \quad B(g) + H^+(g) = BH^+(g)
\end{align*}
\]

have been determined by several groups of workers (13–15). The values of $\Delta H^0_{ps}$, i.e., minus the proton affinity, given in Table 3, are averages and based on PA = 207 kcal mol$^{-1}$ for NH$_3$, 224 kcal mol$^{-1}$ for pyridine, and 229 kcal mol$^{-1}$ for trimethylamine. Thus, the $\Delta H^0_{ps}$ values taken for PS and DABCO are respectively, 1030 and 970 kJ mol$^{-1}$, these values being rounded to the nearest 5 kJ mol$^{-1}$.

We can now obtain the valuable enthalpies of transfer of BH$^+$ ions from the gas phase to water, $\Delta H^0_{pw}(BH^+)$, and to Me$_2$SO, $\Delta H^0_{ps}(BH^+)$, by using relations derived from the thermodynamic cycles relating protonation processes in the gas phase and Me$_2$SO or water. For example, from eqs. [4] and [10], we derive

\[
\begin{align*}
\text{[11]} & \quad \Delta H^0_{gs}(BH^+) = \Delta H^0_{gs}(B) + \Delta H^0_{ps}(H^+) + \Delta H_{ps}^0 - \Delta H_{gs}^0 \\
\Delta H^0_{gs}(BH^+) & \quad \text{is taken as } -1155 \text{ kJ mol}^{-1}, \text{ which is based on } \Delta H^0_{ps}(H^+) = -25 \text{ kJ mol}^{-1} \text{ and } \Delta H^0_{pw}(BH^+) = -1130 \text{ kJ mol}^{-1} \text{ } (-270 \text{ kcal mol}^{-1}) \text{ (12). } \Delta H_{gs}^0 \text{ is } -\Delta H_{gs}^0, \text{ the enthalpy of sublimation. } \Delta H_{sub}^0 \text{ is calculated for DABCO as } +65 \text{ kJ mol}^{-1} \text{ from a literature value at } 65^\circ \text{C (16) corrected to } 25^\circ \text{C (17). } \Delta H_{sub}^0 \text{ for PS was estimated as follows. The enthalpy of fusion of PS } \text{ (t$_f$ = 48°C) was estimated as } +20 \text{ kJ mol}^{-1}, \text{ from a heat of solution in Me$_2$SO, } +25 \text{ kJ mol}^{-1}, \text{ minus a small enthalpy of solution of a non-associated liquid in Me$_2$SO taken as } +5 \text{ kJ mol}^{-1} \text{ (18). The enthalpy of vaporization } \Delta H^0_{vap} \text{ of liquid PS at } 25^\circ \text{C, } +70 \text{ kJ mol}^{-1}, \text{ was obtained from a correlation line between } \Delta H_{gs}^0 \text{ and normal boiling points } \text{ t$_b$ for tertiary amines (19) and an estimated } \text{ t$_b$ } \sim 320^\circ \text{C. Finally, } \Delta H_{sub}^0 \text{ is obtained as } +90 \text{ kJ mol}^{-1} \text{ which is interestingly near the value for}
\end{align*}
\]
Free energies of transfer (kJ mol⁻¹) of B and BH⁺ from water to Me₂SO at 25°C

<table>
<thead>
<tr>
<th>B or BH⁺</th>
<th>PS</th>
<th>PSH⁺</th>
<th>DABCO</th>
<th>DABCOH⁺</th>
<th>Me₂N⁺</th>
<th>Me₂NH⁺</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG°(B or BH⁺)</td>
<td>-28</td>
<td>-21</td>
<td>+16</td>
<td>-3</td>
<td>+5.3</td>
<td>-5.4</td>
<td>-19</td>
</tr>
</tbody>
</table>

*Standard state as hypothetical 1 M solution.

<table>
<thead>
<tr>
<th>B</th>
<th>ΔH°(B)</th>
<th>ΔH°(BH⁺)</th>
<th>ΔH°(BH⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>+24.3 ± 1.0</td>
<td>+30 ± 5</td>
<td>-48.5 ± 0.6</td>
</tr>
<tr>
<td>DABCO</td>
<td>+19.4 ± 0.4</td>
<td>-24.6 ± 0.4</td>
<td>-53 ± 1</td>
</tr>
<tr>
<td>DABCOH⁺</td>
<td>-38 ± 2</td>
<td>-12.56 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>

*Reference 10.

Enthalpies of solution and enthalpies of protonation (kJ mol⁻¹) of PS and DABCO at 25°C

<table>
<thead>
<tr>
<th>B</th>
<th>ΔH°(B)</th>
<th>ΔH°(B)</th>
<th>ΔH°(DABCOH⁺)</th>
<th>ΔH°(DABCOH⁺)</th>
<th>ΔH°(DABCOH⁺)</th>
<th>ΔH°(DABCOH⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>+24.3 ± 1.0</td>
<td>+30 ± 5</td>
<td>-48.5 ± 0.6</td>
<td>-65 ± 4</td>
<td>-1030b</td>
<td></td>
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<tr>
<td>DABCO</td>
<td>+19.4 ± 0.4</td>
<td>-24.6 ± 0.4</td>
<td>-53 ± 1</td>
<td>-30.54 ± 0.04a</td>
<td>-970c</td>
<td></td>
</tr>
<tr>
<td>DABCOH⁺</td>
<td>-38 ± 2</td>
<td>-12.56 ± 0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 5. ¹³C shift values (ppm) of PS, PSH⁺, and PSH₂⁺ in Me₂SO and water

<table>
<thead>
<tr>
<th>¹³C</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-9</th>
<th>C-10</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS (Me₂SO)</td>
<td>151.3</td>
<td>113.8</td>
<td>126.5</td>
<td>122.5</td>
<td>120.9</td>
<td>138.4</td>
<td>45.3</td>
</tr>
<tr>
<td>PSH⁺ (Me₂SO)</td>
<td>145.6</td>
<td>122.8</td>
<td>128.0</td>
<td>130.0</td>
<td>120.0</td>
<td>135.9</td>
<td>46.9</td>
</tr>
<tr>
<td>PSH⁺ (H₂O)</td>
<td>144.3</td>
<td>121.9</td>
<td>127.8</td>
<td>130.0</td>
<td>118.9</td>
<td>135.8</td>
<td>46.6</td>
</tr>
<tr>
<td>PSH₂⁺ (H₂O)</td>
<td>135.4</td>
<td>124.4</td>
<td>128.2</td>
<td>135.4</td>
<td>116.9</td>
<td>138.3</td>
<td>51.5</td>
</tr>
</tbody>
</table>

*Standard deviation usually better than 0.1 ppm.

1,8-dimethylnaphthalene, +83 kJ mol⁻¹ (20). Although our ΔH°(sub) value is obviously a crude estimate, the error is not unlike that on PA values, 5–10 kJ mol⁻¹. Our calculated enthalpies of transfer from the gas phase are listed in Table 4.

Nuclear magnetic resonance data

The ¹³C limit chemical resonance shifts obtained for PSH⁺ and PSH₂⁺ from our data in 10–18 M H₂SO₄ are summarized in Table 5. The ¹³C shift values for PS and PSH⁺ in Me₂SO are also given. The spectra corresponding to Me₂SO solutions containing molar ratios of acid to PS between 0 and 1 showed signals for both PS and PSH⁺. Apparently the exchange between the nonprotonated and protonated forms is too slow to be observed on the nmr time scale at room temperature.

H signals for both PS and PSH⁺ were also observed in solutions with molar ratios of acid to PS between 0 and 1 and the proton of PSH⁺ appeared at unusually low field, 18.36 ppm. Further addition of acid did not cause shift of the PSH⁺ proton, so that the exchange between PSH⁺ and protonated Me₂SO (HCF₃SO₃ is a strong acid in Me₂SO) is also slow. The PSH⁺ spectrum shows a doublet signal for the methyl protons. The splitting (J = 2.4 Hz) is due to coupling with the PSH⁺ proton.

In contrast, the study of the protonation of DABCO by ¹³C nmr, using the molar ratio method, indicated exchange between DABCO and both protonated species both in water and in Me₂SO. The plots of the ¹³C shifts against the molar ratio of acid-base consisted of three straight lines whose intersections corresponded to molar ratios 1.0 and 2.0. The C-1 shift values for DABCO, DABCOH⁺, and DABCOH₂⁺, deduced from the graphs, are respectively 48.2, 45.3, 44.1 ppm in Me₂SO and 46.0, 44.9, and 44.4 ppm in water.

Discussion

Ionization constants and free energies of transfer

We will consider the ionization constants Kₐ of PSH⁺ and DABCOH⁺ first, since they are our initial raw data. We will then discuss the solvent effect on Kₐ in terms of free energy of transfer of B and BH⁺.

The data in Table 1 show that on passing from water to Me₂SO the pKₐ change is -4.5 for PSH⁺ and +0.1 for DABCOH⁺, thus confirming our preliminary findings that while in water PS is a much better base than DABCO, the reverse holds true in Me₂SO. Our previously determined ΔpKₐ for dimethylaniline (-2.7) and for trimethylamine (-1.4) (18) listed in Table 1 for comparison, suggest that, at least in part, the pKₐ changes for PSH⁺ and DABCOH⁺ in Me₂SO are in line with what is expected for related amines in the aromatic and aliphatic series. However, PS and DABCO must have some additional specific structural factors which would account for their ΔpKₐ being larger than for the simple parent amines considered. For DABCO at least, it is clear that its diamine nature plays a part in explaining its ΔpKₐ = +0.1 since its monoamine analog, quinuclidine, has a ΔpKₐ = -1.2 (Table 1) very close to that of Me₂N, -1.4.
The very weak basicity of PSH$^+$ is noteworthy with a corresponding $pK_a$ value of $-9.0 \pm 0.2$ (half protonation in $15.2\, M\, H_2SO_4$, $m^* = 1.12 \pm 0.04$ (11)). The extraordinary stability of PSH$^+$ (1) with respect to protonation and deprotonation as shown by both its $pK_a$ values, is totally different from what is observed both for DABCOH$^+$ (Table 1) and for BH$^+$ ions in the $\alpha,\omega$-diamines series where there is no “dicoordination” of the proton (7).

Turning now to the free energies of transfer of B and BH$^+$ in Table 2, we note first the highly contrasted $\Delta G^T$ values for both bases, PS and DABCO. The high and negative $\Delta G^T$ for PS is typical of aromatics behaviour with their very low solubility in water and high solubility in Me$_2$SO. The situation is completely reversed for DABCO with $\Delta G^T = +16\, kJ\, mol^{-1}$, indicating that DABCO is more strongly solvated by water through H-bonding to both nitrogens. Looking next at the values of $\Delta G^T(BH^+)$, we find that PSH$^+$ exhibits a strong preference for Me$_2$SO while DABCOH$^+$ is only slightly better solvated by Me$_2$SO. To conclude this free energy analysis of the solvent effect, the much reduced basicity of PS when passing from water to Me$_2$SO comes from three nearly equal contributions of some 23 kmol$^{-1}$, those on PS and H$^+$ being opposed by that on PSH$^+$. For DABCO, the absence of solvent effect on its basicity is due to nearly equal and opposite effects on the neutral base and H$^+$.

**Enthalpies of transfer**

Our values of the enthalpies of transfer $\Delta H^T$ of PS, DABCO, PSH$^+$, and DABCOH$^+$ from water to Me$_2$SO (Table 4) present interesting results when compared with previous data (18, 21) for aliphatic and aromatic amines. First, the small $\Delta H^T$ for PS is typical of what is observed for aromatics (for $C_7H_6$, $\Delta H^T = -0.3\, kJ\, mol^{-1}$) so that, given the high negative value of $\Delta G^T$, there must be a very large compensating positive entropy of transfer, as is common to aromatics, and which reflects the peculiarities of water as a solvent. For DABCO, $\Delta H^T$ is large and positive indicating much stronger interactions with water, as was already clear with $\Delta G^T$. Again the $\Delta H^T$ value for DABCO is near that for the aliphatic amine Me$_3N$; the $\Delta G^T$ values for both bases are also positive (21) and almost identical. The negative $\Delta H^T$ values for all the BH$^+$ ions which are listed in Table 4 indicate some 15–20 $kJ\, mol^{-1}$ stabilization in Me$_2$SO though much less for DABCOH$^+$.

Finally, if we turn our attention to the enthalpies of transfer of a series of BH$^+$ ions from the gas phase to Me$_2$SO in Table 4, we draw some highly valuable conclusions. We note first that the values of $\Delta H^T$ for different nitrogen bases, B = DABCO, Me$_3N$, Py, and $\phi$NMe$_2$ are all within $-280 \pm 5\, kJ\, mol^{-1}$ while $\Delta H^T$ (PSH$^+$) is some 40 kmol$^{-1}$ less exothermic. We previously found (18, 21) that the exothermic heat of solution of substituted ammonium ions decreases with the number of N—H protons which can H-bond to Me$_2$SO, the size of the substituent being of lesser importance. The average decrease of the heat of solution of the gaseous ions per H-bond was about 35 kmol$^{-1}$. Then it is clear that while DABCOH$^+$, Me$_3$NH$^+$, PyH$^+$, and $\phi$NMe$_2$H$^+$ all form one H-bond with Me$_2$SO, PSH$^+$ does not normally H-bond to the solvent. If the solvation of the PSH$^+$ cation is non-specific, its heat of solution $\Delta H^T = -239\, kJ\, mol^{-1}$ should be near that of ions such as the tetraalkylammonium. Unfortunately, these latter values are not well established because they depend on some assumptions for the calculation of lattice enthalpies of related salts (22). Our comparisons of enthalpies of solution of BH$^+$ ions in Me$_2$SO (Table 4) could have been made with water as the solvent. The values of $\Delta H^T$ (BH$^+$) are easily calculated from our data in Table 4 with $\Delta H^T = \Delta H^T(BH^+) - \Delta H^T(BH^+)$ for B = Me$_3N$, Py, and $\phi$NMe$_2$. We obtain an enthalpy of solution in water of $-262\, kJ\, mol^{-1}$ while for DABCO the value is much more exothermic, $-280\, kJ\, mol^{-1}$, largely because of H-bonding of the second nitrogen of this diamine to water (there was no such H-bonding with Me$_2$SO). For B = PS, $\Delta H^T(BSH^+) = -224\, kJ\, mol^{-1}$ which is much less exothermic and is close to the rough estimate given by Taft ($-210\, kJ\, mol^{-1}$) (23) for “limiting physical ion-dipole and ion — induced dipole solvation of univalent cations which do not involve specific cation—molecule chemical bonding”. We, therefore, conclude that the proton of PSH$^+$ is involved in a strong intramolecular H-bond which precludes H-bonding to water, or even to more basic Me$_2$SO as we have seen. Further support of this point comes from the remarkable correlation of Taft et al. (23) which suggests that the solvation behaviour of PSH$^+$ in water is more like that of resonance-stabilized carbonium ions.

The exceptionally slow rate of proton transfer from PSH$^+$ to OH$^-$ also implies that there is an unusually strong intramolecular H-bond in PSH$^+$ (2). The lack of exchange on the nmr time scale between PS, PSH$^+$, and acids in Me$_2$SO and other solvents (1, 24) is as well indicative of unusual properties of the proton in PSH$^+$ and the $^1H$ nmr spectra of PSH$^+$ in Me$_2$SO is compatible with the presence of a strong H-bond with H$^+$ in a bridge between the nitrogen atoms.

**The proton sponge acid—base system as a reference**

There is a most interesting consequence of the apparent lack of specific chemical interactions between PSH$^+$ and Me$_2$SO or water, and presumably between PSH$^+$ and other solvents. We propose to use the PSH$^+/PS$ acid—base system as a reference system to obtain values of $\Delta G^T(H^+)$, the free energy of transfer of H$^+$ between solvents, and hence obtain values of $\Delta G^T$ for other cations and anions. Equation [2] can be rearranged to give

$$[12] \quad \Delta G^T_1(H^+) = \Delta G^T_1(PH^+) - \Delta G^T_1(PH^+)$$

where $t$ stands for transfer from solvent 1 to solvent 2 and $\Delta G^T_1$ and $\Delta G^T_2$ are the free energies of protonation in solvents 1 and 2, respectively. Assuming

$$[13] \quad \Delta G^T_1(PH^+) = \Delta G^T_1(PS)$$

we obtain

$$[14] \quad \Delta G^T_1(H^+) = \Delta G^T_1(PH^+) - \Delta G^T_2(PH^+)$$

For example, with water and Me$_2$SO we calculate from our data in Table 1 $\Delta G^T_1(H^+) = -26\, kJ\, mol^{-1}$. The extrathermodynamic assumption corresponding to eq. [13] is equivalent to supposing first that PS is an excellent neutral analog of PSH$^+$ and second that the electrostatic contribution $\Delta G^T_2(PSH^+)$ is negligible (12). The first assumption is the direct consequence of our finding that PSH$^+$ does not give any specific interaction with the solvent, and the second assumption is reasonable as long as the solvent dielectric constant is not too low. Although more data with other solvents are obviously needed to assess completely the validity of our proposed extrathermodynamic assumption, it is interesting to note that the corresponding $\Delta G^T_1(H^+)$ value for the transfer from water to Me$_2$SO, $-26\, kJ\, mol^{-1}$, is in acceptable agreement with the $\Delta G^T_1(H^+)$. 

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1For naphthalene, $\Delta H^T = -11\, kJ\, mol^{-1}$. 

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2Interactions between nitrogens of PS and water, or other H-bond donor solvents, are likely to be minimal.
value \(-19 \text{ kJ mol}^{-1}\) deduced from the widely used TATB assumption, i.e. \(\Delta G^0(\text{Asf}_4^+) = \Delta G^0(Bf_4^+)\), considering that the ferrocene assumption used by electrochemists gives a \(-32 \text{ kJ mol}^{-1}\) value (12) and the Hammett type hypothesis \(\Delta G^0(BH^+) = \Delta G^0(B)\) where B is a Hammett base) leads to \(-9 \text{ kJ mol}^{-1}\) (12). One advantage of our proposed assumption is its directness: we only need the \(pK_a\) values of the PSH\(^+\)/PS system in both solvents to calculate \(\Delta G^0(H^+)\) while the other assumptions usually require a large number of experimental determinations which lead to an increased margin of error. It is clear that the PSH\(^+\)/PS system can also be used as a reference to establish an enthalpy scale for the transfer of \(H^+\) between solvents. By assuming

\[\Delta H^0_t(PS) = \Delta H^0_t(PSH^+)\]

we calculate for \(\Delta H^0_t(H^+)\) (eq. [8]) \(-16 \text{ kJ mol}^{-1}\) for the water–Me\(_2\)SO transfer, a value which also is in reasonable agreement with \(-25 \text{ kJ mol}^{-1}\) deduced from the TATB assumption. Here, again, our extrathermodynamic assumption leads to more directly accessible values of \(\Delta H^0_t(H^+)\) than does the TATB assumption.

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