**α-Glycyl Cation, Radical, and Anion (H$_2$NCH$^+$/−COOH): Generation and Characterization in the Gas Phase**

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The title species are synthesized in the gas phase and their unimolecular chemistry is determined by a combination of tandem mass spectrometry methods. Dissociative electron ionization of the α-amino acids valine, leucine, isoleucine, or serine produces the α-glycyl cation, H$_2$NCH$^+$COOH, in high yield and purity. At threshold, this ion dissociates by CO loss to form the proton-bound complex HC≡N⋯H$^+$⋯OH$_2$ via a tight 1,4-H migration that is associated with a high reverse barrier. After collisional activation, additional channels open, most notably the formation of the complementary and structure-characteristic fragments H$_2$NCH$_1$ (ionized aminocarbene) and "COOH and the elimination of OH. Charge reversal and neutralization–reionization of H$_2$NCH$^+$COOH conclusively show that α-glycyl anion, H$_2$NCH$^−$COOH, and α-glycyl radical, H$_2$NCHCOOH, are stable species residing in deep potential energy wells. In the microsecond time window of the experiments, a small fraction of the α-glycyl radical decomposes by sequential elimination of H$_2$O and CO. The α-glycyl anions arising by charge reversal of the cation or reionization of the radical partly undergo rearrangement losses of H$_2$ and H$_2$O, direct cleavages to "COOH, OH$^−$, and H$_2$N$^−$, and consecutive fragmentation of these primary product anions.  

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Free radicals bearing the −N–C–C(O)− frame have been implicated as intermediates in the oxidative damage of α-amino acids and proteins, a process of immense importance in molecular biology, toxicology, and medicine [1]. For this reason, a large number of theoretical studies have inquired the structures and thermochemical properties of relevant model systems, derived from glycine [2–5] and other α-amino acids [6]. Of particular interest has been the prototype species, viz. the α-glycyl radical (Scheme 1), which is presumed to arise upon the oxidation of glycine in acidic solutions or the solid state [7–10]. Theory predicts a high thermodynamic stability for this C-centered radical because of its captodative substitution pattern by electron-withdrawing and electron-donating groups (Scheme 1) [9, 11]. Thus far, α-glycyl radicals have been detected among the irradiation products of aqueous glycine solutions [7, 8] or glycine crystals [10] by electron spin resonance (ESR). Gaseous H$_2$NCHCOOH has also been observed in a recent neutralization–reionization mass spectrometry (NRMS) [12–14] study by O’Hair et al., albeit in admixture with other C$_2$H$_2$NO$_2$ isomers [15]. The present investigation reports a series of new NRMS experiments that yield pure α-glycyl radicals and provide detailed insight on their intrinsic (i.e., gas phase) chemistry.

In NRMS, a reactive intermediate is synthesized in the gaseous state by neutralization of the corresponding mass-selected cation or anion and its unimolecular chemistry is determined from the mass spectra obtained after reionization to positive and/or negative ions [16–18]. The α-glycyl cation (H$_2$NCH$^+$COOH) and anion (H$_2$NCH$^−$COOH), both of which can be resonance stabilized by the substituents attached to the α-carbon (Scheme 1), are stable species according to ab initio calculations by O’Hair et al. [15]; hence, either ion is suitable for NRMS studies. H$_2$NCH$^+$COOH and H$_2$NCH$^−$COOH are available by electron and negative chemical ionization of glycine, respectively [15]. Extensive labeling and careful tandem mass spectrometry (MS/MS) [19, 20] experiments by O’Hair et al. [15] revealed, however, that glycine cogenereates appreciable amounts of other C$_2$H$_2$NO$_2$ isomers during these processes, which compromises the unequivocal characterization of the α-glycyl system. Here, we describe an alternative strategy; dissociative electron ionization of specific α-substituted amino acids is first employed to produce in high purity and yield cation H$_2$NCH$^+$COOH $\leftrightarrow$ H$_2$N=CHCOOH, whose structure and unimolecular reactivity are ascertained by several MS/MS methods,
including metastable ion (MI) characteristics [21], collisionally activated dissociation (CAD) [19, 20], triple-stage mass spectrometry (MS3) [20], and neutral fragment reionization (NfR) [22]. Cation H2NCH+COOH is subsequently used as the starting material for the gas phase preparation and study of radical H2NCHCOOH as well as anion H2NCH−COOH via neutralization and charge reversal (CR) [23, 24], respectively.

### Experimental

All experiments were performed with a modified MicrOmega AutoSpec tandem mass spectrometer of E1BE2 geometry, which has been described in detail [25]. This instrument houses one collision cell (Cls-1) in the field-free region preceding E1 (FFR-1) and two more (Cls-2 and Cls-3), separated by an intermediate ion deflector, in the field-free region between B and E2 (FFR-3). MI, CAD, NfR, and neutralization–reionization (NR) spectra of precursor ions formed in the ion source were acquired using EI of several α-amino acids followed by α-cleavage of the side chain gives rise to the incipient ion [H2NCHCOOH]+ (C2H4NO2+, m/z 74). The amino acids glycine, alanine, valine, leucine, isoleucine, serine, methionine, and phenylalanine were found to yield detectable ion fluxes of m/z 74. Methionine and phenylalanine are not suitable precursors because their C2H4NO2+ ions are contaminated by appreciable amounts of isobaric C2H6S2++ and C4H7+, respectively. Glycine and alanine produce pure C2H4NO2+ cations but in low yield. On the other hand, pure and abundant C2H4NO2+ beams are generated from valine, leucine, isoleucine, or serine, making either of these amino acids an appropriate source for the α-glycyl cation. The set of spectra shown in this study originates from isoleucine, but any of the other acceptable precursors (i.e., those yielding pure C2H4NO2+) leads to indistinguishable spectra.

The pressure of each collision gas was raised until the C2H4NO2+ precursor ion beam intensity was attenuated by 20%, except for “CR−” where the attenuation was 40%. The kinetic energy release of the dish-topped signal from metastable C2H4NO2+ was calculated at half-height (T0.5) and across the dish maxima (Tdish) by established procedures [27, 28]. The spectra shown are multiscan summations and the reproducibility of their relative abundances is better than ±10%. The amino acids used were purchased from Aldrich or Sigma and the collision gases from Linde (oxygen), Liquid Carbonic (helium), or Matheson (trimethylamine); all chemicals were introduced into the mass spectrometer as received.

### Results and Discussion

**Generation of the α-Glycyl Cation**

EI of several α-amino acids followed by α-cleavage of the side chain gives rise to the incipient ion [H2NCHCOOH]+ (C2H4NO2+, m/z 74). The amino acids glycine, alanine, valine, leucine, isoleucine, serine, methionine, and phenylalanine were found to yield detectable ion fluxes of m/z 74. Methionine and phenylalanine are not suitable precursors because their C2H4NO2+ ions are contaminated by appreciable amounts of isobaric C2H6S2++ and C4H7+, respectively. Glycine and alanine produce pure C2H4NO2+ cations but in low yield. On the other hand, pure and abundant C2H4NO2+ beams are generated from valine, leucine, isoleucine, or serine, making either of these amino acids an appropriate source for the α-glycyl cation. The set of spectra shown in this study originates from isoleucine, but any of the other acceptable precursors (i.e., those yielding pure C2H4NO2+) leads to indistinguishable spectra.
Unimolecular Chemistry of α-Glycyl Cation

Metastable [H₂NCHCOOH]⁺ undergoes elimination of CO to produce CH₄NO⁺ (m/z 46). The corresponding peak is broad and dish topped with Tₕ and T₀.₅ values of 0.30 and 0.56 eV, respectively (Figure 1a). The peak shape and large kinetic energy release point out that CO loss proceeds through a tight rearrangement with an appreciable reverse activation energy [21, 27, 28]. More information on this reaction is revealed by the CAD (MS³) spectrum of metastably produced CH₄NO⁺ (Figure 1b), which is dominated by fragments of m/z 19 (H₃O⁺) and 28 (CH₂N⁺). Such MS³ characteristics agree well with the structure of a proton-bound complex between H₂O and HC≡N, i.e. HC≡N···H⁺···OH₂. Because of the higher proton affinity of HCN (713 kJ mol⁻¹) vs. that of H₂O (691 kJ mol⁻¹) [26], such a complex would preferentially decompose to HC≡NH⁺ (m/z 28) + H₂O rather than to HCN + H₂O⁺ (m/z 19), as indeed observed (Figure 1b). The mechanism presented in Scheme 2, which involves a concerted 1,4-H

rearrangement in metastable [H₂NCHCOOH]⁺, reconciles both the large kinetic energy released upon CO loss [21, 27, 28] as well as the structure of the resulting CH₄NO⁺ fragment ion. It should be mentioned at this point that protonated glycine, ¹H₃NCH₂COOH, shows very similar MI features: it mainly loses CO to form the proton-bound complex H₂C≡NH··H⁻··OH₂ via a tight rearrangement associated with a large kinetic energy release [29]. Apparently, ammonium ion ²H₃NCH₂COOH and immonium ion ²H₂NCH⁺COOH ↔ H₂NCH⁺COOH exhibit at threshold parallel unimolecular reactivities.

The loss of CO remains an abundant decomposition channel also after collisional activation, although now many more reactions take place (Figure 2). Based on the mass shifts observed for the perdeuterated α-glycyl cation, the major CAD products of [H₂NCHCOOH]⁺ are assigned the compositions C₂H₃NO⁺ (m/z 57; OH⁻ loss), C₂H₅NO⁺ (m/z 56; H₂O loss), CH₄NO⁺ (m/z 46; CO loss), CHO₂⁺ (m/z 45; CH₃N loss), CH₃N⁺ (m/z 29; CO₂H loss), and CH₂N⁺ (m/z 28; consecutive H₂O loss from m/z 46). The same fragmentation pattern,

Scheme 2.

The numbers in parentheses are heats of formation. ∆H° values and transition state energies are shown in ovals and rectangles, respectively. All energies are in kJ mol⁻¹ and from [26] unless otherwise noted.

Estimated by assuming that the differences in heat of formation between the protonated amines ¹H₃N–CH₂–COOH and ¹H₃N–CH₂–CH₃ and the protonated imines ¹H₂N–CH₂–COOH and ¹H₂N–CH₂–CH₃ are equal.

Lower limit, obtained by equating T₀.₅ with the reverse activation energy.

Estimated from the heats of formation of HCNH⁺ and H₂O by assuming that the stabilization energies of the ion–dipole complexes HCNH⁺···OH₂ and H₂C≡NH⁻··OH₂ (formed from protonated glycine) [29] are identical.
but with lower signal/noise ratio, is obtained when [H₂NCHCOOH]⁺ is formed from glycine ([M–H]⁺ ion). It is noteworthy, that our CAD spectrum of [H₂NCHCOOH]⁺ (Figure 2) differs markedly from that reported for [glycine–H]⁺ by O’Hair et al. [15], which included additional fragments at m/z 30, 58, and 72. O’Hair et al. assigned the extra peaks to isomeric C₂H₄NO₂⁻ ions, such as the ion–molecule complex CH₂=NH₂⁺···OCO from which m/z 30 (CH₂=NH₂) can arise easily [15]; evidently, these isomeric contaminants are not generated under our EI conditions.

For more definitive information about the connectivity of the C₂H₄NO₃⁻ beam exiting our ion source, the complementary CAD products CHO₂⁻ and CH₃N⁻ (their m/z values add up to that of the [H₂NCHCOOH]⁺ precursor ion) were also analyzed by MS³. The MS³ spectrum of CHO₂⁻ (Figure 3) matches within experimental error the CAD spectrum reported for authentic (i.e., source generated) carboxyl cation, H₂O⁻ [22]. Similarly, the MS³ spectrum of CH₃N⁻ (Figure 4) is identical (within experimental uncertainty) with the CAD spectrum of ionized aminocarbene, +H₂NCH [30]; the m/z 13 (CH⁺) and 16 (+H₂N) fragments in Figure 4 readily distinguish this ion from the isomeric +HNCN, as had been shown previously [30, 31]. Ions +H₂NCH and +COOH arise from [H₂NCHCOOH]⁺ by simple cleavage of the C=O bond and, hence, are particularly indicative of the α-glycyl structure, as is the direct cleavage of OH (m/z 57 in Figure 2).

Corroborative evidence that CAD of [H₂NCHCOOH]⁺ mainly liberates the neutrals mentioned above (viz. OH, H₂O, CO, CH₃N, and CO₂H) is provided by the neutral fragment reionization ("N, R⁺") spectrum (Figure 5), which contains the superimposed collision-induced ionization spectra [32] of all these losses. Upon collisional ionization, each neutral generates molecular and fragment ions. The molecular ions are detected at m/z 45 ("CO₂H"), 29 (CH₃N⁺; shoulder of m/z 28), 28 (CO⁺), 18 (H₂O⁺), and 17 (OH⁺). Fragmentation of these molecular species provides extra contributions to CO⁺ and OH⁺ and also accounts for the "N, R⁺" products at m/z 44 (CO₂), 29 (COH⁺), 26–28 (CH₃–N⁺), 16–17 (H₀–O⁺), and 12 (C⁺).

Overall, the ionic and neutral dissociation products of the C₂H₄NO₃⁻ precursor ion and the MS³ data of selected ionic fragments from it are consistent with the α-glycyl structure. Based on these facts, it is concluded that the m/z 74 cation produced from isoleucine (or valine, leucine, and serine) maintains the [H₂NCHCOOH]⁺ connectivity and, hence, is an appropriate reagent for the gas phase synthesis of the α-glycyl radical and anion.

The α-Glycyl Anion

Charge reversal of [H₂NCHCOOH]⁺ (m/z 74) to negative ions ("CR⁻") leads to abundant anions of the same composition ("survivor" anions) as well as fragment anions (Figure 6). This process might produce energetically excited α-glycyl anions that rearrange to the more stable glycinate anion, H₂NCH₂COO⁻ [15, 33]. The
fragmentation pattern of Figure 6 is, however, substantially different from that reported for the collision-induced decomposition of H$_2$NCH$_2$COO$^-$ by Bowie et al. [33]. For example, H$_2$NCH$_2$COO$^-$ yields an abundant fragment by H$^+$ loss (m/z 73) [33], which is absent from Figure 6. Consequently, the anions formed by charge reversal of [H$_2$NCHCOOH]$^-$ are not contaminated by glycinate anions or their fragments and rather reflect the stability and dissociation behavior of α-glycyl anions.

The sizable survivor signal in Figure 6 (m/z 74) affirms that [H$_2$NCHCOOH]$^+$ is a stable ion, as had been predicted computationally by O’Hair et al. [15] (see Scheme 1 for resonance structures). Major fragments arise by rearrangement losses of H$_2$ (m/z 72) and H$_2$O (m/z 56); these presumably have the resonance-stabilized structures HN=CH=(OH)O$^-$ (enolate of iminooacetic acid) and HN–CH=O (amide of amino-acetic acid), respectively. Direct cleavages can account for COOH (m/z 45) [34], OH$^-$ (17), and H$_2$N$^+$ (16). Finally, the fragments at m/z 40–41 (H$_{10}$C=C=O$^-$), 28 (HNCH$^-$) [35], and 26 (CN$^-$) could be formed by consecutive cleavages either from [H$_2$NCHCOOH]$^-$ or the heavier fragment anions.

The α-Glycyl Radical

Neutralization of [H$_2$NCHCOOH]$^+$ followed by reionization of the intermediate neutral to cations ~0.5 μs later gives rise to the “NR$^+$” spectrum of Figure 7. This spectrum contains a sizable survivor cation (m/z 74) and a similar fragmentation pattern to that observed in the CAD spectrum of the [H$_2$NCHCOOH]$^+$ precursor ion (Figure 2), indicating that the “NR$^+$” sequence has regenerated the original α-glycyl cation. Similarly, reionization to anions leads to an “NR$^-$” spectrum with an abundant survivor anion (m/z 74 in Figure 8) and striking resemblance to the “CR$^-$” spectrum of [H$_2$NCHCOOH]$^-$, consistent with the “NR$^+$” and “CR$^-$” processes creating the same anions, viz. [H$_2$NCHCOOH]$^-$ and fragments thereof. The combined “NR$^+$” and “NR$^-$” spectra provide strong evidence that gaseous (i.e., solitary) α-glycyl radical is a stable species, residing in a potential energy well with appreciable barriers towards fragmentation, as implied by the ESR studies in solution and the solid state [7, 8, 10].

The “NR$^+$” spectrum of [H$_2$NCHCOOH]$^+$ from glycine is identical to that of Figure 7 (poorer signal/noise) and substantially different from the “NR$^-$” spectrum reported for [M–H]$^-$ of glycine by O’Hair et al. [15]. Specifically, we observe barely any m/z 30 and less m/z 29 and 44 than present in the “NR$^+$” spectrum of glycine’s [M–H]$^-$. O’Hair et al. produced [glycine–H]$^+$ by negative chemical ionization, which leads to a mixture of H$_2$NCH$_2$COO$^-$, H$_2$NCH$^-$COOH, and HNCH$_3$COOH [15], and is neutralized to a mixture of C$_2$H$_4$NO$_2$ radicals. Reionization of the H$_2$NCH$_2$COO$^-$ and HNCH$_3$COOH components adequately accounts for the described discrepancies.

Our “NR$^+$” and CAD spectra of [H$_2$NCHCOOH]$^+$ (Figures 7 and 2) show some differences in their relative fragment ion abundances, which can largely be ex-
plained by the different internal energy distributions transferred upon "NR" via vis CAD [36]. The double-collision "NR" event generally deposits higher average internal energies, partly because of Franck–Condon effects during the neutralizing and reinouncing collisions [37]. As a result, more consecutive fragmentations and less rearrangement dissociations take place upon "NR" than CAD. Indeed, the rearrangement losses of H2O (m/z 56) and CO (46) have lower relative abundances in Figure 7 ("NR") than in Figure 2 (CAD). On the other hand, the more unsaturated fragments, such as CO2 (m/z 44) and HCNH+ (28), have enhanced relative abundances upon "NR" which can promote consecutive hydrogen losses. Another reason for some discrepancies between the "NR" and CAD spectra of [H2NCHCOOH]+ could be partial dissociation of the intermediate α-glycyl radical in the "NR" experiment. More information on this topic is unveiled by comparison of the "NR" and "CR" spectra, as discussed below.

The unimolecular reactivity of α-glycyl radical can be appraised by a method recently introduced by Schwarz et al. [34]. The approach is based on comparing charge reversal ("CR") and neutralization–reionization spectra involving charge inversion ("NR"). In "CR", cations are converted into anions in the same collision cell; at the nearly single collision conditions employed in this study, most anions are formed by double electron transfer in one collision; a few double-collision events may also take place, as upon "NR", but in faster succession so that a stable neutral intermediate may not have sufficient time for dissociation. Under these circumstances, the anions present in the "CR" spectrum mainly originate from charge-inverted ions. In contrast, "NR" uses two spatially and temporally well separated collisions; now, the ultimate fragment anions may result both from dissociations of the intermediate neutral as well as from the reionized species. Subtracting the normalized "CR" spectrum (i.e., the fragmentations of the anions) from the normalized "NR" spectrum (i.e., the convoluted fragmentations of neutrals and anions) leads to the neutral ion decomposition difference spectrum ("NIDD") [34], in which the fragments from the neutrals appear with positive intensities and those from the ions with negative intensities.

Table 1 lists the "NIDD" spectrum of [H2NCHCOOH]+. The differences are mainly negative, indicating that most "NR" fragments arise after reionization. On the other hand, the positive differences for m/z 28 and 56 suggest that these products are also formed at the neutral stage. Scheme 3 provides a plausible pathway, involving the elimination of H2O from α-glycyl radical to yield the ketene imine radical, [HN=CH–CO] (56 Da), which can further decompose to HNCH + CO (both 28 Da). Reionization of HNCH+/CO and [HN=CH–CO] contributes m/z 28 and 56 peaks, thereby increasing their relative abundances in the "NR" as compared to the "CR" the spectrum (Table 1); H2O gives no visible signal, because it cannot form a stable negative ion [26]. It is noteworthy that the survivor anion (m/z 74) also appears on the positive scale in the +NIDD spectrum (Table 1). The higher relative abundance of this ion upon "NR" (where it is formed after sequential electron addition) vs. "CR" (where it is formed mainly in one step) is ascribed to a better Franck–Condon factor and, hence, a lower internal excitation during the stepwise process.

Upon reionization to cations (cf. "NR" spectrum of Figure 7), the neutral dissociation products H2O (18 u) and HNCH/CO (28 u) provide contributions to m/z 18 and 28, respectively. However now, HN=CH–CO (56 u) does not yield an appreciable m/z 56 peak; presumably the incipient iminoacylium cation emerging after reionization, viz. HN=CH–CO+, undergoes facile loss of CO, in analogy to the closely related aminoacylium ion H2N–CH2–CO+, which has been shown to be a transient species, dissociating to +H2NCH2 + CO [29, 38].

Conclusions

The importance of α-amino acid and peptide radicals in pathogenic processes has prompted several recent studies on the gas phase chemistry of the prototype α-glycyl system [15, 39]. The combined MS/MS experiments presented in this study provide strong evidence that gaseous α-glycyl cation, radical, and anion are stable species. The unimolecular reactivity observed for these compounds is a direct consequence of their electronic distributions. The unpaired electron of the radical can

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**Table 1. +NIDD spectrum of α-glycyl cation, [H2NCHCOOH]+**

<table>
<thead>
<tr>
<th>m/z</th>
<th>+NR (%%)</th>
<th>+CR (%%)</th>
<th>+NIDD (Δ%%)</th>
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</thead>
<tbody>
<tr>
<td>16</td>
<td>3.2</td>
<td>4.5</td>
<td>−1.3</td>
</tr>
<tr>
<td>17</td>
<td>3.9</td>
<td>5.0</td>
<td>−1.1</td>
</tr>
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<td>12.6</td>
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</tr>
<tr>
<td>28</td>
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</tr>
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<td>44.7</td>
<td>31.7</td>
<td>+13.0</td>
</tr>
</tbody>
</table>

*Relative to total ions in spectrum (Σ = 100%).
*Entry for "NR" minus entry for "CR". For a thorough description of the method see [34].
be delocalized over the entire glycine backbone (cf. Scheme 1), which strengthens both the N–C° and C°–C(O) bonds; as a result, the favored dissociation of α-glycyl radical involves cleavage of other bonds, viz. H–N and C(O)–OH (Scheme 3). In sharp contrast, the charge of the α-glycyl ions can be delocalized only into one of the C° substituents. The electron-donating amine group provides resonance stabilization to the cation, increasing the N–C° bond order (Scheme 1); it is, therefore, not surprising that the major fragmentations of [H₂NCHCOOH]⁺ originate from scission of the C°–C(O) and C(O)–OH bonds. On the other hand, the electron-withdrawing carboxyl group stabilizes the anion (an enolate system); now, the C°–C(O) bond order rises (Scheme 1) and [H₂NCHCOOH]⁺ preferentially decomposes by breakup of the N–C° and C(O)–OH (as well as H–N and H–C) bonds (vide supra). It is worth noting that cation +CH₂COOH [40] and anion H₂NCHF₂ [41] where a positive and negative charge are exposed to an electron-withdrawing and electron-donating substituent, respectively, do not exist. Adding both these substituents to C° leads to stable H₂NCHOH and H₂NCH₂COOH, indicating that the stabilizing effect of the substituent that can spread out the charge outweighs the destabilizing effect of the other substituent. Finally, the high stability of the α-glycyl system, in particular of the radical, strongly suggests that such species and related peptide systems may have considerable lifetimes in vivo.

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