metric analysis of **2** in argon shows a gradual weight loss (ca. 35%) in the region 25–700 °C and a slight weight loss in the region 700–1000 °C.[14]

Pyrolysis of a sample (7.5 g) of **2** at 900 °C in vacuo (24 h) and then at 1200 °C in air (2 h) results in the formation of a white crystalline solid **4** (4.4 g) and Et_2O, NH_3, and NH_4Cl as identified by mass spectrometry and infrared spectroscopy. Elemental analysis[15] of **4** yields $B/N = 1.15$. An infrared spectrum is very similar to a spectrum obtained from commercial h-BN.[16] An X-ray powder pattern of **4** is consistent with the powder pattern for turbostratic modified h-BN.[17] TEM analysis[18,19] of **4** shows regions of well-developed crystallinity interspersed with amorphous material. The crystalline BN grains are approximately 5–10 nm on a side and 30–40 nm long, and the BN (002) lattice fringes are clearly visible. EDS[18,19] analysis shows a Si peak in all regions of the sample. The BN aggregates are porous with pores ~2 nm in diameter. There is no evidence for microporosity, and the BET[18] surface area is 34 $m^2\,g^{-1}$. Additional characterization details are provided in the Supplementary Material.

A sample of **4** was treated with 40% aqueous HF solution for 15 min at 25 °C to remove any boron oxides and silica formed.[20] The remaining white powder **5** was washed with distilled water and air dried. Infrared spectra show no changes in the region 1600–400 cm^{-1} compared to the spectrum of **4**, and the X-ray powder pattern of **5** shows no noticeable changes. The microstructure of **5**, as revealed by TEM analyses (Figure 1), appears less porous with sharper lattice fringes, as if removal of the intervening amorphous material allows the grains to collapse together. EDS analyses show a complete absence of Si in most regions. Carbon arc emission spectroscopy shows silicon present at a level of 0.03–0.05%.[21]

These preliminary studies indicate that an oligomeric borazinylamine gel can be prepared in high yield, and this gel provides a useful precursor for the formation of hexagonal boron nitride. It is also very important to note that this chemistry provides a system which is adaptable to sol-gel processing.[22] Although several features require additional study, it is apparent that the amine cross-linking of borazene fragments offers a beneficial and important advance in the use of borazenes as sources for BN. It is interesting to note that some investigators have suggested that the presence of silica in boron nitride improves its processing characteristics as well as prevents hydrolysis of boron nitride.[23] Therefore, the presence of organosilicon in our synthesis may prove beneficial. Additional studies of chemically modified borazenes and other cross-linking reagents are in progress.

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Supplementary Material Available: Figures showing infrared spectra, TGA and DTA traces, infrared spectra, X-ray powder patterns, TEM photographs, and EDS patterns (12 pages). Ordering information is given on any current masthead page.

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[14] TGA traces obtained in air are similar to those obtained in UHP argon, except above 1000 °C a slight weight gain is observed. This suggests a degree of oxidation of boron and residual silicon.

[15] Elemental Anal. Found: B, 36.7; N, 41.2. Analyses for Si and Cl were not obtained. Accurate elemental analyses are difficult to obtain due to incomplete dissolution of the samples.

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[18] Abbreviations used in the text are defined as follows: TEM = transmission electron microscopy; EDS = energy dispersive X-ray spectroscopy; BET = Brunauer, Emmett, and Teller method for surface area measurement; TGA = thermal gravimetric analysis; DTA = differential thermal analysis.

[19] EDS analyses were performed by using a Tracor Northern 5500 system with a high take-off detector. The sample tilt was 0° during X-ray analysis. The microscope used was a JEOL JEM-2000 FX operated at 200 kV. The point resolution is ~0.3 nm.

[20] HF solutions (40%) are unreactive toward h-BN. Kubo, T.; Inoc, H.; Ochiai, T. Jpn. Kokai. Tokkyo Koho 79 145725, **1979**; *Chem. Abstr.* **1980**, *92m*, 134047d.

[21] Trace analyses obtained from Spectra Co., San Diego, CA.

[22] Transparent plugs of the gel **2** have been formed in several organic solvents, and these have been found to withstand critical point drying in liquid carbon dioxide.

[23] Tsapuk, A. K.; Popobeda, L. G.; Kovalevskii, N. N. *Poroshkovaya Met.* **1978**, *18*, 51; *Chem. Abstr.* **1978**, *88*, 196260.

The Order of Proton Affinities of the 20 Common L-α-Amino Acids

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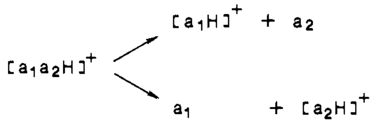
On the basis of the unimolecular decomposition of cluster ions the order of proton affinity (PA) of the 20 common L-α-amino acids is suggested. The results are shown in Table I, where the PA decreases from arginine to glycine. The order obtained agrees with the PA's that have been measured for six of the amino acids.[1]

A protonated dimer of two different amino acids a_1 and a_2 can be observed in the FAB spectrum of a mixture of the two amino acids.[2] It decomposes unimolecularly according to



(1)

The relative rates of the competing reactions in eq 1 can be determined from the relative abundances of $[a_1H]^+$ and $[a_2H]^+$ in the mass-analyzed ion kinetic energy (MIKE)[3] spectrum of the protonated dimer.[4] The order of the rates of the two reactions in eq 1 is the same as the order of the PA's of a_1 and a_2 when the reverse activation energies and the entropy effects of the two reactions can be ignored.

The reverse activation energies can be ignored if they are either close to zero or very similar in magnitude. Assuming that the proton is bridging the two amino acids in the protonated dimer, this will indeed be the case.[5]

Although the structures of the protonated monomers can be guessed with some assurance, this is not the case for the structures of the protonated dimers. Hence the entropy effect is more difficult to assess. For the amino acids where equilibrium measurements on proton exchange reactions have been carried out no appreciable entropy effect has been noticed.[1a]

When the α-NH_2 group is the site of protonation, charge-induced dipole interaction with the side chain leads to stabilization

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[1] (a) Meot-Ner (Mautner), M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1979**, *101*, 686. (b) Locke, M. J.; McIver, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 4226.

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[3] (a) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1977. (b) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1023A.

[4] (a) The protonated dimers were generated by fast atom bombardment (Xe, ~9 keV) of a mixture of two L-α-amino acids (Sigma) in 1 M trichloroacetic acid in glycerol (87%). The mass spectrometer employed was a Varian 311A (BE geometry). The intensities of the peaks in the MIKE spectrum (average of 3–5 scans) were corrected for the energy dependent yield of secondary electrons at the multiplier. For analyses of daughter ions with mass differences of 1 or 2 the decomposition was studied in the third field free region of a ZAB-3F (BEB geometry).

[5] Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279.

Table I[a]

PA[b]		Gly	Ala	Cys	Ser	Val	Asp	Leu	Thr	Ile	Phe	Met	Tyr	Asn	Pro	Glu	Trp	[Gln	Lys][c]	His	Arg
	Arg																Arg		Arg	Arg	
	His																His	His	His		
	[Lys][c]		Lys		Lys		Lys				Lys				Lys	Lys[d]	Lys				
	Gln]										Gln	Gln			Gln	Gln[d]	Gln				
	Trp														Trp	Trp					
	Glu		Glu				Glu				Glu			Glu	Glu						
218.4	Pro					Pro					Pro	Pro	Pro	Pro							
	Asn										Asn	Asn	Asn								
	Tyr									Tyr	Tyr	Tyr									
	Met									Met	Met										
215.1	Phe		Phe		Phe	Phe	Phe	Phe	Phe	Phe											
	Ile					Ile	Ile[d]		Ile												
	Thr						Thr	Thr													
214.5	Leu				Leu	Leu	Leu[d]														
	Asp		Asp	Asp	Asp	Asp															
213.9	Val		Val	Val	Val																
	Ser		Ser	Ser																	
	Cys		Cys																		
212.2	Ala	Ala																			
208.2	Gly																				

[a] Each amino acid indicated to the right of the heavy line can be assigned to the most abundant ion in the MIKE spectrum of the cluster ion which contains the amino acid at the top of the column combined with that to the left in the row; e.g., decomposition of the cluster ion with the composition $[\mathrm{Ser{\cdot}Lys{\cdot}H}]^+$ yields primarily $[\mathrm{Lys{\cdot}H}]^+$ and hence PA(Lys) > PA(Ser). [b] Values (in kcal/mol) from ref 1a. [c] Order is undetermined. See text. [d] Analyzed on the ZAB-3F.

of the positive charge. Charge-dipole interaction with the carboxylic acid group and for some of the amino acids, (e.g., Ser, Cys, Asp, and Asn) also with the side chain, may give some destabilization.[6] For Arg, Lys, Gln, and Glu the protonated species fulfill the geometrical requirements for ring-formed structures which include basic sites in the side chain.[7] In these cases an entropy effect is to be expected in proton exchange experiments.

In the protonated dimer the same interactions will be present, but owing to the charge dispersion each will be much weaker than in the protonated monomer. This is illustrated by the study on protonation reactions of trifunctional amines under equilibrium conditions.[8] They show that when a proton is solvated by two of the basic sites on the amine, solvation by the third does not occur even when allowed by the geometry. A similar effect operating in the protonated amino acid dimer would mean that apart from solvating the proton with its most basic site each amino acid would have few conformational restraints.

Overall it appears that available experimental evidence supports the hypothesis that the entropy effect in the decomposition reaction of the protonated dimers can be ignored when establishing the order of amino acid PA's. It is also clear that positive evidence is needed. This can best be supplied by equilibrium measurements.

The order for Gln (MH^+: 147.0699) and Lys (MH^+: 147.1134) remains undetermined. Analysis of the decomposition of the cluster ion $[\mathrm{Gln{\cdot}Lys{\cdot}H}]^+$ demands high resolution for the separation of the cluster as well as for analysis of the fragments.

For Gly, Ala, Ser, Cys, and Thr the PA's have been calculated.[9] The calculated values have the same magnitude as those obtained experimentally. For the groups Gly, Ala, and Cys, Ser, Thr the order is in agreement with the order presented here, but the overall order is not.

In order to determine proton affinities it has hitherto been necessary to evaporate a sample of the compound to be studied. This has prevented the study of compounds of high polarity. Just as desorption ionization methods have enabled the analysis of polar compounds they should enable the study of their gas-phase chemistry.

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Registry No. H-Gly-OH, 56-40-6; H-Ala-OH, 56-41-7; H-Cys-OH, 52-90-4; H-Ser-OH, 56-45-1; H-Val-OH, 72-18-4; H-Asp-OH, 56-84-8; H-Leu-OH, 61-90-5; H-Thr-OH, 72-19-5; H-Ile-OH, 73-32-5; H-Phe-OH, 63-91-2; H-Met-OH, 63-68-3; H-Tyr-OH, 60-18-4; H-Asn-OH, 70-47-3; H-Pro-OH, 147-85-3; H-Glu-OH, 56-86-0; H-Trp-OH, 73-22-3; H-Gln-OH, 56-85-9; H-Lys-OH, 56-87-1; H-His-OH, 71-00-1; H-Arg-OH, 74-79-3.

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(6) These effects are reviewed in the following: Taft, R. W. *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; 1983; Vol. 14, p 247.

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Highly Reduced Organometallics. 19.[1] Synthesis of Carbonyl Anions of Titanium(0) from Titanocene Dicarbonyl. The First Structural Characterization of a Carbonyl Hydride of Titanium, $(C_5H_5)Ti(CO)_2(Me_2PCH_2CH_2PMe_2)H$

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Reductive labilization of poor or nonacceptor ligands on transition-metal compounds has been demonstrated to be a versatile synthetic route to highly reduced anions and other organometallics in the past decade.[2] Jonas and his group have established that metallocenes of the first row transition metals are particularly useful in this regard. One or two cyclopentadienyl groups can often be selectively removed from metallocenes by reduction in the presence of a variety of neutral ligands to access totally new classes of organometallic materials.[3]

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