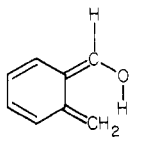

I

sorptions similar to enol I. The observed excitation spectra of OHBA and OHAP are indeed similar to the absorption spectrum of I.

The B spectrum has no large Stokes shift and its excitation spectrum is only slightly shifted from the absorption spectrum, which seems to be in favor of the open conformation. This spectrum is seen for OHBA in EtOH and MeOH, not in PrOH and BuOH. Thus strong solvation of alcohol seems to be needed for the appearance of this spectrum. In the strongly solvating protic solvents OHBA may exist in differently solvated structures. In the more strongly solvated species the $^1n\pi^*$ state of OHBA is further blue shifted and its $^1\pi\pi^*$ state may become the S_1 state. The B fluorescence may come from the S_1 state of such a species.

4. Summary

The Stokes shifted fluorescence of OHBA and OHAP in nonpolar solvents take place from the excited states of the proton or hydrogen-transferred forms (S_1') of the closed conformers which are likely to be the enol forms. At 77 K the transfer rates are rather slow and the nonradiative decays are dominant in the decay processes of the excited states (S_1). The decay rate constants of the transferred form (S_1') are given by the sums of the temperature-independent radiative decay rate constants and the temperature-dependent nonradiative decay rate constants. The main species of OHBA and OHAP in alcohols are open conformers which phosphoresce at low temperature. However, fluorescence spectra similar to those found in nonpolar solvents are also obtained in alcohols. It is suggested that the fluorescence originates from OHBA and OHAP which exist in the enol forms in the ground state and the strongly solvated open conformers of OHBA. The closed conformer of OHBA is converted into the open conformer by UV irradiation in nonpolar solvents at 77 K.

Acknowledgment. We express our sincere thanks to Professor T. Okada of Osaka University for his valuable discussions concerning the proton transfer and to Dr. S. Yamauchi of Kyoto University for his counsel on the fluorescence quantum yield. We thank Miss E. Hamada of Kyoto University for transforming papertape outputs from the minicomputer into cards for deconvolutions. We are indebted to Professor A. Maeda of Kyoto University for the use of the Hitachi MPF-2A fluorescence spectrometer. This research was partly supported by a grant from the Ministry of Education of Japan.

Registry No. OHBA, 90-02-8; OHAP, 118-93-4; MS, 119-36-8; OHBP, 117-99-7.

Effect of Solvation on the Acid/Base Properties of Glycine

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Abstract: The gas-phase acidity and basicity of glycine and several of its methyl-substituted isomers have been measured by pulsed ion cyclotron resonance (ICR) mass spectrometry. The amino acids were introduced into a heated, ultra-high-vacuum chamber using a direct insertion probe. Their partial pressures were measured directly, and these values were used in calculating equilibrium constants for gas-phase proton-transfer reactions. The proton affinity of glycine ($\Delta H°$ for $GlyH^+ \rightarrow H^+ + Gly$) is 213 kcal/mol, and the heterolytic bond dissociation energy ($\Delta H°$ for $Gly \rightarrow H_2NCH_2CO_2^- + H^+$) is 342 kcal/mol. Glycine is a zwitterion in the crystalline state and in aqueous solution, but the pulsed ICR experiments indicate that it is not a zwitterion in the gas phase. Thermodynamic cycles have been constructed for transfer of the protonated and deprotonated forms of glycine from the gas phase to aqueous solution. The heat of solvation for $^+H_3NCH_2CO_2H$ is -87.1 kcal/mol, and the heat of solvation of $H_2NCH_2CO_2^-$ is -90.7 kcal/mol.

It is widely known that in aqueous solution and in the crystalline state α-amino acids have the structure of a dipolar ion, or zwitterion. They are appreciably soluble only in water and do not melt until they decompose at almost 300 °C, which is consistent with the "salt-like" dipolar ion structure. There are two ionizable groups in aqueous solution having pK_a values around 2 and 9. Taking glycine as an example, the first pK_a at 2.3 is what one expects for ionization of a carboxyl group.

$$^+NH_3CH_2CO_2H = H^+ + {}^+NH_3CH_2CO_2^- \qquad \Delta G°_{aq} = 3.2 \text{ kcal/mol} \quad (1)$$

This pK_a value is consistent with that of acetic acid ($pK_a = 4.8$) and the presence of a strong electron-withdrawing effect of the positive ammonium group which stabilizes the glycine dipolar ion.[1] The second acid dissociation for glycine has a pK_a of 9.6 and corresponds to the reaction:

$$^+NH_3CH_2CO_2^- = H^+ + NH_2CH_2CO_2^- \qquad \Delta G°_{aq} = 13.3 \text{ kcal/mol} \quad (2)$$

This is similar to the ethylammonium ion which has a pK_a of 10.7. Thus, in aqueous solution the basicity of glycine (the reverse of reaction 1) is similar to that of acetate ion, and its acidity (reaction 2) is similar to that of an alkylammonium ion.

Little is known about the acid/base properties of the α-amino acids in the gas phase, yet comparisons of the gas-phase and solution-phase data would be of fundamental importance. It would be interesting to know if zwitterions exist in the gas phase and how the hydration enthalpies of the protonated and deprotonated α-amino acids compare with simpler analogues.

Recently we reported the first measurements of the gas-phase acidity and basicity of glycine.[2] Using a pulsed ion cyclotron resonance (ICR) mass spectrometer with an ultra-high-vacuum

(1) See, for example: Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids;" Wiley: New York, 1961; Vol. 1, Chapter 4, pp 497-500.

(2) Locke, M. J.; Hunter, R. L.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 272-273.

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chamber, equilibrium constants were measured for various gas-phase proton-transfer reactions. For example, the acidity (proton donor ability) of glycine in the gas phase relative to formic acid was determined by measuring the equilibrium constant for the reaction:

$$HCO_2^- + Gly = NH_2CH_2CO_2^- + HCO_2H \qquad (3)$$

The partial pressures of formic acid and glycine were measured directly with an ionization gauge, and the equilibrium relative abundance of the two anions was measured using an ICR trapped ion analyzer cell.[3,4] The gas-phase basicity (proton acceptor ability) of glycine was measured relative to several reference bases in reactions such as

$$^+NH_3CH_2CO_2H + CH_3NH_2 = CH_3NH_3^+ + Gly \qquad (4)$$

Moet-Ner, Hunter, and Field have also reported the proton affinities for several aliphatic α-amino acids measured with a pulsed high-pressure mass spectrometer (HPMS).[5]

In this paper we report further pulsed ICR results for the acid/base chemistry of glycine and three of its methyl-substituted isomers. These data provide convincing chemical evidence that in the gas phase glycine is not a zwitterion. Substituent effects on gas-phase acidity and basicity are discussed, and the gas-phase data are combined with solution-phase thermodynamic data to calculate the solvation enthalpies for the glycine anion and cation.

Experimental Section

The acidity and basicity measurements reported in this paper were performed with a pulsed ion cyclotron resonance (ICR) mass spectrometer which was constructed in our laboratory at the University of California at Irvine. The pulsed ICR technique utilizes the cyclotron resonance principle for mass analysis of gaseous ions stored in a one-region trapped ICR cell.[3] A pulsed mode of operation is used for ion formation, trapping, double resonance irradiation, and mass analysis. At a typical operating pressure of 5×10^{-6} torr, ions are stored for about 1 s by a uniform magnetic field of 1.2 T and a weak electric field (0.5 V/cm). The ions suffer on the order of 100 ion–neutral collisions while stored in the ICR cell, which is generally sufficient to thermalize them to the temperature of the neutral gas. Many of the experimental techniques utilized for this study are similar to those used for construction of the gas-phase acidity scale[6-8] and the proton affinity scale.[9-11]

Owing to the low volatility of the α-amino acids, a specially designed ultrahigh-vacuum chamber had to be used. The chamber is wrapped with pressure-sensitive heating tape (Clayborne Labs, size A-16-2 tape). Bakeout temperatures up to 250 °C could be achieved, but during experiments the temperature was set at 110 °C to avoid thermal degradation of the amino acids. The chamber is pumped by a 150-L/s ion pump capable of base pressures in the low 10^{-9} torr range. The trapped ion analyzer cell is mounted inside the chamber and positioned between the pole caps of a large electromagnet.

A crystalline amino acid sample was placed in a Teflon sample cup and admitted into the chamber using a heated direct insertion probe. Usually about 1 mg of sample was used so that the vapor pressure would remain stable for several hours. The probe, at room temperature, was inserted into the heated vacuum chamber (about 109 °C) and degassed until the background pressure dropped to a steady reading, typically about 2×10^{-8} torr. The probe was then slowly heated until the amino acid sample contributed a steady partial pressure of about 1×10^{-6} torr.

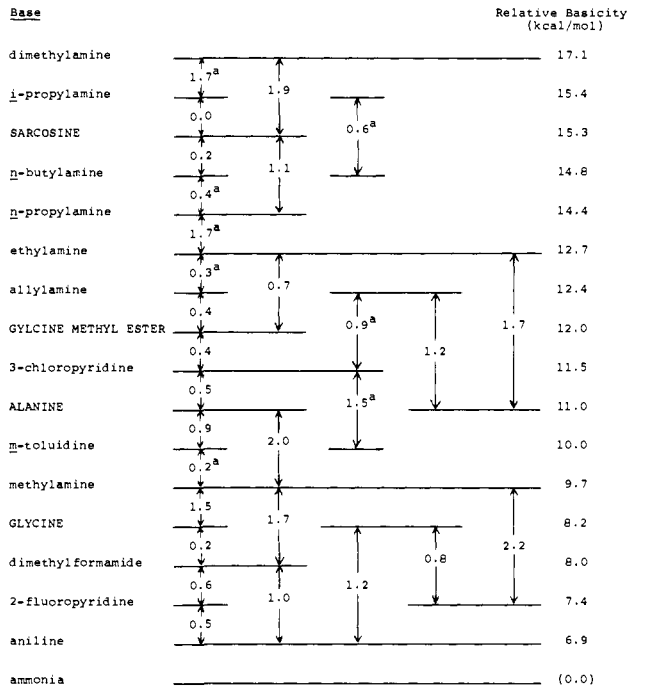

Figure 1. Scale of gas-phase basicities for several amino acids and reference compounds previously studied by ICR. The strongest bases are at the top of the scale. Each number listed is the result of a separate determination of $\Delta G°$ (kcal/mol) for proton-transfer reactions of the type $AH^+ + B = BH^+ + A$ at 380 K. Superscript "a" indicates a value taken from ref 11.

Typical probe temperatures were about 40 to 70 °C. Under identical conditions employing an empty sample cup, no significant increase in pressure was noted, even when the probe was heated in excess of 250 °C. Positive ion ICR mass spectra at an electron impact energy of 20 eV were acquired both with and without samples present as a check for impurities, especially water. After the amino acid pressure had stabilized, a suitable reference acid or base was admitted to the vacuum chamber through a variable-leak valve. Pressure measurements were made with a Bayard-Alpert ionization gauge and were corrected for the relative ionization cross sections for each compound using the method of Otvos and Stevenson.[12]

To determine equilibrium relative basicities, positive ions were produced by a pulsed electron beam and stored in a trapped ion analyzer cell for reaction periods as long as 2 s. The ICR signals for both the protonated amino acid and the protonated reference base were monitored as a function of trapping time. A quench pulse was applied to the side plates at the end of the reaction period to eliminate all ions from the reaction cell, and the reaction sequence was then repeated.

A similar procedure was followed to determine equilibrium relative acidities except that all DC voltages applied to the plates of the ICR cell were reversed in polarity, thus allowing only negative ions to be trapped in the cell. Methyl nitrite was added to a pressure of about 1×10^{-8} torr to capture low-energy electrons and produce CH_3O^- (m/z 31) which rapidly abstracts a proton from the amino acids.[13] Upon addition of a suitable reference acid, the ICR signals for the M − 1 negative ions for both the amino acid and the reference acid were monitored as a function of reaction time.

Ion cyclotron double resonance was used to confirm that the proton-transfer reactions were fast compared to the time scale of the ICR experiment.[14] In addition, all experiments were performed at a constant magnetic field strength of 1.2 T, and the ions were detected with a capacitance bridge detector.[15] Under these conditions the trapping efficiency of the analyzer cell and the detection sensitivity is the same for all ions.

Materials. All compounds used in this study were commercially available and were assayed for purity by their positive ion and negative ion ICR mass spectra. Glycine, alanine, sarcosine, glycine methyl ester,

(3) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1978**, *49*, 111–118.
(4) McIver, R. T., Jr. *Sci. Am.* **1980**, *243*, 186–196.
(5) Meot-Ner, M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1979**, *101*, 686–689.
(6) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046–6056.
(7) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017–4029.
(8) Bartmess, J. E.; McIver, R. T., Jr. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979, Vol. 2, Chapter 11.
(9) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417–5429.
(10) Aue, D. H.; Bowers, M. T. In ref 8, Chapter 9.
(11) Taft, R. W. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Wiley-Halsted: New York, 1975; p 31, with small temperature corrections based on additional unpublished results.
(12) Otvos, J. W.; Stevenson, D. P. *J. Am. Chem. Soc.* **1955**, *78*, 546–551.
(13) Jaeger, K.; Henglein, A. *Z. Naturforsch. A* **1967**, *22*, 700–704.
(14) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334–3338.
(15) McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65–84.

Table I. Thermodynamic Data for Glycine and Its Methyl-Substituted Isomers[a]

compound (AH)	GB[b]	PA[c]	$\Delta G°_{acid}$[d]	$\Delta H°_{acid}$[e]	$\Delta H°_{sub}$	$\Delta H_f°(AH)_s$	$\Delta H_f°(AH_2^+)$	$\Delta H_f°(A^-)$
glycine $NH_2CH_2CO_2H$	204.6	213.0	335.5	342.4	32.6[f]	−128.4[h]	58.4	−120.6
alanine $NH_2CH(CH_3)CO_2H$	207.4	215.8	333.8	340.7	33.0[f]	−134.7[h]	49.7	−128.2
sarcosine $CH_3NHCH_2CO_2H$	211.7	219.4	334.7	341.5	34.9[g]	−122.7[i]	60.0	−113.5
glycine methyl ester $NH_2CH_2CO_2CH_3$	208.4	216.8						

[a] All values in kcal/mol at 298 K. [b] Gas-phase basicity: $\Delta G°$ for $AH_2^+ = AH + H^+$, relative to ammonia at 196.4 kcal/mol.[11] [c] Proton affinity: $\Delta H°$ for $AH_2^+ = AH + H^+$, relative to ammonia at 205.0 kcal/mol.[11] [d] Gas-phase acidity: $\Delta G°$ for $AH = A^- + H^+$, relative to benzoic acid at 333.0 kcal/mol.[7] [e] Heterolytic bond dissociation energy: $\Delta H°$ for $AH = A^- + H^+$, relative to 339.9 kcal/mol for benzoic acid.[7] [f] Reference 26. [g] Reference 32. [h] Reference 33. [i] Reference 34.

and benzoic acid were dried under vacuum at about 50–70 °C. All reference acids and bases were distilled under reduced pressure and additionally purified by three freeze–pump–thaw cycles on the vacuum line of the ICR inlet system.

Results

Pulsed ICR data for the relative gas-phase basicities of glycine, alanine, sarcosine, glycine methyl ester, and several reference bases are shown in Figure 1. The strongest bases are at the top of the figure. Each value is the average of at least three determinations of the free-energy changes

$$\Delta G° = -RT \ln K \quad (5)$$

which are calculated from the measured equilibrium constants for reactions such as

$$BH^+ + A = AH^+ + B \quad (6)$$

where B is a reference base and A is an amino acid. All the reference bases have been previously studied by pulsed ICR to determine their gas-phase basicities relative to ammonia.[9-11] Equilibrium constants were measured at various temperatures from 320 to 385 K, but $\Delta G°$ was found to vary by less than ±0.2 kcal/mol, which is within the experimental uncertainty of ±0.3 kcal/mol. Such a small dependence of $\Delta G°$ on temperature has also been noted previously in comparing pulsed ICR measurements at 320 K with pulsed high-pressure mass spectrometry measurements at 600 K.[7,9]

Based upon a value of 205.0 kcal/mol for the proton affinity of ammonia ($\Delta H°_{298}$ for $NH_4^+ = NH_3 + H^+$), the proton affinities for glycine and its methyl-substituted isomers are as shown in Table I. These $\Delta H°$ values were calculated using the experimentally measured $\Delta G°$ values shown in Figure 1 and the estimated entropy change calculated from the ratio of the rotational symmetry numbers for each species shown in reaction 6.[8-10,16] The entropy change is thus given by

$$\Delta S° = -R \ln \frac{(\sigma_{AH^+})(\sigma_B)}{(\sigma_{BH^+})(\sigma_A)} \quad (7)$$

where σ is the internal rotational symmetry number for each species. In the case of alanine (species A) vs. ammonia (species B) the symmetry numbers are as follows: alaninium ion, 3 (one axis of threefold symmetry about the C–N bond); ammonia, 3 (one axis of threefold symmetry); ammonium ion, 12 (four axes of threefold symmetry); and alanine, 1 (no symmetry about the C–N bond). The symmetry of the methyl group in alanine has not been included because it is also present in the alaninium ion, and its contribution cancels. Substituting these values into eq 7 gives 0.57 eu and at 380 K, $T\Delta S°$ is 0.22 kcal/mol. This value was also used for glycine and glycine methyl ester, but for sarcosine $T\Delta S°$ is 0.98 kcal/mol.

Our data for the relative gas-phase acidities for several of these amino acids are shown in Figure 2. Each value refers to $\Delta G°$ for proton-transfer equilibria such as

$$AH + B^- = BH + A^- \quad (8)$$

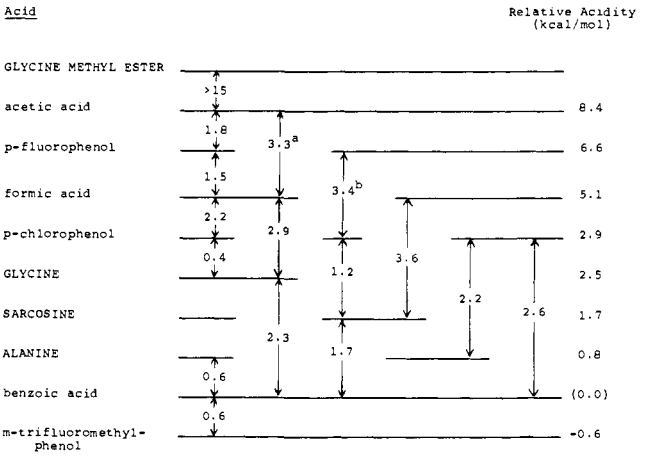

Figure 2. Scale of gas-phase acidities for several amino acids and various reference compounds previously studied by ICR. The strongest acids are at the *bottom* of the scale. Each number listed is $\Delta G°$ (kcal/mol) for proton-transfer reactions such as $A^- + BH = B^- + AH$ at a temperature of 380 K. Superscripts "a" and "b" indicate values from ref 8 and 7, respectively.

All reference acids used in the multiple determinations have been studied previously by pulsed ICR.[6-8] Heterolytic bond dissociation enthalpies are given in Table I, based upon a value of 339.9 kcal/mol for the heterolytic bond dissociation enthalpy of benzoic acid ($\Delta H°_{298}$ for $C_6H_5CO_2H = C_6H_5CO_2^- + H^+$).[17] Entropy contributions were estimated using rotational symmetry numbers.

Discussion

Meot-Ner et al. have measured proton affinities for several α-amino acids using pulsed high-pressure mass spectrometry.[5] Since reagent gas pressures in HPMS are about 10^6 times greater than those used in ICR experiments, the partial pressures of the amino acids could not be measured directly in the HPMS source. Instead, Moet-Ner et al. relied on an indirect method based on ion–molecule kinetics to estimate the pressures of the amino acids and thereby calculated equilibrium constants. Generally their results are 1 to 2 kcal/mol lower than the pulsed ICR values, when the data are adjusted to a common value for the absolute proton affinity of ammonia. This discrepancy could be explained by a systematic error of a factor of 3 in the pressures of the amino acids measured at 570 K in the HPMS source. Considering the difficulty of these experiments, the HPMS and pulsed ICR results are in good agreement.

Methyl-Substituent Effects. Several studies in the literature provide a basis for predicting the effect on the gas-phase basicity of substituting a methyl group for a hydrogen.[9-11,18] The pre-

(16) Cummings, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9.

(17) Acidities reported in Table I are based on a value $\Delta G° = 328.0$ kcal/mol for the reaction $HCl \rightarrow H^+ + Cl^-$ at 298 K taken from ref 39. In addition, the gap between HCl and benzoic acid is reported in ref 7 as 4.6 kcal/mol at 380 K, and with a small entropy correction becomes 5.0 kcal/mol at 298 K.

(18) Staley, R. H.; Taagepera, M.; Henderson, W. G.; Koppel, I.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 326–330.

dominate effect of methyl substitution is to increase the basicity of a molecule. For example, substitution of methyl for hydrogen on the nitrogen of a primary amine increases its gas-phase basicity by about 7 kcal/mol (i.e., methylamine vs. dimethylamine, or ethylamine vs. methylethylamine). Such a large effect results only when substitution occurs at the site of protonation, i.e., on nitrogen itself. If substitution occurs at a position more remote for the site of protonation, such as on the α carbon of a primary amine, the increase in basicity is smaller, about 3 kcal/mol (i.e., methylamine vs. ethylamine, or ethylamine vs. isopropylamine).

Previous studies also provide a basis for predicting the effect on acidity of methyl for hydrogen substitution.[8,19,20] Methyl substitution can increase gas-phase acidity, as in the cases of methanol vs. ethanol (+3.1 kcal/mol) and acetic acid vs. propionic acid (+1.2 kcal/mol). But decreases in acidity are also observed, as in the cases of phenol vs. *p*-methylphenol (−1.2 kcal/mol) and acetylene vs. propyne (−4.7 kcal/mol).

Using these observations, it is possible to predict the effect of methyl for hydrogen substitution on the gas-phase acid/base chemistry of glycine. In order to make any predictions, two possible structures of neutral glycine in the gas phase must be considered: the nonionic α-amino carboxylic acid and the zwitterion. The predicted effects of methyl substitution on the acid/base chemistry of both of these structures are quite different, as discussed below.

The gas-phase basicity reactions for glycine zwitterion and alanine zwitterion are shown in reactions 9 and 10, respectively.

$$^{+}NH_3CH_2CO_2^{-} + H^{+} = {}^{+}NH_3CH_2CO_2H \quad (9)$$

$$^{+}NH_3CH(CH_3)CO_2^{-} + H^{+} = {}^{+}NH_3CH(CH_3)CO_2H \quad (10)$$

The question to consider is which reaction is more exothermic. We would select reaction 9 for the following reasons. First, all of the amino acid species above are stabilized by polarization induced by the positive and negative charge centers. Polarization stabilization caused by the positive charge is about the same for a zwitterion and its protonated form since the site of positive charge is the same. However, only the zwitterions are stabilized by negative charge polarization and alanine zwitterion is stabilized to a greater extent than the glycine zwitterion because of the additional methyl group. The expected result, therefore, of the increased stability of alanine zwitterion is to lower the exothermicity of reaction 10 and thereby cause the basicity of alanine zwitterion to be *less* than that of glycine zwitterion. Similar considerations can be applied to the sarcosine zwitterion (reaction 11). The stabilization would be expected to be less than in alanine

$$^{+}NH_2(CH_3)CH_2CO_2^{-} + H^{+} = {}^{+}NH_2(CH_3)CH_2CO_2H \quad (11)$$

because the methyl group is at a greater distance from the carboxylate group. Equation 12 summarizes the predicted order of basicity for the amino acids as zwitterions.

$$\text{glycine} > \text{sarcosine} > \text{alanine} \quad (12)$$

An analogous analysis can also be made for the gas-phase acidity of the amino acids as zwitterions. Reactions 13 and 14

$$^{+}NH_3CH_2CO_2^{-} = H^{+} + NH_2CH_2CO_2^{-} \quad (13)$$

$$^{+}NH_2(CH_3)CH_2CO_2^{-} = H^{+} + NH(CH_3)CH_2CO_2^{-} \quad (14)$$

show the acidity reactions for glycine zwitterion and sarcosine zwitterion, respectively. Which is the stronger acid in the gas phase? We would expect glycine zwitterion to be stronger because polarization stabilization due to the negative charge centers is the same, but the positive charges on nitrogen preferentially stabilize the sarcosine zwitterion relative to the glycine zwitterion. This effect would increase the endothermicity of reaction 14 and make sarcosine zwitterion a *weaker* acid than glycine zwitterion in the gas phase. In the case of alanine zwitterion (reaction 15), the

$$^{+}NH_3CH(CH_3)CO_2^{-} = H^{+} + NH_2CH(CH_3)CO_2^{-} \quad (15)$$

added methyl group also stabilizes the zwitterion but to a lesser extent than in sarcosine since it is further from the positive charge on nitrogen. Equation 16 shows our predicted order of gas-phase acidities for the zwitterionic amino acids.

$$\text{glycine} > \text{alanine} > \text{sarcosine} \quad (16)$$

The acid/base properties of the *nonionic* forms of these amino acids can also be predicted in the same manner. Since alkyl amines are stronger bases than carboxylic acids in the gas phase, protonation of the nonionic amino acids is expected to occur on nitrogen rather than oxygen, as shown in the reactions:

$$NH_2CH_2CO_2H + H^{+} = {}^{+}NH_3CH_2CO_2H \quad (17)$$

$$NH_2CH(CH_3)CO_2H + H^{+} = {}^{+}NH_3CH(CH_3)CO_2H \quad (18)$$

$$NH(CH_3)CH_2CO_2H + H^{+} = {}^{+}NH_2(CH_3)CH_2CO_2H \quad (19)$$

The relative gas-phase basicities of these three amino acids can be predicted simply by considering the proximity of the methyl group to the positive charge on nitrogen. On this basis, the expected order is

$$\text{sarcosine} \gg \text{alanine} > \text{glycine} \quad (20)$$

These considerations assume that the effect of a methyl group on the nonionic amino acid (the neutral molecule) is negligible compared with its stabilizing effects in the ion due to both the charge-induced dipole polarization interaction and the electron-donating inductive effect.

Similar considerations can be used to predict the relative gas-phase acidities of the nonionic forms of the amino acids:

$$NH_2CH_2CO_2H = H^{+} + NH_2CH_2CO_2^{-} \quad (21)$$

$$NH_2CH(CH_3)CO_2H = H^{+} + NH_2CH(CH_3)CO_2^{-} \quad (22)$$

$$NH(CH_3)CH_2CO_2H = H^{+} + NH(CH_3)CH_2CO_2^{-} \quad (23)$$

Deprotonation certainly would occur at the carboxyl group, and the proximity of the negative charge to the added methyl group suggests the following acidity order:

$$\text{alanine} > \text{sarcosine} > \text{glycine} \quad (24)$$

These predictions for the acid/base properties of the nonionic and zwitterionic forms of the amino acids can be compared with the experimental results shown in Figures 1 and 2. From the basicity data shown in Figure 1, two trends are evident. First, the gas-phase basicities of the amino acids are more similar to their amine analogues than to their oxygen analogues (the proton affinity of acetic acid is more than 20 kcal/mol less than methylamine).[11] Secondly, the methyl substituent effects agree with the order predicted for the nonionic forms (eq 20) and disagree with that predicted for the zwitterionic forms (eq 12).

Two trends are also evident from the gas-phase acidity data in Figure 2. First, the gas-phase acidities of the amino acids are similar to acetic acid and quite different from ethylamine (methylamine is more than 50 kcal/mol less acidic than acetic acid).[8] Secondly, the order of acidities agrees with the predictions made for the nonionic forms (eq 24) and disagrees with that predicted for the zwitterionic forms (eq 16). Three major conclusions may be drawn from these observations: (1) in the gas phase, glycine, alanine, and sarcosine exist as nonionic α-amino carboxylic acids; (2) protonation in the gas phase occurs on the amino group; (3) deprotonation in the gas phase occurs from the carboxyl group.

Predictions about the gas-phase acid/base behavior of glycine methyl ester, the third methyl-substituted isomer of glycine, have not been included in the above discussion, since this isomer cannot exist as a zwitterion. However, it is interesting to note that the gas-phase basicity of glycine methyl ester (Figure 1) is similar to the other methyl-substituted isomers of the glycine. This provides additional evidence that the gaseous amino acids exist in the nonionic form. The gas-phase acidity for glycine methyl ester is estimated to be about 20 kcal/mol less than glycine. This

(19) Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 6572–6575.
(20) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6056–6063.

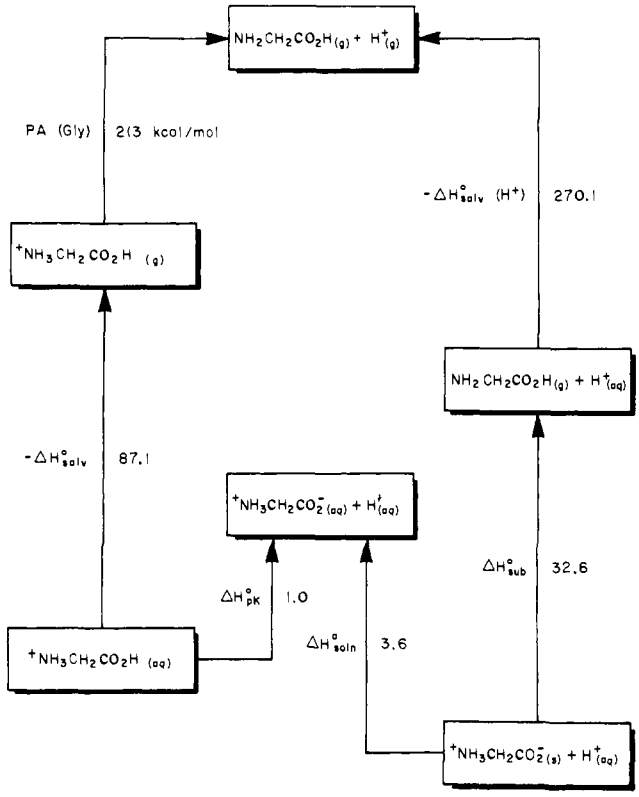

Figure 3. Thermodynamic cycle for calculation of the single ion enthalpy of transfer (gas-phase to aqueous solution) for protonated glycine (all values in kcal/mol).

large decrease in acidity is consistent with that observed for acetic acid vs. methyl acetate (22.5 kcal/mol) and confirms the earlier assumption that the carboxyl group is most easily deprotonated.[21]

These experimental results can also be compared with theoretical estimates of the proton affinities for glycine and alanine made recently by Wright and Borkman.[22] Their results assign values of 222.3 and 225.8 kcal/mol to glycine and alanine, respectively. These calculated *absolute* proton affinities differ from the ICR experimental results substantially, by about 10 kcal/mol. However, their calculated *relative* values (alanine 3.5 kcal/mol more basic than glycine) agree reasonably well with our experimental result of 2.7 kcal/mol (Table I).

Heats of Solvation. Our values for the gas-phase acidity and basicity of glycine can be used to calculate the energetics for transfer of the ions from the gas phase to aqueous solution:

$$A^+(g) \rightarrow A^+(aq) \qquad \Delta H^\circ = \Delta H^\circ_{solv} \qquad (25)$$

A thermodynamic cycle for protonated glycine is shown in Figure 3. Beginning with crystalline glycine, the heat of solution is 3.6 kcal/mol.[23] Protonation in aqueous solution produces the structure $^+NH_3CH_2CO_2H$ and is exothermic by 1.0 kcal/mol.[24] Going the other direction, glycine crystals can be sublimed to produce glycine vapor. There are three literature values for the heat of sublimation: 31.2 (Takagi et al.[25]), 32.6 (Svec et al.[26]); and 23.0 kcal/mol (Friedman et al.[27]). We have selected the value 32.6 kcal/mol as being the one most consistent with our own experiments. The next step, removing the proton from aqueous solution, requires 270.1 kcal/mol, and then combining a gaseous proton and gaseous glycine releases 213 kcal/mol (the PA of glycine).[28] The cycle is completed by transfer of the positive ion $^+NH_3CH_2CO_2H$ from the gas phase to aqueous solution, for which we calculate −87.1 kcal/mol. In Table II the heats of solvation for the other protonated amino acids are compared with

Table II. Solvation Enthalpies for Protonated Amino Acids and Amines[a]

compound (AH)	PA[b]	$\Delta H^\circ_{i-(aq)}$[c]	$\Delta H^\circ_{solv-(AH)}$	$\Delta H^\circ_{solv-(AH_2^+)}$
glycine $NH_2CH_2CO_2H$	213.0	1.0[d]	−29.0[f]	−87.1
alanine $NH_2CH(CH_3)CO_2H$	215.8	1.2[d]	−30.9[f]	−86.4
sarcosine $CH_3NHCH_2CO_2H$	219.4	1.7[d]	−32.4[f] (est)	−84.8 (est)
glycine methyl ester $NH_2CH_2CO_2CH_3$	216.8	7.6[d]		
methyl amine CH_3NH_2	214.6	13.2[e]	−10.8[g]	−79.5
dimethylamine $(CH_3)_2NH$	221.7	12.0[e]	−12.7[g]	−73.1
trimethylamine $(CH_3)_3N$	226.2	8.8[e]	−12.6[g]	−65.3
ethylamine $C_2H_5NH_2$	217.5	13.7[e]	−13.1[g]	−79.4
diethylamine $(C_2H_5)_2NH$	226.8	12.7[e]	−15.3[g]	−71.3
triethylamine $(C_2H_5)_3N$	233.5	10.3[e]	−16.8[g]	−63.7

[a] All values kcal/mol at 298 K. [b] Proton affinity: ΔH° for $AH_2^+ = AH + H^+$, relative to ammonia at 205.0 kcal/mol.[11] [c] Aqueous ionization enthalpy: ΔH° for $AH_2^+ = AH + H^+$. [d] Reference 24. [e] Reference 35. [f] Calculated as the difference of the enthalpy of solvation[23] and the sublimation enthalpy.[26] The enthalpy of solution for sarcosine is estimated to be 2.5 kcal/mol. [g] Reference 36.

Table III. Solvation Enthalpies for Deprotonated Amino Acids and Carboxylic Acids[a]

compound (AH)	ΔH°_{acid}[b]	$\Delta H^\circ_{i-(aq)}$[c]	$\Delta H^\circ_{solv-(AH)}$	$\Delta H^\circ_{solv-(A^-)}$
glycine $NH_2CH_2CO_2H$	342.4	10.6[d]	−29.0[g]	−90.7
alanine $NH_2CH(CH_3)CO_2H$	340.7	10.8[d]	−30.9[g]	−90.7
sarcosine $CH_3NHCH_2CO_2H$	341.5	9.7[d]	−32.4[g] (est)	−94.1 (est)
formic acid HCO_2H	345.1	0.0[e]	−11.2[h]	−86.2
acetic acid CH_3CO_2H	348.4	−0.1[e]	−12.6[h]	−91.0
propanoic acid $C_2H_5CO_2H$	347.3	−0.2[e]	−14.2[h]	−91.6
fluoroacetic acid FCH_2CO_2H	338.2	−1.7[f]	−17.0[f]	−86.8
chloroacetic acid $ClCH_2CO_2H$	334.0	−1.1[f]	−15.2[f]	−80.2
bromoacetic acid $BrCH_2CO_2H$	335.8	−1.0[f]	−15.3[f]	−82.0

[a] All values kcal/mol at 298 K. [b] Heterolytic bond dissociation energy: ΔH° for $AH = A^- + H^+$, relative to 339.9 kcal/mol for benzoic acid.[7] [c] Aqueous ionization enthalpy: ΔH° for $AH = A^+ + H^+$. [d] Reference 24. [e] Reference 31. [f] Reference 30. [g] Calculated as the difference of the enthalpy of solution[23] and the sublimation enthalpy.[26] The enthalpy of solution for sarcosine is estimated to be 2.5 kcal/mol. [h] Reference 36.

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Table IV. Estimating Heats of Solvation by the Summation Method[a]

compound	ΔH°_{solv}[b]	estimated values for ΔH°_{solv}[b]	error
$NH_2CH_2CO_2^-$	−90.7	CH_3NH_2 (−10.8) + HCO_2^- (−86.2) = −97.0	6.3
$NH_2CH(CH_3)CO_2^-$	−90.7	$CH_3CH_2NH_2$ (−13.1) + HCO_2^- (−86.2) = −99.3	8.6
		CH_3NH_2 (−10.8) + $CH_3CO_2^-$ (−91.0) = 101.8	11.1
$^+H_3NCH_2CO_2H$	−87.1	$CH_3NH_3^+$ (−79.5) + HCO_2H (−11.2) = −90.7	3.6
$^+H_3NCH(CH_3)CO_2H$	−86.4	$CH_3CH_2NH_3^+$ (−79.4) + HCO_2H (−11.2) = −90.6	4.2
		$CH_3NH_3^+$ (−79.5) + CH_3CO_2H (−12.6) = 92.1	5.7
$^+H_3NCH_2CO_2^-$	−58.0	$CH_3NH_3^+$ (−79.5) + HCO_2^- (−86.2) = −165.7	107.7

[a] All values kcal/mol at 298 K. [b] Values taken from Tables II and III.

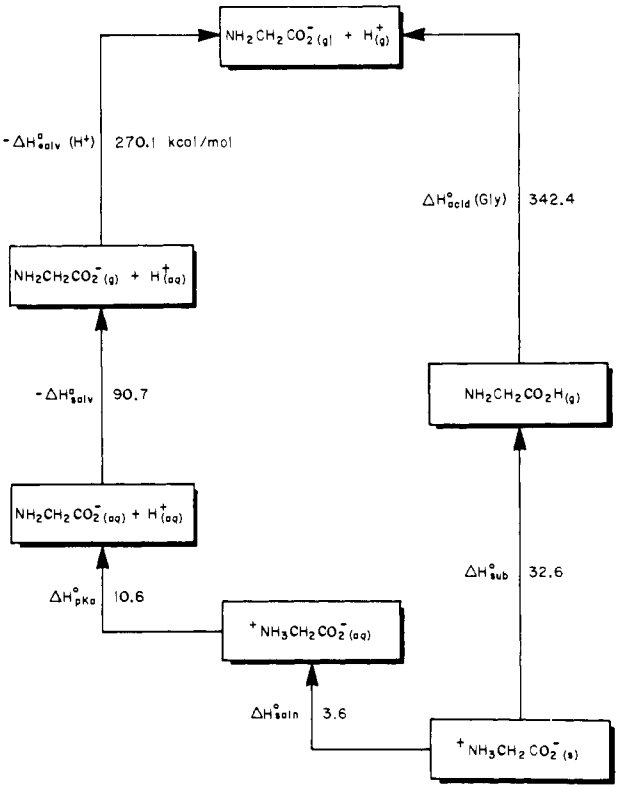

Figure 4. Thermodynamic cycle for calculation of the single ion enthalpy of transfer (gas phase to aqueous solution) for deprotonated glycine (all values in kcal/mol).

values for other ions reported in the literature.[29-31] The solvation enthalpy for protonated alanine is almost 1 kcal/mol less than for protonated glycine, and both of these are about 7 kcal/mol greater than the other primary amines, methylamine and ethylamine.

A similar thermodynamic cycle is shown in Figure 4 for transfer of deprotonated glycine from the gas phase to aqueous solution. The calculated enthalpy of solvation for $NH_2CH_2CO_2^-$ is −90.7 kcal/mol. Table III summarizes the available thermochemical data for the deprotonated forms of the other amino acids and related carboxylic acids.[29-31] The most important conclusion from these data is that heats of solvation for the deprotonated forms of glycine, alanine, and acetic acid are practically the same.

Recently Haberfield[38] estimated the solvation enthalpies of bifunctional molecules such as $NH_2CH_2CO_2^-$ as the sum of the solvation enthalpies of separate parts of the molecule, such as $\Delta H^\circ_{solv}(CH_3NH_2)$ plus $\Delta H^\circ_{solv}(HCO_2^-)$. Several examples of this additivity approach to solvation enthalpies are shown in Table IV, and it is apparent that in general the experimental ion solvation enthalpies are lower by about 5 kcal/mol than the sum of the solvation enthalpies of separate parts of the molecule. This is most likely due to stabilization of the gaseous ion by polarization and intramolecular hydrogen bond formation.

The enthalpy of transfer for neutral glycine from the gas phase to aqueous solution is the difference of the heat of sublimation (32.6 kcal/mol) and the heat of solution for the solid (3.6 kcal/mol). This gives ΔH° = −29.0 kcal/mol for the process

$$NH_2CH_2CO_2H(g) \rightarrow {}^+NH_3CH_2CO_2^-(aq) \qquad (26)$$

An alternative cycle for this process first involves an intramolecular proton transfer to form a gaseous zwitterion followed by solvation of the zwitterion. Experimental data are not available for either of these steps; however, formation of the zwitterion in the gas phase by intramolecular proton transfer has been estimated by theoretical calculations to be endothermic by about 29 kcal/mol.[21b] Combining this value with ΔH° for reaction 26 gives a solvation enthalpy of the glycine zwitterion of about −58 kcal/mol. As expected, this value is considerably greater than the heat of solution of a nonionic species such as methylamine ($\Delta H^\circ_{solv}(CH_3NH_2)$ = ¦0.8 kcal/mol in Table II), but less than that for the purely ionic species (>60 kcal/mol) which are shown in Tables II and III.

Heats of Formation. Heats of formation for protonated and deprotonated glycine in the gas phase can be calculated from the ICR measurements. The heat of formation for protonated glycine can be calculated from the enthalpy change for reaction 17, which is given by

$$\Delta H^\circ = \Delta H_f^\circ({}^+NH_3CH_2CO_2H) - \Delta H_f^\circ(H^+) - \Delta H_f^\circ(Gly) \qquad (27)$$

where ΔH° is the negative of the proton affinity of glycine (−213.0 kcal/mol) and the heat of formation for a gaseous proton is $\Delta H_f^\circ(H^+)$ = 367.2 kcal/mol.[39] The heat of formation of gaseous neutral glycine can be estimated from literature values for the enthalpies of formation for crystalline glycine (ΔH_f°(gly) = −128.4 kcal/mol) and of sublimation (ΔH°_{sub} = 32.6 kcal/mol).[26,33] Combining these three gives the gas-phase heat of formation for the positive ion: $\Delta H_f^\circ({}^+NH_3CH_2CO_2H)(g)$ = 58.4 kcal/mol. This same approach can be used to calculate the heat of formation of deprotonated glycine in the gas phase. The enthalpy change for reaction 21 is

$$\Delta H^\circ_{acid} = \Delta H_f^\circ(NH_2CH_2CO_2^-) + \Delta H_f^\circ(H^+) - \Delta H_f^\circ(Gly) \qquad (28)$$

Combining the value from Table I for ΔH°_{acid} = 342.4 kcal/mol,

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for glycine, with the previously discussed values for $\Delta H_f°(H^+)$ and $\Delta H_f°(Gly)$ gives $\Delta H_f°(NH_2CH_2CO_2^-)(g) = -120.6$ kcal/mol. Results of similar calculations for the other amino acids used in this study are shown in Table I.

Conclusion

The gas-phase ion chemistry of low volatility molecules can be studied in pulsed ICR spectrometers by heating the analyzer system and adding the samples via a direct insertion probe. Only moderate heating is required since the ICR cell normally requires pressures in the range 10^{-7} to 10^{-5} torr.

In the gas phase glycine exists as a nonionic molecule in contrast with the zwitterionic structure which is dominant in the solid phase and in aqueous solution. This has been proven by examining methyl-substituent effects, and these effects in substituted glycines are typical of what has been found in previous studies for other classes of compounds.

The enthalpy of transfer of protonated glycine from gas phase to aqueous solution is -87.1 kcal/mol, and for $NH_2CH_2CO_2^-$ the solvation enthalpy is -90.7 kcal/mol. The enthalpies of formation for protonated and deprotonated glycine are found to be 58.4 and -120.6 kcal/mol, respectively.

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Registry No. Glycine, 56-40-6; alanine, 56-41-7; sarcosine, 107-97-1; glycine methyl ester, 616-34-2.

ENDOR Study of VO^{2+} Adsorbed on Y Zeolite

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Abstract: Over the past two decades electron paramagnetic resonance (EPR) has been used extensively in studies of the structure of transition metal ion exchanged zeolites. Use is made of the fact that data on g values and metal ion hyperfine splitting constants provide an insight into the structure of the cation binding site. In this contribution it will be shown that electron nuclear double resonance (ENDOR) makes it possible to measure the interactions between the unpaired electrons and nuclear spins in the vicinity of the paramagnetic cation. Generally, these interactions remain unresolved in the EPR spectra of these amorphous systems. The experimental results demonstrate that the ENDOR technique can be used to study cation solvation in the zeolite cavities and changes in cation environment induced by removal of solvent molecules or co-adsorbed molecules. It is shown that subtle structural changes that do not register in the EPR spectrum can have a profound effect on the ENDOR spectra. The results presented here suggest that ENDOR can be of great value in studies of transition metal ion adsorption on zeolites as well as other porous surfaces.

Zeolites are used as catalysts in a variety of chemical reactions. Their catalytic activity can be modified by cation exchange and changes in cation binding site. For this reason the study of the relation between structure and activity continues to be an important area of research. In cases where the exchanged cation is a transition metal ion, data on g values and metal ion hyperfine couplings derived from EPR spectra have proven to be a valuable source of structural information.[1-5] A more complete insight into the structure of these systems could be provided by measurement of hyperfine splitting constants of nuclear spins in the vicinity of the paramagnetic center.[6] Unfortunately, EPR measurements generally do not give access to this information. It will be shown that these interactions can be measured by using electron nuclear double resonance (ENDOR).

To explore the utility of ENDOR in this field of research the oxovanadium(IV) Y zeolite system was chosen for the following reasons. (1) Work performed in this laboratory has established that ENDOR spectra of vanadyl complexes in amorphous solids are obtained readily.[7-10] It has been demonstrated that the spectra give detailed information on hyperfine as well as quadrupole interaction components. (2) VO^{2+} adsorbed on Y zeolite has been the focus of an earlier EPR study by Martini and co-workers.[11] These workers proposed specific models for the various VO^{2+} complexes that could be generated. This offers the opportunity to investigate whether or not ENDOR can contribute new information that aids in the elucidation of the structure of the system.

Experimental Section

Linde Type NaY zeolite obtained from Alfa was used as received. Adsorption of VO^{2+} was achieved by stirring 5 g of zeolite with 100 mL of a 0.02-M solution of $VOSO_4 \cdot 5H_2O$ under an argon atmosphere for about 1 week. The exchanged zeolites were kept hydrated by storage in a water-vapor-saturated atmosphere. Evacuation (10^{-2} torr) at room temperature yielded the (partially) dehydrated samples used in this investigation.

EPR and ENDOR spectra were recorded with a Varian E9 X-band spectrometer with the home-built ENDOR accessory described before.[7,9] The optimum temperature for recording of the ENDOR spectra was found to be around 20 K. Other instrumental conditions were as follows: microwave power 5 mW, radio frequency power ~300 W, 10 kHz frequency modulation with a deviation of ±50 kHz.

Data and Discussion

The EPR spectrum of hydrated, VO^{2+}-exchanged Y zeolite recorded at 100 K is presented in Figure 1. The spectrum closely resembles that reported by Martini et al.[11] On the basis of the EPR parameters derived from the spectrum ($g_\parallel = 1.938$, $g_\perp = 1.986$, $A_\parallel = -0.0178$ cm^{-1}, $A_\perp = -0.0070$ cm^{-1}), these authors assigned the spectrum to the $VO(H_2O)_5^{2+}$ complex. The room-temperature spectrum of the hydrated system shows some line broadening and slight shifts of peak positions. This was attributed[11] to residual molecular motion of the complex. The penta-

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