orbitals. Upon bonding to the two CO molecules, the Be 2s orbital mixes with its low-lying 2p orbitals to form sp^2 hybrid orbitals, two of which are used to form bonds with the carbon lone pair orbital of the CO, while the third is occupied by one of the unpaired electrons. The second unpaired electron occupies a b_1 orbital perpendicular to the plane of the molecule, which is a Be 2p type orbital that is involved in a π back-bonding interaction with the CO π^* orbital.

The $^3B_1$ state of $Be(CO)_2$ is analogous to the lowest $^3B_1$ state of methylene on the basis of the nature and type of the highest occupied orbitals. Formation of $Be_2(CO)_4$ from two $Be(CO)_2$ molecules in their $^3B_1$ states results in a Be-Be double bond. An analysis of the two highest occupied orbitals of $(CO)_2BeBe(CO)_2$ shows significant bonding between the two Be atoms. The highest occupied (b_{3u}) orbital is π bonding between the Be atoms, with each Be also involved in π back-bonding with the π^* orbitals of the CO. The second highest occupied orbital (a_g) is a σ type bonding orbital. The triplet state arising from the one-electron excitation to the π^* orbital of $(CO)_2BeBe(CO)_2$ is 16.2 kcal below the singlet state at the HF level of theory. The inclusion of electron correlation effects reverses the order of the states with the ^1A_g below the triplet state by 10.6 kcal at the MP2 level of theory.[10]

The binding energy of $(CO)_2BeBe(CO)_2$ is computed with respect to dissociation to two $Be(^1S)$ and four CO molecules as well as to two $^3B_1$ $Be(CO)_2$ fragments. The computed binding energies are given in Table I. Even at the HF level, the interaction energy between the two $Be(CO)_2$ fragments in $(CO)_2BeBe(CO)_2$ is 15.5 kcal. Note that the Be_2 molecule shows no binding at this level of theory.[11] The complete fragmentation of $(CO)_2BeBe(CO)_2$ into two Be atoms and four CO molecules requires 36.0 kcal at the HF level of theory. At the MP4(SDQ) level, the strength of the Be-Be bond in this molecule is 50.0 kcal, and the complete fragmentation requires 68.3 kcal. The contributions of electron correlation to the binding energy of both $Be(CO)_2$ and $(CO)_2BeBe(CO)_2$ are large, indicating the need to reoptimize the geometry of these molecules to include electron correlation effects.[10] This trend is consistent with other studies of CO binding to metal atoms.[12]

At the HF level of theory the BeBe distance in $(CO)_2BeBe(CO)_2$ is only 1.938 Å, which is considerably shorter than the experimental bond distance of 2.45 Å in Be_2,[13] the shortest Be-Be distance of 2.226 Å in Be metal,[14] and the Be-Be bond length of 2.124 Å in HBeBeH at the same level of theory.[15] The computed harmonic vibrational frequency for the Be-Be stretch for this molecule of 942 cm^{-1} is more than 4 times larger than the experimental value of the vibrational frequency of Be_2 at 223 cm^{-1} and is also larger than the Be-Be stretching frequency of 645 cm^{-1} in HBeBeH at the same level of theory. The barrier for rotation about the Be-Be bond, computed at the HF geometry of the ground state by the GVB method[16] correlating only the pair of electrons in the π bond, is 6.70 kcal. The computed properties of the Be-Be bond, bond distance, bond energy, vibrational stretching frequency, and barrier to rotation, all lend support to the idea of a double bond between the Be atoms in this molecule.

The nature of the bonding and the stability of $(CO)_2BeBe(CO)_2$ demonstrate that it is indeed possible to form strong double bonds between Be atoms. The bonding in this molecule where two formally s^2 closed subshells interact arises from the mixing of the empty p orbitals with the occupied s orbitals, i.e., hybridization. A ligand field of D_{2h} symmetry is shown to induce strong bonding between two Be atoms which are weakly bound in the Be_2 molecule.

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Proton Affinities of the 20 Common α-Amino Acids†

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We report the first measurement of the gas-phase basicities ($-\Delta G$ of protonation) of all of the 20 common α-amino acids, from which we can derive their proton affinities ($-\Delta H$ of protonation). The basicities are determined by observing the occurrence or nonoccurrence of reaction 1, and its reverse reaction, in which A represents an amino acid, B a reference base, and AH^+ and BH^+ their respective protonated forms. The observation of proton

$$A + BH^+ \rightarrow AH^+ + B \quad (1)$$

transfer between the protonated molecule of a base and an amino acid implies a negative free energy for reaction 1. The reverse reaction is observed if the free energy of reaction 1 is positive.

The α-amino acids are low-volatility compounds and thus are difficult subjects for the type of gas-phase equilibrium experiments generally utilized to measure gas-phase basicity or proton affinity.[1] To date, values of the proton affinity of only 6 of the 20 common α-amino acids have been published.[2,3] Meot-Ner et al. used high-pressure mass spectrometry to measure the gas-phase basicity of six amino acids (glycine, alanine, valine, leucine, phenylalanine, and proline), and they also used variable-temperature studies to directly measure the enthalpy of the proton-transfer reaction and thus the proton affinities of three of the amino acids.[2] Locke and McIver measured the gas-phase basicities of glycine and alanine with ion cyclotron resonance spectrometry.[3] In these studies, for the cases where enthalpies were not measured directly, proton affinity values were obtained from the gas-phase basicity data by estimating the entropy of the reaction, which was found to be a small or negligible correction.

In this study, we use Fourier transform ion cyclotron resonance spectrometry to observe the reaction of laser-desorbed, neutral amino acid molecules with a series of protonated reference bases, as in reaction 1. With this technique, called laser desorption/chemical ionization (LD/CI), low-volatility or nonvolatile compounds can be utilized as the neutral partner in studies of ion-molecule reactions.[4] The reverse of reaction 1 is examined by forming a protonated molecule of an amino acid by matrix-assisted laser desorption of the amino acid,[5] followed by reaction with a

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Table I. Gas-Phase Basicities (GB) and Proton Affinities (PA) of the 20 α-Amino Acids (italics) and Reference Bases

amino acids	reference base	GB (350 K)[a,b]	PA[a,c]
	acetophenone	200.7 ± 1.5	210.0 ± 1.5
Gly		*202.4 ± 3.2*	*211.7 ± 3.2*
	pyrrole	204.1 ± 1.5	213.4 ± 1.5
Cys		*205.4 ± 2.8*	*214.6 ± 2.7*
	2-fluoropyridine	206.6 ± 1.5	215.7 ± 1.5
	methylamine	209.2 ± 1.5	219.6 ± 1.5
Ser, Asp		*210.3 ± 2.6*	*220.2 ± 2.1*
	3-fluoropyridine	211.3 ± 1.5	220.7 ± 1.5
Ala, Val		*212.3 ± 2.5*	*222.1 ± 2.9*
	ethylamine	213.2 ± 1.5	223.4 ± 1.5
Leu, Ile		*214.8 ± 3.1*	*225.0 ± 3.1*
	isopropylamine	216.3 ± 1.5	226.5 ± 1.5
Phe, Tyr, Asn		*217.4 ± 2.6*	*227.2 ± 2.2*
	pyridine	218.4 ± 1.5	227.8 ± 1.5
Thr, Met, Gln, His		*219.5 ± 2.6*	*228.5 ± 2.2*
	tert-butylamine	220.5 ± 1.5	229.2 ± 1.5
Pro, Trp		*221.9 ± 2.9*	*231.0 ± 3.3*
	trimethylamine	223.3 ± 1.5	232.7 ± 1.5
Glu		*223.7 ± 1.9*	*240.6 ± 1.9*
	diethylamine[d]	224.1 ± 1.5	233.5 ± 1.5
Lys		*226.0 ± 3.4*	*242.6 ± 3.4*
	di-*n*-propylamine[d]	227.9 ± 1.5	237.3 ± 1.5
	triethylamine[d]	230.2 ± 1.5	239.6 ± 1.5
	tri-*n*-butylamine[d]	233.8 ± 1.5	243.2
Arg		*>233.8*	*>243.2*

[a] All values are in kcal/mol. [b] Relative GB values of the reference bases are from ref 7 and are adjusted for 350 K. The absolute GB values are based on a value of 198.2 kcal/mol for NH_3 at 350 K. [c] PA values of the reference bases are from ref 7. [d] Relative GB and PA values are from ref 1 and are referenced to the values of GB and PA of trimethylamine from ref 7.

neutral volatile base.[6] Use of a series of reference bases with small differences in gas-phase basicity allows an amino acid to be bracketed within a narrow range. Most of the reference bases used in this study were chosen from a recently published ladder of proton affinities and gas-phase basicities.[7] The study that produced the revised ladder of basicities eliminated systematic errors in the upper end of the proton affinity scale previously in use[8] and yielded measurements in agreement with proton affinity values obtained from absolute determinations at various positions in the ladder.

The gas-phase basicities and proton affinities measured for the 20 α-amino acids are listed in Table I, along with the literature values for the reference bases used in this study. For most of the amino acids, the entropy of reaction 1 can be calculated from changes in the rotational symmetry numbers (σ) of the reactants and products according to eq 2.[9] The amino acids and reference

$$\Delta S_{rot} = R \ln [\sigma_A \sigma_{BH^+} / \sigma_{AH^+} \sigma_B] \quad (2)$$

bases used in this study have low symmetry, yielding rotational entropy values of approximately ±2 cal/mol·K. At the temperature of the system in this study, 350 K,[10] the contribution of entropy to the free energy of reaction 1 is ±0.7 kcal/mol. The uncertainty in the assignment of the gas-phase basicities of the amino acids, determined by the spacings between the gas-phase basicities of the reference bases, is ±2.5 kcal/mol on average. The contribution of entropy, caused by changes in rotational symmetry, to the free energy of reaction 1 is much smaller than the uncertainty in the assignment of the free energy and can be neglected, so that $\Delta H = \Delta G$ for reaction 1. This assumption has been verified in a previous study of amino acid proton affinities.[2] A notable exception to this simplification occurs when an intramolecular hydrogen-bonded cyclization occurs, as has been observed for α,ω-diamines.[11] Lysine (2-carboxy-1,5-pentanediamine) fulfills the geometric requirement for such a cyclization. The formation of the hydrogen bond in cyclized diamines causes a substantial increase in their gas-phase basicities and proton affinities relative to monoamines of similar polarizability. The difference in gas-phase basicity between lysine and the structurally similar monoamine, leucine (2-carboxyisopentylamine), 11.2 ± 3.2 kcal/mol, is approximately the same as that between 1,5-pentanediamine and *n*-pentylamine, 10.7 ± 1.5 kcal/mol,[1] suggesting the intramolecular cyclization of protonated lysine. The entropy of cyclization for lysine should be approximately equal to that of 1,5-pentanediamine (ΔS_{cyc} = −20.5 cal/mol·K).[1] The enthalpy of protonation of lysine via reaction 1 is equal to the free energy plus $T\Delta S$ = −7.2 kcal/mol at 350 K. The proton affinity value of lysine in Table I has been adjusted to account for cyclization of the protonated molecule.[12]

Table II. A Comparison of the Proton Affinity Values of Six α-Amino Acids with Published Values[a]

	current study[b]	Meot-Ner[c]	Locke and McIver[d]
glycine	204.0–207.4	208.2	210.3
alanine	211.5–214.0	212.2	213.1
valine	211.5–214.0	213.9	
leucine	214.0–216.5	214.5	
phenylalanine	216.5–218.1	215.1	
proline	218.8–222.1	218.4	

[a] All values are in kcal/mol. [b] Values from this study have been adjusted to match the proton affinity ladder from ref 9. [c] PA values are from ref 2 and are based on the proton affinity ladder of ref 9. [d] PA values are from ref 3 and are adjusted to match the proton affinity ladder from ref 9.

The difference in gas-phase basicities between glutamic acid and aspartic acid (ΔGB = 13 kcal/mol) is much greater than for the corresponding amides, glutamine and asparagine (ΔGB = 2 kcal/mol). The structures of these amino acids differ by one methylene group in the side chain, and so only a small difference in gas-phase basicity is expected, as is observed for the amides. The anomalously high gas-phase basicity of glutamic acid suggests cyclization of its protonated form. The proton affinity assignment has been adjusted to account for the entropy of cyclization (ΔS_{cyc} = −21.5 cal/mol·K, as for 4-hydroxybutanamine,[1] $T\Delta S_{cyc}$ = −7.5 kcal/mol). Interestingly, the gas-phase basicity of glutamine does not suggest cyclization of that amino acid.

Arginine is the most basic of the amino acids, presumably because of the strongly basic guanido group present in its side chain. It is more basic than any of the reference bases that are used in this study. As a result, we can only set a lower limit on the gas-phase basicity of this amino acid, 234 kcal/mol, and on the proton affinity, 243 kcal/mol. Although arginine has the

(6) For formation of protonated molecules by matrix-assisted laser desorption, amino acids were mixed 1:1000 with sinapinic acid and desorbed with the 248-nm line of an excimer laser. The desorbed ions were thermalized by 20–100 collisions with argon, admitted through a pulsed valve, prior to their reaction with the reference bases.

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appropriate geometry to form an intramolecular hydrogen bond, there is insufficient data on the gas-phase basicities of guanidine compounds to determine whether cyclization occurs for this amino acid on the basis of the measurements reported here.

Table II compares prior measurements of the proton affinities of six amino acids with the measurements reported here. To facilitate the comparison, the proton affinity values in the table are referenced to the proton affinity ladder used in the earliest study.[2] We find excellent agreement with Meot-Ner's measurements of the proton affinities of alanine, valine, leucine, and proline and close agreement for glycine and phenylalanine.[2] Likewise, we find excellent agreement with the proton affinity value of alanine reported by Locke and McIver.[3] Our value for the proton affinity of glycine is lower than, but similar to, that measured by Locke and McIver. The comparisons show no systematic differences between ours and prior measurements. Our relative ordering of the proton affinities of the amino acids agrees with that proposed by Bojensen with a few notable exceptions.[13] Bojensen places histidine as the second most basic amino acid, while we find it sixth on our list. In Bojensen's study, glutamine is more basic than glutamic acid, opposite to our finding. We find alanine, methionine, and threonine to be more basic than does Bojensen. While the exact reason for the differences between the two measurements is not known, it should be emphasized that the measurements reported here are based on well-established ion–molecule techniques and theory. Bojensen relates ion abundances in a metastable ion mass spectrum to thermodynamic properties of the product ions, a technique proposed by Cooks and co-workers for measuring relative proton affinities of closely related, monofunctional compounds.[14] The discrepancies between our measurements and those of Bojensen may be a limitation of Cook's method, which has never been tested with structurally diverse, polyfunctional molecules such as the amino acids.

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Different Reaction Paths Taken by Hydrogen Isotopes

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Kinetic isotope effects usually reveal differences in *degree* but not in *kind*. However, in studying the chemistry of muonium (hydrogen's light isotope with a positive muon as nucleus) we find it to behave as a nucleophile in its reactions with aromatic N-heterocyclic solutes in water. This contrasts with the electrophilic character of ^{1}H.[1,2] Muonium (Mu) has one-ninth the atomic mass of ^{1}H but virtually the same reduced mass, ionization energy, size, etc. as all hydrogen isotopes. Hitherto Mu has shown kinetic and spectroscopic isotopic effects which are understandable in terms of its different atomic mass from that of ^{1}H;[3] but in the present study it shows a different *type* of reaction.

Recently we found that Mu produces the free radical which arises from addition into the aromatic ring of pyrazine at its C atoms.[4] Now we report the rate constants measured for that reaction and Mu's reaction with other N-heterocyclic compounds. Table I gives our observed rate constants (k_M) for reaction of Mu with benzene, pyridine, and the 1,2-, 1,3-, and 1,4-diazines. These data were obtained by measuring the chemical decay rate of muonium using the muon-spin-rotation technique[5] on millimolar aqueous solutions of these compounds at natural pH. They are compared in Table I with the published data for reaction of ^{1}H atoms with the same solutes under similar conditions. Since Mu adds to a ring C,[4] whereas ^{1}H attaches at the more electronegative N atoms,[6] these data have been normalized in columns 3 and 5 of Table I by dividing k_M by the number of C sites on the solutes and k_H by the number of N sites.

Table I. Rate Constants[a] for the Reaction of Muonium Atoms with Aromatic N-Heterocyclic Solutes in Water at ~295 K. Comparison with Published Data on ^{1}H[b]

solute	k_M	k_M/C	k_H	k_H/N	k_M/k_H
benzene	33 ± 3	5.5	9	(1.5)[c]	3.7
pyridine	58 ± 4	12	7.8[d]	7.8	7.4
pyridazine	50 ± 3	12.5	2.7[e]	1.4	18.5
pyrimidine	37 ± 2	9	0.92[f]	0.46	40.2
pyrazine	77 ± 5	19	3.0[g]	1.5	25.7

[a] All k values are in units of 10^8 dm^3 mol^{-1} s^{-1}; k_M/C and k_H/N are described in the text. See footnotes c to g for pH dependence. [b] Reference 8. [c] Calculated as k_H per C atom. [d] The 7.8 refers to natural pH. At pH ~1, however, $k_H = 1.7 \times 10^8$ M^{-1} s^{-1} for pyridine where >99% of the solutes were protonated; so protonation decreases k_H by ~4.5-fold. This contrasts with Mu, where k_M increased from 58 to 74 (×10^8) on changing from pH ~7 to pH 1.2, for pyridine. Thus k_M/k_H increases from 7.4 at pH ~7 to 44 at pH ~1. [e] k_H measured at pH ~1, where ~99% of the solutes have one of their N atoms protonated; so the number of unprotonated N atoms is half that relevant to the k_M data. [f] k_H measured at pH ~1, where ~65% of the solutes have one of their N atoms protonated. [g] k_H measured at pH ~1, where ~30% of the solutes have one of their N atoms protonated.

Mu is seen to react 3.7 times faster than ^{1}H with benzene. This is not inconsistent with Mu's 3-fold-higher mean thermal velocity stemming from its one-ninth atomic mass: a kinetic isotope effect expected for diffusion-limited reactions.[3] The overall rate constants ratio, k_M/k_H, then increases to 7.4 due to the presence of one ring N, and up to 40 with two N atoms. This ratio rises partly by k_M increasing and partly by k_H decreasing.

The enhancement of k_M by ring nitrogens implies that Mu is "nucleophilic", because N draws electron density from the C atoms where Mu reacts. Preliminary results even suggest that there is a direct proportionality between $-\log(k_M)$ and the Hückel molecular orbital localization energy on each C.[7] By contrast, the presence of the ring N of pyridine seems to switch H's reaction site from C to N (as seen through ESR data[6]). This results in a minor overall decrease in k_H (but an increase per atom where reaction takes place). The presence of a second N atom then reduces the rate further. Also, ^{1}H has already been shown to display a negative Hammett ρ parameter,[1,2] and the differences between the diazines have been interpreted as consistent with this electrophilic character.[1]

There is additional information to be gleaned from the pH dependence of these rate constants arising from protonation of the solute. For pyridine, which is the only N-heterocycle for which data are available, k_M/k_H jumps from 7.4 at pH ~7 to 44 at pH ~1. Almost all of this jump (see footnotes to Table I) emerges from a decrease in k_H. This consequently corroborates the view that reaction of H, but not Mu, occurs on the N atom.

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