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Internal and External Solvation of Polyfunctional Ions

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Abstract: In protonated difunctional amines, $X(CH_2)_nNH_3^+$, intramolecular solvation of the protonated function creates hydrogen bonded cyclic structures. The enthalpy of cyclization, $-\Delta H_{cyc}°$, increases with increasing ring size from $n = 2$ to $n = 4$. Intramolecular H bonding is weaker than H bonding in dimer ions because of ring strain, constrained geometry of the H bond, and polarization of the X function. The combined effect of these factors, denoted as $\Delta H_{strain}°$, weakens the intramolecular bond by ca. 17, 8, and 4 kcal mol^{-1} when $n = 2$, 3, and 4, respectively. The entropy of cyclication, $\Delta S_{cyc}°$, becomes more negative as the ring size increases, from −8 to −14 to −17 cal mol^{-1} K^{-1} for $n = 2$, 3, and 4, respectively. Comparison of protonated diamines and amino alcohols shows that $\Delta H_{strain}°$ and $\Delta S_{cyc}°$ are similar in rings of the same size in the two types of ions. In protonated triamines $NH_2(CH_2)_nNH_2^+(CH_2)_nNH_2$, $n = 2$ or 3, $\Delta H_{strain}°$ and $-\Delta S_{cyc}°$ indicate that only one small H-bonded ring is formed. However, the thermochemistry suggests that in $NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2$ at temperatures below 400 K the proton will shift from the secondary to a primary amine function to form a large H-bonded ring. The thermochemistry of hydration of polyfunctional ions shows that hydration decreases the stability of the internal H bond. For example the exothermicity of ring closure for the naked $NH_2(CH_2)NH_3^+$ ion is 14.2 kcal mol^{-1} but it decreases to 10.5 and 8.8 kcal mol^{-1} when the ion is solvated by one or two water molecules, respectively. Further hydration makes the entropy of ring closure more negative. As a result, the overall stability of the internal H bond is decreased by increasing solvation. For example, the temperature required for thermal opening of the H-bonded ring is calculated as 966 K for naked $NH_2(CH_2)_3NH_3^+$ but only 420 K for the ion solvated by four H_2O molecules. Kinetic studies show that H^+-transfer reactions to the diamines, which are exoergic only if the product ions are cyclic, proceed near unit collision efficiency. This shows that the intramolecular H bond is formed within the lifetime of the reaction complex. In a case when the reverse rather than forward reaction is exoergic, e.g., in H^+ transfer from $HO(CH_2)_3NH_3^+$ to $(CH_3)_3N$, the exoergic step proceeds near *unit collision efficiency*, even though this is an *endothermic* reaction.

Introduction

Intramolecular solvation of protonated functional groups has been observed to enhance the gas-phase basicities or acidities of several types of polyfunctional molecules. Such phenomena were observed in diamines,[1] polyamines,[2] amino alcohols, halogenated amines,[1] diaminonaphthalenes,[3] and some cyclohexanediols.[4] These observations suggest that intramolecular solvation is a common occurrence in gas-phase ions, and it should be prevalent in many biological molecules which have several functional groups. Despite the common occurrence, however, the entropy and enthalpy effects of intramolecular hydrogen bonding in gaseous ions were determined only in a few diamines. Yamdagni and Kebarle,[5] who performed these measurements, found that the enthalpies and entropies of protonation of diamines $NH_2(CH_2)_nNH_2$, $n = 2$–7, were consistent with the formation of internally hydrogen-bonded cyclic structures in the ions.

In contrast to the gas phase, in solution the external solvent may compete with the intramolecular functional groups to solvate the protonated function. Specifically, the solvent may delocalize the charge from the protonated function, thereby weakening its ability to engage in internal solvation. Also, the structure of the solvent may be different about the internally bonded vs. open polyfunctional ions. Through these effects the solvent may alter the relative stabilities of the internally bonded vs. open forms and in the extreme case cause the opening of the internal hydrogen bond.

We expect that the thermochemistry of the stepwise solvation of polyfunctional ions will clarify the factors involved in the competition between internal and external solvation. The thermochemistry of the internal and external solvation of protonated amine groups will be reported in this paper.

Experimental Section

Measurements were performed on the Rockefeller University Chemical Physics Mass Spectrometer, operated in the pulsed ionization mode.[6] Equilibrium and kinetic measurements were done by using the usual

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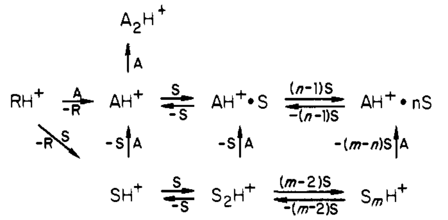
Table I. Enthalpies, Entropies, and Free Energies of Proton-Transfer Reactions $B_1H^+ + B_2 \rightleftarrows B_2H^+ + B_1$ and Proton Affinities of Diamines and Amino Alcohols[a]

		$-\Delta H°$ [b]		$-\Delta S°$ [b]		$-\Delta G°_{330}$ [c]			
B_1	B_2	this work	YK[e]	this work	YK	this work	YK	AB	PA of B_2 [d]
Me_2NH	$NH_2(CH_2)_2NH_2$	5.3	9.6	5.8	12.7	3.4	5.4	3.2	227.8
Et_2NH		−0.2		4.5		−1.7		−1.4	226.9
Pr_2NH		−2.9		4.0		−4.2		−3.7	226.5
pyridine		5.0		6.0		3.0		2.9	227.4
Me_3N	$NH_2(CH_2)_3NH_2$	9.0	13.0	13.3	20.6	4.6	6.2	4.4	235.3
Pr_2NH		5.8		10.8		2.2		1.7	235.2
Pr_2NH	$NH_2(CH_2)_4NH_2$	10.1		14.3		5.4		4.7	239.5
Me_2NH	$NH_2(CH_2)_2OH$	0.2		0.3		0.1			220.7
Me_3N	$NH_2(CH_2)_3OH$	3.5		11.9		−0.4		−0.5	229.8
pyridine	$NH_2(CH_2)_4OH$	12.9		16.1		7.6			235.3
i-$Pent_3N$	$NH_2(CH_2)_3NH(CH_2)_3NH_2$	10.2		13.4		6.8			247.5
i-$Pent_3N$	$NH_2(CH_2)_2NH(CH_2)_2NH_2$	0.2		5.0		−1.5			237.5

[a] $\Delta H°$, $\Delta G°$, and PA in units of kcal mol^{-1}; $\Delta S°$ in units of cal K^{-1} mol^{-1}. [b] Error estimates from average of standard deviations of slopes and intercepts of van't Hoff plots: for $\Delta H°$, ±0.4 kcal mol^{-1}; for $\Delta S°$, ±0.7 cal K^{-1} mol^{-1}. [c] For this work and YK (Yamdagni and Kebarle[5]) values calculated from $\Delta G°_{330} = \Delta H° - 330\Delta S°$. For AB (Aue and Bowers[1]) values obtained directly from ICR gas-phase basicity data. [d] Using PA values of reference bases as given by Aue and Bowers,[1] but adjusted to $PA(NH_3) = 207$ kcal mol^{-1} as reference standard. [e] Yamdagni and Kebarle.[5]

Scheme I



procedures;[6] i.e., ions were generated by a 10-μs ionizing electron pulse, and the relative concentrations of reactant and product ions were followed as a function of reaction time to 100–1000 μs. Variation of ion intensities with approach to equilibrium yielded kinetic results, and at longer times, constant product/reactant ion intensities, combined with known neutral partial pressures, yield equilibrium constants. Proton-transfer equilibria were measured in mixtures containing *i*-C_4H_{10} or CH_4 as the major carrier gas and small quantities (0.1–1%) of a sample and a reference amine. When the samples were volatile compounds, mixtures were prepared by premixing the components in 5-L bulbs at room temperature. When the samples had low vapor pressures, they were mixed with the reference compounds and carrier gas in a heated bulb. In either case, the prepared mixtures were then allowed to flow to the ion source. Total source pressures were 0.5–2.0 torr. In all proton-transfer equilibria the pressure ratios of the sample and reference bases were varied by factors of 2–6 to confirm that the equilibrium constants were independent of the mixture ratios.

When the hydration of the protonated amines was studied, a small amount of the amine, usually about 0.1% or less in the carrier gas, was admitted to the source, where the total pressure was again 0.5–2.0 torr. Water vapor was admitted from another flow line and used at partial pressures of 0.005–0.50 torr in the source.

In solvation reactions, especially at lower temperatures, a problem arises in that the dimer A_2H^+ becomes a major ion, and its formation competes with the solvation equilibrium. In these solvation systems complex schemes of reactions may take place. Taking RH^+ as the protonating reactant ion, i.e., *t*-$C_4H_9^+$ or CH_5^+, A as the amine, and S as the solvent, we write Scheme I. In such a complex system, there is a danger that the relative concentrations of the two ions in the equilibrium pair of interest (e.g., $AH^+ + S \rightleftarrows AH^+{\cdot}S$) may become approximately constant for a long period of time due to a kinetic steady-state situation. This steady-state ion ratio may be significantly different from the true equlibrium ion ratio, yet interpreted as such. In order to clarify this point, we examined with a computer the calculated behavior of a large variety of simulated systems of the kind shown in Scheme I. The conclusion drawn from these simulations is that the steady-state ion ratio deviates significantly, i.e., by more than 5%, from the true equilibrium ratio only if a reaction is present which depletes one of the ions in the equilibrium of interst at a rate which is at least 10 times greater than the rates of either the forward or inverse reaction in the equilibrium. Since in our systems the most important depleting reactions involve the formation of A_2H^+, we worked at low concentrations of A to minimize this side reaction. Simulation of the actual reaction systems indicates that our equilibrium measurements were carried out under conditions where the time-independent ion ratios did not deviate from the true equilibrium values by more than 5%.

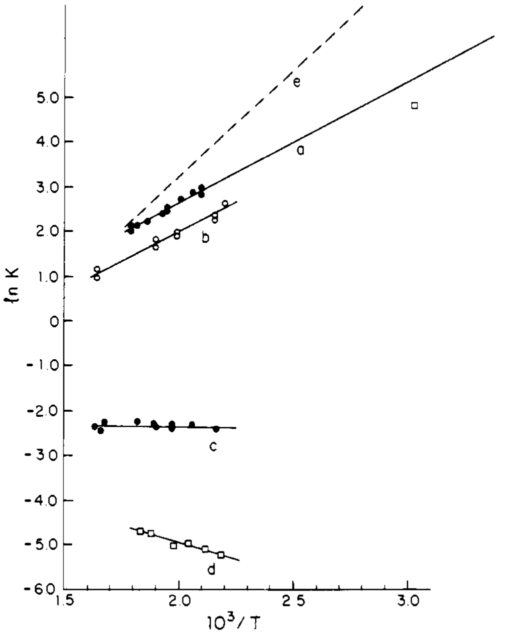


Figure 1. van't Hoff plots for $B_1H^+ + B_2 \rightleftarrows B_2H^+ + B_1$, where B_2 = 1,2-diaminoethane (DAE) and the reference base B_1 is (a) $(CH_3)_2NH$, (b) pyridine, (c) $(C_2H_5)_2NH$, (d) $(n\text{-}C_3H_7)_2NH$, and (e) $(CH_3)_2NH$ from ref 5. Point indicated by the open box for a is calculated from ICR values from the basicities of DAE and $(CH_3)_2NH$ as reported by Aue and Bowers.[1]

Materials used in these studies were purchased from Aldrich, Matheson Gas Products, and Pfaltz and Bauer and were used as purchased. The mass spectra were checked in each case to assure the absence of significant impurities.

Results

Temperature studies were performed on proton-transfer equilibria between diamines or amino alcohols and reference bases. van't Hoff plots obtained in these measurements are shown in Figures 1 and 2. The thermochemical results are summarized in Table I.

Two of the reactions in Table I, i.e., reaction 1 and reaction 5, were studied previously by pulsed high-pressure mass spectrometry by Yamdagni and Kebarle (YK).[5] Also, basicities of some diamines and amino alcohols were obtained at lower pressures and temperatures by Aue and Bowers,[1] who used ion cyclotron resonance (ICR) techniques. We observe (Figures 1 and 2 and Table I) that a significant difference exists between $\Delta H°$

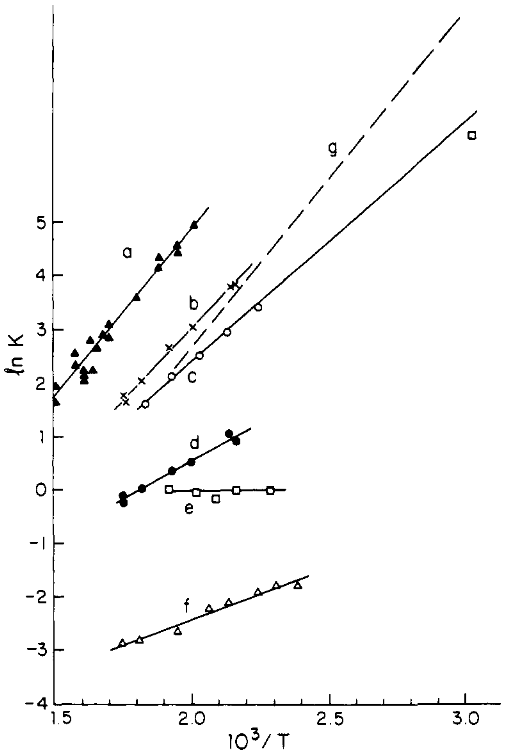


Figure 2. van't Hoff plots for $B_1H^+ + B_2 \rightleftarrows B_2H^+ + B_1$, for the following reaction systems (B_1, B_2): (a) pyridine, $HO(CH_2)_4NH_2$; (b) $(C_3H_7)_2NH$, $NH_2(CH_2)_4NH_2$; (c) $(CH_3)_3N$, $NH_2(CH_2)_2NH_2$; (d) $(C_3H_7)_2NH$, $NH_2(CH_2)_3NH_2$; (e) $(CH_3)_2NH$, $HO(CH_2)_2NH_2$; (f) $(CH_3)_3N$, $HO(CH_2)_3NH_2$; (g) $(CH_3)_3N$, $NH_2(CH_2)_3NH_2$ (from ref 5). Point indicated by the open box for c is from Aue and Bowers.[1]

and $\Delta S°$ values from our results and those of YK for reactions 1 and 5, although the equilibrium constants for both reactions agree well at about 600 K (see Figures 1 and 2). The difference between our present results and those of YK is puzzling, since in general results obtained by the pulsed high-pressure technique in the two laboratories are in good agreement. For example, in the same reaction systems where we measured reaction 5 the dimer $(Me_3N)_2H^+$ was also formed and we measured the association equilibrium $Me_3NH^+ + Me_3N \rightleftarrows [Me_3N]_2H^+$. We obtained for this association reaction $\Delta H° = -22.4 \pm 1.2$ kcal mol^{-1} and $\Delta S° = -29.3$ cal K^{-1} mol^{-1}, which are in good agreement with the values of YK, -22.5 kcal mol^{-1} and -32.0 cal K^{-1} mol^{-1}, respectively.

While our values for the diamines differ from those of YK, our results are in good agreement with ICR data of Aue and Bowers.[1] Thus, from our $\Delta H°$ and $\Delta S°$ values we can calculate $\Delta G°$ at the effective temperature of ICR measurement, which we take as 330 ± 10 K. In Table I we compare our $\Delta G_{330}°$ values for reactions 1-7 and 9 with $\Delta G_{330}°$ values from ICR gas-phase basicity data. The average difference between the two sets of data for the eight reactions is only ± 0.35 kcal mol^{-1}, and the largest difference is 0.7 kcal mol^{-1}. In comparison, the $\Delta G_{330}°$ values as calculated from the data of YK for reactions 1 and 5 differ from the ICR values by 2.2 and 1.8 kcal mol^{-1}, respectively. (See also Figures 1 and 2.) Thus our data agree better with ICR than the results of YK. We should note, however, that the differences between the three sets of data for $\Delta G_{330}°$ are of the same order of magnitude as the combined error limits.

As another test of the consistency of our data, we note that we obtained the PA of 1,2-diaminoethane relative to four reference bases (Table I). The standard deviation of the four PA values obtained in this manner is only 0.6 kcal mol^{-1}.

Discussion

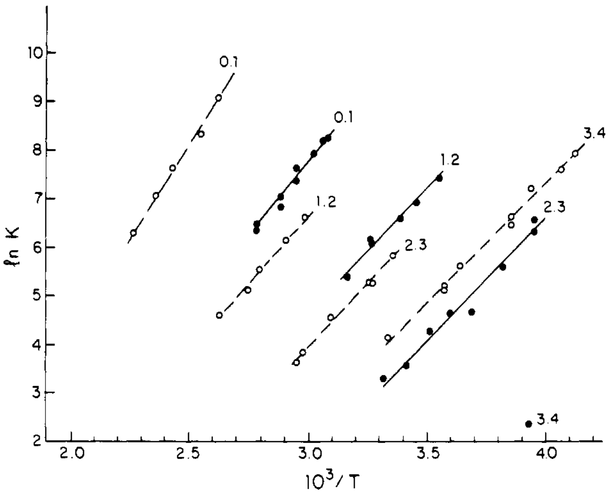


Figure 3. van't Hoff plots for the hydration equilibria $BH^+\cdot(n-1)(H_2O) + H_2O \rightleftarrows BH^+\cdot nH_2O$ for the protonated diamine $B = NH_2(CH_2)_3NH_3^+$ (solid circles) and for the protonated model monoamine $B = n\text{-}C_3H_7NH_3^+$ (open circles). $n-1$ and n are indicated in the figure. The single point at the bottom lower right is the one equilibrium point obtained for the (3,4) reaction in the diamine.

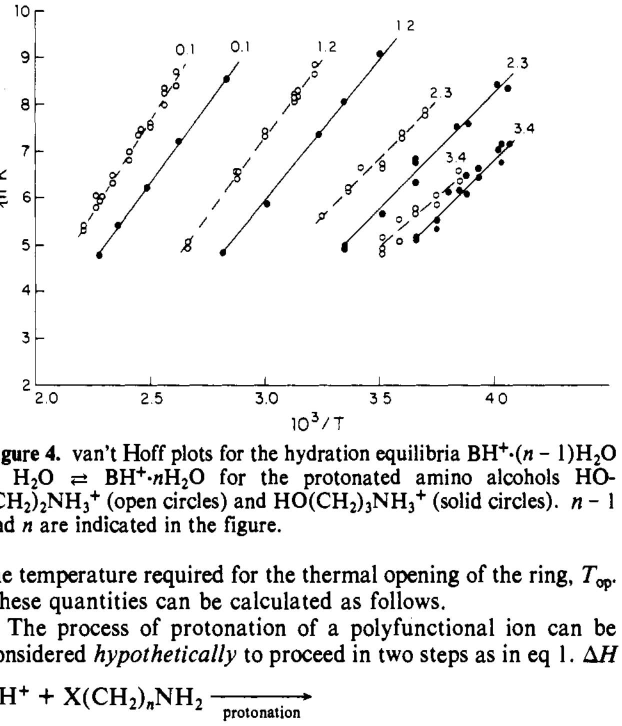


Figure 4. van't Hoff plots for the hydration equilibria $BH^+\cdot(n-1)H_2O + H_2O \rightleftarrows BH^+\cdot nH_2O$ for the protonated amino alcohols $HO(CH_2)_2NH_3^+$ (open circles) and $HO(CH_2)_3NH_3^+$ (solid circles). $n-1$ and n are indicated in the figure.

1. The Thermochemistry of Internal Hydrogen Bonding: Diamines. Internal hydrogen bonding in the protonated diamines results in the formation of cyclic structures. The stabilities of these structures may be represented by the enthalpy and entropy of cyclization, i.e., $\Delta H_{cyc}°$ and $\Delta S_{cyc}°$, the ring strain, $\Delta H_{strain}°$, and the temperature required for the thermal opening of the ring, T_{op}. These quantities can be calculated as follows.

The process of protonation of a polyfunctional ion can be considered *hypothetically* to proceed in two steps as in eq 1. ΔH

$$BH^+ + X(CH_2)_nNH_2 \xrightarrow[\text{protonation}]{} X(CH_2)_nNH_3^+ + B \xrightarrow[\text{cyclization}]{} \overline{X(CH_2)_nNH_3}^+ + B \quad (1)$$

for the first step should be similar to that for the protonation of a model monoamine of comparable polarizability, i.e., of $CH_3(CH_2)_nNH_2$, since the direct through-bond effect of X on the PA of a remote amine group should be small. On the other hand, the solvation of the charge in the second step should increase the stability of the polyfunctional ion, and we can assign to this process most of the difference between the PAs of this compound and the model monoamine. Therefore we calculate $\Delta H_{cyc}°$ from eq 2.

$$-\Delta H_{cyc}° = PA(X(CH_2)_nNH_2) - PA(CH_3(CH_2)_nNH_2) \quad (2)$$

Similarly, $\Delta S_{cyc}°$ can be found from the difference between $\Delta S°$ of proton transfer to a model monoamine and the polyfunctional amine, after corrections for small entropy effects due to rotational symmetry. Values of $\Delta H_{cyc}°$ and $\Delta S_{cyc}°$ obtained in this manner are given in Table II.

We observe that the values of $\Delta H_{cyc}°$ range between -5 and -17 kcal mol^{-1}. These enthalpies for internal hydrogen bonding

Table II. Heats[a] and Entropies[b] of Hydration Reactions $BH^{+}\cdot(n-1)H_2O + H_2O \rightleftarrows BH^{+}\cdot nH_2O$, Heats and Entropies of Cyclization of the Naked Ions BM^{+} and of the n-fold Hydrated Ions $BH^{+}\cdot nH_2O$, Temperatures Required for Thermal Opening of the Cyclic Structures, and Strain Energies of the Cyclic Ion

BH^{+}	n	$\Delta H_{hydratn}{}^{\circ}$	$\Delta S_{hydratn}{}^{\circ}$	$-\Delta H_{cyc}{}^{\circ}$	$-\Delta S_{cyc}{}^{\circ}$	$T_{op}{}^{c}$	$\Delta H_{strain}{}^{\circ}$
$NH_2(CH_2)_2NH_3^+$	0			6.7	8.0	838	16.7
	1	14.7	23.9	6.3	10.4	606	
	2	12.0	23.9	6.7	13.0	550	
	3	11.0	27.4	7.4	17.3	428	
$NH_2(CH_2)_3NH_3^+$	0			14.2	14.7	966	8.8
	1	11.4	19.8	10.5	13.0	808	
	2	9.9	20.2	8.8	11.9	739	
	3	10.4	28.1	8.9	16.9	527	
	4	(9.4)[d]	(28.0)	(8.4)	(20.0)	(420)	
$NH_2(CH_2)_4NH_3^+$	0			17.9	17.1	1047	5.1
	1	(11.0)[e]	(20.0)	(13.8)	(15.6)	(885)	
$NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2$	0			7.1	6.8	1044	15.9
$NH_2(CH_2)_3NH_2^+(CH_2)_3NH_2$	0			17.1	14.8	1155	5.9
$HO(CH_2)_2NH_3^+$	0						
	1	15.4	23.1				
	2	13.4	25.8				
	3	9.8	20.8				
	4	8.3	19.3				
$HO(CH_2)_3NH_3^+$	0			8.8	11.9	739	8.2
	1	13.3	20.8	7.0	11.2	625	
	2	11.6	23.2	7.0	13.1	534	
	3	9.9	23.7	6.6	13.7	482	
	4	9.9	25.9	6.6	14.7	449	
$HO(CH_2)_4NH_3^+$				13.7	16.9	811	3.3
$CH_3(CH_2)_2NH_3^+$	1	15.1	21.5				
	2	11.6	21.3				
	3	10.3	23.1				
	4	9.9	24.9				

[a] In units of kcal mol^{-1}. [b] In units of cal K^{-1} mol^{-1}. [c] In K. [d] Obtained from the measured values of $\Delta G^{\circ} = -2.2$ kcal mol^{-1} at 254 K, and assuming $\Delta S^{\circ} = -28.0$ cal K^{-1} mol^{-1} as in the preceding solvation step. [e] Obtained from the measured value of $\Delta G^{\circ} = -4.8$ kcal mol^{-1} at 309 K assuming $\Delta S^{\circ} = -19.8$ cal K^{-1} mol^{-1} as in the analogous solvation step of $NH_2(CH)_3NH_3^+$.

between protonated and neutral amine functions are significantly smaller than the dissociation energies of protonated amine dimers such as $CH_3NH_3^+\cdot CH_3NH_2$, where $\Delta H_D{}^{\circ} = 21.2$ kcal mol^{-1}.[5] We can suggest several reasons for the weakening of the internal hydrogen bond. First, the σ-bond frame of the polyfunctional amine can prevent the two amine functions from obtaining the optimal geometry for hydrogen bonding. Second, the formation of the hydrogen bond induces strain in the σ-bond frame. Third, in $X(CH_2)_nNH_3^+$ the protonated group may induce a positive charge in X, which will therefore be less available for hydrogen bonding than in the neutral component of a dimer ion.

We represent the weakening of the internal bond from whatever cause by $\Delta H_{strain}{}^{\circ}$ and calculate it from eq 3, where 23 kcal mol^{-1}

$$\Delta H_{strain} = 23 + \Delta H_{cyc} \text{ kcal mol}^{-1} \qquad (3)$$

represents the average strength of bonding in amine dimer ions. Values of $\Delta H_{strain}{}^{\circ}$ are given in Table II. We should note that the methods used here to evaluate $\Delta H_{cyc}{}^{\circ}$, $\Delta S_{cyc}{}^{\circ}$, and $\Delta H_{strain}{}^{\circ}$ are similar to those used by YK.

A useful measure of the overall stability of the internal hydrogen bond can be obtained by calculating the temperature necessary for thermal opening of this bond. Specifically, we want to calculate the temperature, T_{op}, at which half of the population of the $X(CH_2)_nNH_3^+$ ions will be in the open form, i.e., where $K_{op} = 1$. T_{op} is then simply obtained from eq 4. Values of T_{op} are listed in Table II.

$$T_{op} = \Delta H_{cyc}{}^{\circ}/\Delta S_{cyc}{}^{\circ} \qquad (4)$$

Using the values of $\Delta H_{cyc}{}^{\circ}$, $\Delta S_{cyc}{}^{\circ}$, $\Delta H_{strain}{}^{\circ}$, and T_{op}, we shall now compare the thermochemistry of internal hydrogen bonding in the various diamine ions in Table II. First, we note that $\Delta H_{strain}{}^{\circ}$ is especially large (16.7 kcal mol^{-1}) in the smallest ion, $NH_2(CH_2)_2NH_3^+$. Inspection of a molecular model shows that in this ion the $N-H^+$ bond is prevented from aligning in a colinear geometry with the lone pair of the neutral N atom; in fact the $N-H^+\cdots N$ angle must stay as small as 110°. Also, $-\Delta S_{cyc}{}^{\circ}$ for this ion is very small (8.0 cal K^{-1} mol^{-1}), which indicates that the hydrogen bond is weak and much of the freedom of internal rotations of the open structure is preserved as low-frequency torsions in the cyclic form. As the chain length increases, the $-N-H^+\cdots N$ geometry comes closer to optimal and the bond becomes stronger, which is manifested by increasing values of $-\Delta H_{cyc}{}^{\circ}$, $-\Delta S_{cyc}{}^{\circ}$, and T_{op} and by decreasing values of $\Delta H_{strain}{}^{\circ}$ (Table II).

Since internal hydrogen bonding creates cyclic structures, it is reasonable to compare $\Delta H_{strain}{}^{\circ}$ and $\Delta S_{cyc}{}^{\circ}$ to the strain and entropy involved in the formation of σ-bonded rings such as cycloalkanes. Indeed, such a comparison was given by YK. For example, $NH_2(CH_2)_2NH_3^+$ will form formally a five-membered ring; $\Delta S_{cyc}{}^{\circ}$ for this ion is less negative by ca. 5 cal K^{-1} mol^{-1} than the entropy of cyclization of $\dot{C}H_2(CH_2)_3\dot{C}H_2$ to form cyclopentane. Similarly, $\Delta S_{cyc}{}^{\circ}$ for $NH_2(CH_2)_3NH_3^+$ and $NH_2(CH_2)_4NH_3^+$ are less negative by 7 and 4 cal K^{-1} mol^{-1} than those involved in the formation of cyclohexane and cycloheptane from the corresponding diradicals.[5] In fact, the $\Delta S_{cyc}{}^{\circ}$ for these diamine ions agree better with entropies of reactions which form cycloalkane rings one member smaller, i.e., $NH_2(CH_2)_2NH_3^+$ vs. cyclobutane, etc. In this case the differences in $\Delta S_{cyc}{}^{\circ}$ for the diamines and the corresponding hydrocarbons are only 3, 2, and 4 cal K^{-1} mol^{-1}, respectively. On the other hand, the agreement of $\Delta H_{strain}{}^{\circ}$ values for cycloalkanes and protonated diamines is not very good. $\Delta H_{strain}{}^{\circ}$ values are 26, 6, 0, and 6 kcal mol^{-1} for C_nH_{2n}, $n = 4-7$, respectively.[5] $\Delta H_{strain}{}^{\circ}$ values in the protonated diamine series corresponding to $n = 5-7$ are 16.7, 8.8, and 5.1 kcal mol^{-1}. The agreement is poor regardless of whether the ions are compared with cycloalkanes of the same ring size or rings one member smaller. As we noted above, $\Delta H_{strain}{}^{\circ}$ in the ions contains geometrical and polarization factors which are unique to the intramolecular H bonds in ions, and we believe that our finding of better quantitative agreement for $\Delta S_{cyc}{}^{\circ}$ values for the two classes of compounds than for $\Delta H_{strain}{}^{\circ}$ values is quite reasonable.

2. Intramolecular Solvation in Amino Alcohols. We have extended our measurements of the thermochemistry of ionic cyclization to two other types of polyfunctional molecules, namely, amino alcohols and triamines. We expect that $\Delta S_{cyc}{}^{\circ}$ and $\Delta H_{strain}{}^{\circ}$ will be comparable in various types of polyfunctional ions with equal ring sizes. We shall test these predictions with amino alcohols and triamines.

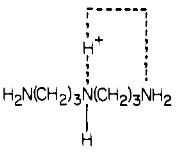
To evaluate $\Delta H_{\text{strain}}^\circ$ in the amino alcohols, we must use the diissociation energy of a dimer ion such as $CH_3NH_3^+\cdot CH_3OH$ as a model for an unstrained internal H bond. $\Delta H_{\text{dissociatn}}^\circ$ for this dimer is not available; however, comparing such dimers as $NH_4^+\cdot NH_3$ vs. $NH_4^+\cdot OH_2$[7] and $CH_3NH_3^+\cdot NH_3$[5] vs. $C_3H_7NH_3^+\cdot OH_2$, we observe that the $NH^+\cdots O$ bond is weaker by 5–7 kcal mol^{-1} than $NH^+\cdots N$. We shall therefore assume 23 − 7 = 15 kcal mol^{-1} for the unstrained $NH^+\cdots O$ bond and calculate $\Delta H_{\text{strain}}^\circ$ for the amino alcohols as eq 5. The values listed in Table

$$\Delta H_{\text{strain}}^\circ = 17 + \Delta H_{\text{cyc}}^\circ \tag{5}$$

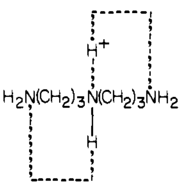
II for $X(CH_2)_3NH_3^+$ and $X(CH_2)_4NH_3^+$ show that within these approximations, $\Delta H_{\text{strain}}^\circ$ is similar for diamine and amino alcohol ions of the same chain lengths. Also, $\Delta S_{\text{cyc}}^\circ$ for the diamines and analogous amino alcohols is similar.

Since $\Delta S_{\text{cyc}}^\circ$ and $\Delta H_{\text{strain}}^\circ$ values of diamines and amino alcohols are similar we may apply $\Delta S_{\text{cyc}}^\circ$ and $\Delta H_{\text{strain}}^\circ$ of $NH_2(CH_2)_2NH_3^+$ to explain the behavior of $HO(CH_2)_2NH_3^+$. The observed values of ΔH° and ΔS° for reaction 8 (Table I) suggest that this ion does not form a cyclic structure. We expect that the strain in the cyclic form of this ion would be about the same as in $NH_2(CH_2)_2NH_3^+$, i.e., ca. 16–17 kcal mol^{-1}. Then $-\Delta H_{\text{cyc}}^\circ$ will be 0 to −1 kcal mol^{-1}, while $-\Delta S_{\text{cyc}}^\circ$ in analogy with $NH_2(CH_2)_2NH_3^+$ will be ca. 8 cal K^{-1} mol^{-1}. From these values T_{op} = 0–125 K, and at the experimental temperatures the ion should be predominantly in the open form, as is indeed observed.

3. Intramolecular Solvation in Triamines. The protonation of triamines is interesting since here the possibilities exist that (a) either one or two internal rings will form and (b) the most stable protonation site will shift due to internal solvation. We shall now observe that despite these possibilities, in the two triamines the measured thermochemistry indicates that only one ring is formed and no proton shift occurs. First, in $H_2N(CH_2)_3NH(CH_2)_3NH_2$ the central secondary amine function should have the highest *PA*, and we use $(n\text{-Pr})_2NH$ as the model monoamine. The derived values of $\Delta H_{\text{cyc}}^\circ$ and especially $\Delta S_{\text{cyc}}^\circ$ for this protonated triamine ion (Table II) are then found to be similar to the values for the diamine $NH_2(CH_2)_3NH_3^+$. This suggests that only one internal ring is formed, i.e., the structure is A rather than B.



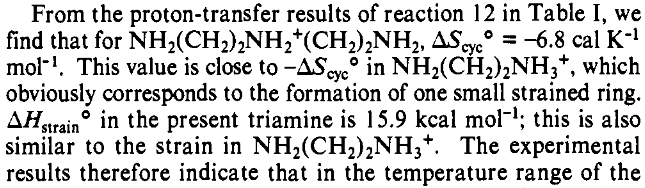
A



B

Based on trends in ion clustering,[7] we expect that bonding of a second solvating $-NH_2$ group to the central $-NH_3^+$ group should be weaker by ca. 7 kcal mol^{-1} than bonding of the first solvating group. However, $\Delta S_{\text{cyc}}^\circ$ for the second ring should be similar to that for the first ring. Then for the second ring we predict $\Delta H_{\text{cyc}}^\circ \simeq -15$ cal K^{-1} mol^{-1} and T_{op} = 670 K. Within the accuracy of the present estimates it is reasonable that the second ring should be unstable at the experimental temperatures of 500–650 K.

An interesting aspect of the protonation of triamines is that here the possibility exists for shift of the protonation site due to internal solvation. Such shift is especially plausible in the case of $NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2$ for the following reason. Here the unsolvated protonation site should be the central $-NH-$ function. Solvation of the proton by one terminal amine group would form one small ring similar to that in $NH_2(CH_2)_2NH_3^+$, where we found large ring strain. However, if the proton shifts to a terminal $-NH_2$ group, solvation by the other terminal $-NH_2$ group would allow the formation of a larger H-bonded ring. On the basis of the results in diamines, this shift would allow more efficient solvation of the proton but would be opposed by a more negative entropy of cyclization. We can calculate the thermochemistry of the proton shift by using the sequence of hypothetical reactions in eq 6.



$$NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2 \xrightarrow{\text{open}} NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2 \xrightarrow{\text{shift}} NH_2(CH_2)_2NH(CH_2)_2NH_3^+ \xrightarrow{\text{close}} NH_2(CH_2)_2NH(CH_2)_2NH_3^+ \tag{6}$$

The thermochemistry for the opening of the small ring (first step) may be estimated from $\Delta H_{\text{cyc}}^\circ$ and $\Delta S_{\text{cyc}}^\circ$ of $NH_2(CH_2)_2NH_3^+$. The thermochemistry for H^+ shift in the open ion can be estimated from the difference between the PA's of the model secondary and primary monoamines $(n\text{-}C_3H_7)_2NH$ and $n\text{-}C_6H_{13}NH_2$.[1] $\Delta S_{\text{cyc}}^\circ$ for closure of the large ring can be estimated by using the $\Delta H_{\text{cyc}}^\circ$ and $\Delta S_{\text{cyc}}^\circ$ for $NH_2(CH_2)_4NH_3^+$, the largest diamine we measured. Using these estimates for the individual steps in reaction 6, we find $\Delta H_{\text{shift}}^\circ = -2.9$ kcal mol^{-1} and $\Delta S_{\text{shift}} = -9.9$ cal K^{-1} mol^{-1}. These results show that above 394 K the small ring will be more stable, but at lower temperatures the proton will shift to a primary terminal function to form the large internal ring.

From the proton-transfer results of reaction 12 in Table I, we find that for $NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2$, $\Delta S_{\text{cyc}}^\circ = -6.8$ cal K^{-1} mol^{-1}. This value is close to $-\Delta S_{\text{cyc}}^\circ$ in $NH_2(CH_2)_2NH_3^+$, which obviously corresponds to the formation of one small strained ring. $\Delta H_{\text{strain}}^\circ$ in the present triamine is 15.9 kcal mol^{-1}; this is also similar to the strain in $NH_2(CH_2)_2NH_3^+$. The experimental results therefore indicate that in the temperature range of the present measurements, 470–600 K, *one small* ring is formed in the protonated triamine. This is in agreement with the thermochemical estimates for reaction 6.

4. The Hydration of Polyfunctional Ions. The solvation of a protonated functional group by either an intramolecular or an external group delocalizes some of the charge from the protonated function and thereby weakens bonding to further solvent groups. Therefore we may expect that intramolecular solvation will weaken the bonding to external solvent molecules and vice versa. In this section we shall examine quantitatively the effects of internal solvation on interactions with external solvent molecules.

When an H_2O molecule bonds to a protonated cyclic diamine, it constitutes the second solvent of the protonated function, the first solvation resulting from the cyclization. To assess quantitatively the effect of the internal H bond on the interaction with the solvent, we compare, for example, reaction 7 with the hydration

$$NH_2(CH_2)_3NH_3^+ + H_2O \rightarrow NH_2(CH_2)_3NH_3^+\cdot H_2O \tag{7}$$

of a protonated monoamine, i.e., reaction 8. We observe that

$$CH_3(CH_2)_2NH_3^+ + H_2O \rightarrow CH_3(CH_2)_2NH_3^+\cdot H_2O \tag{8}$$

$-\Delta H^\circ$ for reaction 7 is smaller by 3.7 kcal mol^{-1} than that for reaction 8. In fact, $-\Delta H^\circ$ for (7) is very similar to $-\Delta H^\circ$ for the addition of the second solvent molecule to $CH_3(CH_2)_2NH_3^+$. Similarly, the enthalpy of the second solvation step of the diamine is similar to that of the third solvation step of the monoamine. On further solvation the differences between the two ions level out.

We thus observe that internal H bonding weakens the interaction with an external solvent. We may expect that increasingly efficient internal bonding will cause increasing internal charge delocalization, which should increasingly weaken bonding to the

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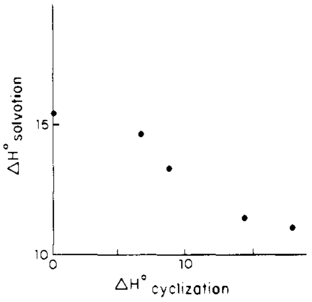


Figure 5. Relation between the enthalpy of cyclization and enthalpies of hydration of polyfunctional ions: (1) $HO(CH_2)_2NH_3^+$; (2) $NH_2(CH_2)_2NH_3^+$; (3) $HO(CH_2)_3NH_3^+$; (4) $NH_2(CH_2)_3NH_3^+$; (5) $NH_2(CH_2)_4NH_3^+$.

external solvent molecule. Indeed, we observe that $-\Delta H_{\text{solvation}}°$ of $HO(CH_2)_2NH_3^+$, the ion which is not internally solvated, is strongest in the polyfunctional amine series, and a general trend of decreasing enthalpies of solvation with increasing strong internal solvation is observed (Figure 5).

The internally bonded, cyclic structures of the polyfunctional ions affect also their entropies of solvation compared with those of monofunctional ions. Thus entropies of hydration of protonated monofunctional ions tend to become more negative by 1–4 cal K^{-1} mol^{-1} upon the addition of each consecutive H_2O molecule into the first hydration shell.[7] This has been assigned to steric hindrance between the H_2O molecules that hinders internal rotation about the hydrogen bond. In comparison, in the hydration of $NH_2(CH_2)_2NH_3^+$ and of $NH_2(CH_2)_3NH_3^+$ we observe that the first two steps have similar $\Delta S°$ values; however, $\Delta S°$ for the third step is significantly more negative. This behavior can be related to the fact that the first two H_2O molecules can here bond each to a proton on a different nitrogen atom in the $-H_2N^+—H\cdots NH_2-$ system, and therefore do not constrain each other; however, the third water molecule will constrain the rotation of both of the two previously added H_2O molecules.

5. The Effects of Hydration on the Stability of the Intramolecular Hydrogen Bond. In the preceding section we noted some enthalpy and entropy effects of the internal H bond on external solvation. Conversely, the external solvent will also delocalize charge from the protonated function, thereby weakening the internal bond. To measure this effect, we are interested in the thermochemistry of cyclization of the *n*-fold solvated polyfunctional ion, i.e., see eq 9, compared with the naked ion, i.e., see eq 10.

$$BH^+\cdot nH_2O_{\text{open}} \rightarrow BH^+\cdot nH_2O_{\text{cyc}} \qquad (9)$$

$$BH_{\text{open}}^+ \rightarrow BH_{\text{cyc}}^+ \qquad (10)$$

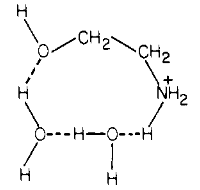
Reaction 9 cannot be observed directly, since at the experimental temperatures the open form BH_{open}^+ is not stable. However, we may use the thermochemical cycle (11). Reaction I is the cyclization of the naked ion; $\Delta H_{\text{cyc}}°$ for this reaction was determined above. Reaction II is the *n*-fold hydration of the cyclic $X(CH_2)_nNH_3^+$ ion; $\Delta H_{\text{II}}°$ is obtained as the sum of enthalpy changes for the first *n* hydration steps of the cyclic ions as given in Table II. Reaction III is the *n*-fold solvation of the open $X(CH_2)_nNH_3^+$ ion. $\Delta H_{\text{III}}°$ cannot be measured directly, but it can be estimated by using the hydration of a protonated open monoamine; we use the hydration of $CH_3(CH_2)_2NH_3^+$ as a model for reaction III. Then $\Delta H_{\text{IV}}°$ is calculated from $\Delta H_{\text{IV}}° = \Delta H_{\text{I}}° + \Delta H_{\text{II}}° - \Delta H_{\text{III}}°$. $\Delta H_{\text{IV}}°$ is the enthalpy for the cyclization of the *n*-fold hydrated ion, and it is denoted by $\Delta H_{\text{cyc}}°$ in Table II. Values for $\Delta S_{\text{cyc}}°$ of the hydrated ions are found in an analogous manner. Values of T_{op} for the *n*-fold hydrated ions are calculated for the cyclic ions, as we did before for the naked ions, by $T_{\text{op}} = \Delta H_{\text{cyc}}°/\Delta S_{\text{cyc}}°$. The derived thermochemical quantities are given in Table II, columns 4–6.

$$\begin{tikzcd} BH^+_{\text{open}} + nH_2O \arrow[r, "\text{III}"] \arrow[d, "\text{I}"'] & BH^+\cdot nH_2O_{\text{open}} \arrow[d, "\text{IV}"] \\ BH^+_{\text{cyc}} + nH_2O \arrow[r, "\text{II}"'] & BH^+\cdot nH_2O_{\text{cyc}} \end{tikzcd} \qquad (11)$$

We can now examine the effect of hydration on a strong internal hydrogen bond such as in $NH_2(CH_2)_3NH_3^+$. We find that the strength of the internal bond, as measured by $-\Delta H_{\text{cyc}}°$, decreases from 14.2 to 10.5 kcal mol^{-1} upon the addition of one H_2O molecule to the ion. It further decreases in the doubly solvated ions, then approximately levels off at ca. 8–9 kcal mol^{-1} upon higher solvation. As for the entropy of cyclization, $\Delta S_{\text{cyc}}°$ becomes somewhat less negative in the first two steps, but when the third H_2O molecule forms a highly hindered structure around the cyclic ion, $\Delta S_{\text{cyc}}°$ becomes more negative and thus opposes cyclization. The combined effects of $\Delta H°$ and $\Delta S°$ on the stability of the cyclic form as a function of solvation are expressed in the variation of T_{op}. Four solvent molecules are sufficient to bring T_{op} from 966 down to 420 K. If the trend observed in T_{op} continues, solvation by a few more H_2O molecules will bring T_{op} down to room temperature.

In ions where the internal hydrogen bond is weaker, the effect of solvation on the already weak bond is smaller. Thus $\Delta H_{\text{cyc}}°$ changes only slightly upon solvation in $HO(CH_2)_3NH_3^+$, and it remains effectively constant in $NH_2(CH_2)_2NH_3^+$. However, entropy effects again decrease T_{op} with solvation, which again approaches room temperature upon the addition of three to four H_2O molecules.

Although the ion $HO(CH_2)_2NH_3^+$ is apparently in the open form, its solvation shows some interesting differences from the open model ion, $C_3H_7NH_3^+$, both in the enthalpy and especially in the entropy of solvation. While the first solvation steps are comparable, the bonding of the second water molecule to $HO(CH_2)_2NH_3^+$ is stronger and has a more negative $\Delta S°$ than in the monoamine. One explanation for the difference could be a bridged structure C. Further H_2O molecules could then hydrogen bond in unconstrained positions to the $-NH_3^+$ or to already present H_2O molecules. This would be consistent with the $-\Delta S°$ values which are unusually small for third or fourth solvation steps.



C

Table III. Rate Constants for Proton-Transfer Reactions from Monoamines to Polyfunctional Molecules M, i.e., $BH^+ + M \rightleftarrows MH^+ + B$

BH^+	M	*T*, K	k_f[a]	k_r[a]	$\Delta H°$[b]	$\Delta G°$[b]
$(CH_3)_2NH_2^+$	$NH_2(CH_2)_2NH_2$	540	15.6	2.0	−5.3	−2.2
$(CH_3)_3NH^+$	$NH_2(CH_2)_3NH_2$	449	12.3	0.37	−9.0	−3.0
		499	12.1	1.06	−9.0	−2.4
		547	7.5	1.20	−9.0	−2.0
		581	6.1	2.20	−9.0	−1.3
$(CH_3)_3NH^+$	$HO(CH_2)_3NH_2$	483	1.15	11.3	−3.5	+2.2
		532	0.85	13.2	−3.5	+2.8
		590	0.70	11.8	−3.5	+3.5

[a] In units of 10^{-10} cm^3 s^{-1}. [b] In kcal mol^{-1}. $\Delta G°$ values from measured equilibrium constants.

6. Kinetics of Some Proton Transfer Reactions. In the proton-transfer reactions reported above we observe processes where the proton is transferred from secondary or tertiary reference amines to diamines in which the amine functions are primary amines. These transfer reactions will be exothermic, and therefore possibly fast, only if the cyclic form which stabilizes the proton in the product ion is formed simultaneously with the transfer process. Otherwise, the proton transfer would be endothermic (as well as endoergic) and such reactions are generally slow. Therefore measurement of the rate constants can yield insight into the mechanism of the formation of internal H bonds.

We obtained rate constants for some of the transfer reactions by using the usual techniques for reversible kinetics.[6] In the first two reactions in Table III the forward reaction proceeds with nearly unit collision efficiency, which suggests that the internal H bond is indeed formed within the lifetime of the reaction complex of the transfer reaction.

The third reaction in Table III constitutes an interesting case in that the forward reaction is exothermic but endoergic, while the reverse reaction is endothermic but exoergic. An unusual result is observed in that here the reverse, i.e., *endothermic reaction proceeds with nearly unit collision efficiency*. The present result is to our knowledge the first case where an endothermic reaction proceeds essentially at the collision rate.

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Resonance Raman Spectra of Bacteriochlorophyll and Its Electrogenerated Cation Radical. Excitation of the Soret Bands by Use of Stimulated Raman Scattering from H_2 and D_2

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Abstract: The development of a new experimental method for producing laser wavelengths in the Soret band region of bacteriochlorophyll (BChl) and its electrogenerated cation radical permits a more detailed study of the effect of excitation wavelength on the resonance Raman (RR) spectrum than was previously possible. Stimulated Raman scattering (SRS) from H_2 or D_2 under high pressure is driven with the second or third harmonics of a Nd:YAG laser. Wavelengths ranging from 396.7 to 502.9 nm are generated. The highest energy wavelength is on the shoulder of the strongest Soret transition in neutral BChl. Good quality RR spectra are obtained at this wavelength, and no evidence of photodegradation is observed. In the case of BChl cation radical, however, the effect of excitation wavelength is more dramatic because it is possible to excite near resonance with three different intense electronic transitions by using the available laser lines. In addition, the resulting spectra show clearly that one-electron oxidation of BChl causes distinctive changes in its RR spectrum. Two intense RR bands seen in the $BChl^{+\cdot}$ spectrum are absent (1414 cm^{-1}) or only weakly observed (1340 cm^{-1}) in the corresponding spectra for BChl. These results indicate that selective RR monitoring of the formation and decay kinetics of the cation radical in vivo should be possible by using 416.0-nm excitation together with detection of the 1414- or 1340-cm^{-1} Raman peaks. The RR spectra of BChl and $BChl^{+\cdot}$ are examined in terms of recent ab initio configuration interaction calculations regarding the nature of the electronic transitions in the Soret region. The resonance enhanced Raman spectra agree qualitatively with changes in the molecular geometry which might be expected on the basis of the molecular orbital composition of the excited electronic state relative to the ground state.

Introduction

In the primary photochemical event of photosynthesis it is believed that a complex of two chlorphylls (Chl) or bacteriochlorophylls (BChl), denoted the special pair, undergoes one-electron oxidation to a π-cation radical in which the remaining unpaired electron is delocalized over both molecules of the complex.[2] The fate of the photoejected electron has been the subject of extensive research aimed toward elucidating the mechanism of photoinduced charged separation in plants. From picosecond absorption spectroscopy[3] and electrochemical studies[4] of photosynthetic bacteria as well as the isolated reaction center (RC) pigments, it appears that the electron is first transferred to an intermediate electron acceptor, bacteriopheophytin (BPheo), resulting in the formation of $BPheo^{-\cdot}$ with a lifetime of approxmately 250 ps. The $BPheo^{-\cdot}$ then transfers the electron to what has been termed the primary electron acceptor, a quinone–iron complex.[5,6] Besides the two special pair BChls and the BPheo intermediate, the RC complex contains two additional BChl molecules, called P800, and one additional BPheo. The role, if any, of these remaining pigment moieties in charge separation is uncertain at present. There is some evidence from picosecond time resolved absorption spectroscopy[7] and steady-state optical spectra of RC preparations at low redox potentials[8] that one of the P800 BChl's is also present as its anion radical. However, additional experiments are needed to determine if P800 BChl functions as an intermediate electron acceptor prior to BPheo as has been postulated.[7]

The progress which has been made toward understanding RC photochemistry can be largely attributed to three spectroscopic techniques–electronic absorption, ESR, and ENDOR spectroscopy—which have been used in conjuction with electrochemical,[4,9] potentiometric,[10] or photochemical[11] procedures for generating the cation and/or anion radicals of the photosynthetic pigments, either in solution or in the RC. Each of these spectroscopic approaches, while providing valuable information, has limitations. In the case of absorption spectroscopy, the spectra of $BChl^{-\cdot}$ and $BPheo^{-\cdot}$ in organic solvents have been used on a

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