not exist between λ and solubility. The present systems may be discussed from the standpoint of lattice energy, crystal form, and species of crystals. The results of this investigation indicate that if the rate-determining of distribution of coprecipitation is known, the distribution coefficients can be predicted, and that distribution coefficients are determined by precipitation rate, solubility product, and so on.

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Thermal Decomposition of Aliphatic Monoamino-Monocarboxylic Acids

P. G. Simmonds, E. E. Medley, M. A. Ratcliff, Jr., and G. P. Shulman[1]

Bioscience and Planetology Section, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, Calif. 91103

Products from the thermal decompositions of a selected group of aliphatic monoamino-monocarboxylic acids have been analyzed by combined gas chromatography-mass spectrometry. Careful identification of both major and minor fragments suggests that, with the possible exception of glycine, amino acids of the aliphatic series decompose by a common reaction pathway. The primary decomposition is one of decarboxylation to yield an amine as the major product. Subsequent decomposition or reaction of the amine leads to the formation of nitriles and *N*-alkylaldimines as significant secondary products.

PYROLYSIS STUDIES of amino acids by gas chromatography and gas chromatography–mass spectrometry (GC–MS) have been reviewed by Stack (*1*). Thermal decomposition studies of both crystalline and aqueous solutions of amino acids have also been undertaken by geochemists with a view to establishing a "geothermometric method" for correlating the sedimentary time scale with the thermal environment (*2–4*).

In spite of the attention given to the pyrolysis of amino acids, there is considerable variation in the amount and type of volatile products reported by various investigators. For example, it is unlikely that the presence of amines, reported as major thermal fragments in one study (*5*) and their absence in another (*6*) can be accounted for solely by differences in the pyrolysis conditions. Adsorption of extremely polar fragments, either in the chromatographic column or on other parts of the analytical system, however, would explain many of the observed differences. Incorrect identification of products has also contributed to the lack of agreement between various workers, particularly where only gas chromatographic data have been used for identification. Even where GC–MS has been used, pyrolysis products often remain unidentified, and emphasis has generally been given to those products which could easily be correlated with the structure of the starting materials. As a consequence, there has seldom been any attempt to derive reaction pathways which would account for the formation of the majority of pyrolysis products.

Some progress has been made in developing reaction sequences which account for the thermal decomposition of aromatic and heteroaromatic amino acids (*7*). The use of ^{14}C-labeled amino acids provides excellent evidence that decarboxylation is the predominant decomposition reaction with negligible fragmentation of the aromatic nucleus (*8*). Hydroxyl- (*9*) and sulfhydryl- (*10*) containing amino acids have previously been studied in some detail and it is quite clear that different pyrolysis mechanisms are possible when the amino acid contains functional groups other than amino and carboxyl.

In the present work, we have selected a group of aliphatic monoamino-monocarboxylic acids for more detailed study by pyrolysis GC–MS, with the purpose of developing a unified reaction scheme which would adequately explain their mode of thermal decomposition. This group consists of glycine, alanine, β-alanine, valine, leucine, and isoleucine. Furthermore, it is hoped that the results of this investigation could be used to predict the course of pyrolysis for other monoamino-monocarboxylic acids and might also provide some insight into the more complex decompositions of multi-functional amino acids.

EXPERIMENTAL

Apparatus. The combined technique of pyrolysis–gas chromatography–mass spectrometry used in this investigation has been reported in detail elsewhere (*11*). To summarize the method, approximately 1 mg of crystalline amino acid was weighed into a 2.5-cm by 0.127-cm i.d., 0.158-cm o.d. stainless steel tube. The tube was directly attached to the front end of the chromatographic column, and the sample

[1] Present address, Casa Loma College, Pacoima, Calif.

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was pyrolyzed in a helium atmosphere by heating the sample tube to 500 °C in 10 sec with a small furnace containing a Nichrome heater (8 ohms resistance). Chromatographic separation of the pyrolysate was achieved using both packed and capillary columns. Capillary columns were 152 m long (o.d. 0.158 cm, i.d. 0.076 cm) made from "Chromat finish" stainless steel (Handy and Harman Tube Co., Norristown, Pa.). One column was coated with Carbowax 20M and another with SF96/Igepal (20:1) (*12*). Two packed columns (2.4 m long, i.d. 0.127 cm; o.d. 0.158 cm) were also used, one contained Poropak Q (Waters Associates, Waltham, Mass.) and the other Chromosorb 103 (Johns-Manville).

Individual products were identified by comparison of their mass spectra (Quadrupole 300; EAI, Palo Alto, Calif.) with published spectra (*13*). Where spectra were unavailable, tentative identification was confirmed by synthesis and comparison of the mass spectral fragmentation pattern of the synthesized compound with that of the pyrolysis product. Chromatographic peak intensity was recorded with an ion-current detector whose output signal was continuously displayed on a potentiometric recorder. The relative yield of each pyrolysis product was determined by calibration of the ion current detector with standard mixtures.

Independent chromatographic analyses were performed with a MicroTek Model 2000-R research chromatograph. Peak areas were computed either by triangulation or by weighing. Proton NMR spectra were recorded on a Varian Model A56-60 nuclear magnetic resonance spectrometer (Varian Associates, Palo Alto, Calif.). Infrared spectra were obtained with a Perkin-Elmer Model 421 spectrometer.

Reagents. Neutral amino acids were all A grade, obtained from Calbiochem (La Jolla, Calif.). All other reagents used in syntheses were reagent grade. Glycine 2-^{13}C, 61% enrichment, was purchased from Prochem (Lincoln Park, N.J.). Glycyl-glycine hydrochloride was obtained from Nutritional Biochemicals, Inc. The water content of all amino acids was determined by the Karl Fischer method.

Procedure. Preparation of Schiff's Bases. The Schiff's bases of 2-methyl propionaldehyde and 2-methyl butyraldehyde were prepared by condensation with the corresponding amines, 2-methyl propylamine and 2-methyl butylamine. The synthesis of *N*-(2-methylpropyl)-2-methyl propionaldimine exemplifies the procedure used to prepare the bases. Equivalent amounts (0.1 mole) of 2-methyl propionaldehyde and 2-methyl propylamine were condensed in a 50-ml round bottomed flask maintained at −78 °C. The mixture warmed slowly to room temperature (26 °C) and was allowed to stand for two hours. The imines were recovered by distillation and characterized by NMR and MS analysis.

Diketopiperazines of glycine and valine were prepared by the method of Schott *et al.* (*14*). The products were recrystallized from water and the structures confirmed by IR and MS. Aliquots, 0.5 mg, of each diketopiperazine were taken for subsequent pyrolysis experiments.

RESULTS AND DISCUSSION

Labile or highly polar compounds such as free amines invariably comprise a large fraction of the pyrolysate of amino acids (*5*). Columns suitable for these materials and replicate analyses may therefore be required to ensure a reasonable estimate of their concentrations.

The determination of very minor pyrolysis products (*i.e.*, those present at a concentration of <1%) are generally unimportant in terms of characterizing individual amino acids. Nevertheless, they are often extremely useful in establishing preference for a particular decomposition sequence where their presence would be predicted from a knowledge of the major pyrolysis products.

Table I lists the type of pyrolysis products and their relative concentrations from those amino acids which have been studied. Hydrogen and carbon monoxide were also observed in all pyrolysates but it was not possible to determine accurately their concentrations under the conditions employed.

While it is difficult to explain the formation of some of the products, such as methane and other hydrocarbons, by other than radical intermediates, it is by no means certain that the thermal fragmentation of aliphatic amino acids proceeds exclusively by a radical mechanism.

Unimolecular decomposition or heterolytic cleavage is certainly an acceptable mechanism for the decarboxylation of carboxylic acids; furthermore, it is well known that where an acid can exist in a Zwitterion form, then decarboxylation is greatly favored (*15*).

$$NH_2CH_2CO_2H \rightleftharpoons NH_3^+CH_2CO_2^- \quad (\Delta H_{298} = -11.5 \text{ Kcal/mole})$$

Although the equilibrium constant for the forward reaction is approximately 10^5 at 26 °C, the equilibrium shifts in favor of the acid form at pyrolysis temperature (*16*). Since it was not possible to determine the exact equilibrium mixture at the time of pyrolysis, it is not known to what extent the Zwitterion form participates in the initial decomposition.

An overall reaction sequence which might tentatively account for the formation of the majority of the products is shown in Figure 1. Reactions which are marked by an asterisk would be favored, however, if the decomposition occurred from the Zwitterion form.

There are four primary reactions by which the amino acids apparently decompose. Decarboxylation is clearly the major decomposition pathway as evidenced both from the yield of carbon dioxide and the formation of amines as major products.

Homolysis of the carbon–carbon bond α to the amino group to yield an alkyl radical represents a minor decomposition pathway for most of the amino acids. Thus, propene, isobutene, butene, and their corresponding alkanes are formed from valine, leucine, and isoleucine, respectively. Alkenes predominate over alkanes, presumably by decomposition of the alkyl radical to an olefin and hydrogen radical, or another alkyl radical (*17*).

$$RCH_2CH_2\cdot \rightarrow R\cdot + CH_2{=}CH_2$$

$$RCH_2{-}CH_2\cdot \rightarrow RCH{=}CH_2 + H\cdot$$

The excess of alkenes can also be explained as a result of heterolytic processes which may lead to olefin products. Olefins of various chain length have also been reported recently in the pyrolysis of aliphatic amino acids (*18*).

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(17) F. O. Rice, "Free Radicals," Catholic Univ. of America Press, Washington, D. C., 1958.
(18) O. Kirret, E. Kulik, and M. Luus, *Izv. Akad. Nauk. Est. SSR, Ser. Geol.*, **18,** 307 (1969).

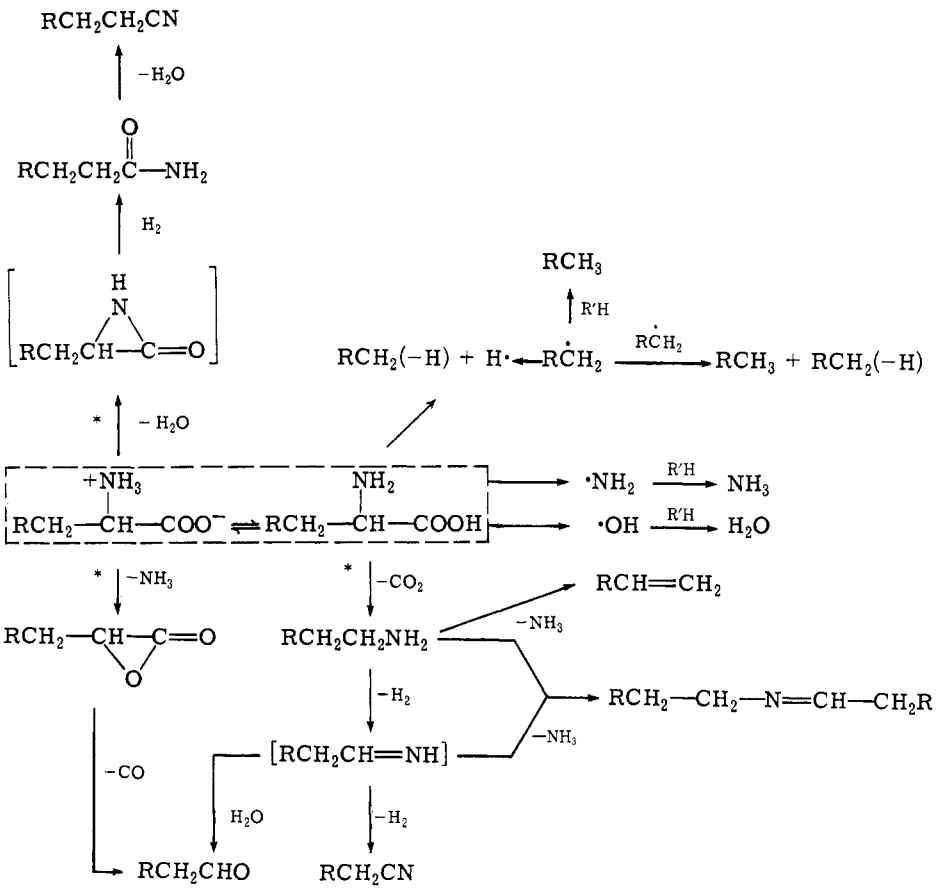
Table I. Relative Concentrations of Pyrolysis Products
(% of total pyrolysate)

Product	Glycine	Alanine	Valine	Leucine	Isoleucine	β-Alanine
CO_2	39.8	43.2	27.9	30.8	31.2	5.1
NH_3	20.5	13.5	12.5	11.6	6.9	18.1
H_2O	22.7	17.0	5.3	8.8	11.2	41.7
HCN	1.6	0.4				
C—CN	12.3	1.6	0.1	3.3	1.4	1.6
C—C—CN	0.7	0.5	0.2	<0.1	1.8	0.6
C=C—CN		1.2		<0.1	0.4	12.1
C—C—CN | C			10.8		1.0	
C=C—CN | C			2.7		1.1	
C—C—C—CN | C			0.9	13.6		
C—C—C—CN | C					4.3	
C—C—C—C—CN | C				0.8		
C—C—C—C—CN | C					1.7	
C—NH_2	0.5					
C—C—NH_2		17.3				0.3
C—C—C—NH_2 | C			21.7			
C—C—C—C—NH_2 | C				21.0		
C—C—C—C—NH_2 | C					19.3	
O ‖ C—C—NH_2	0.8					
O ‖ C—C—C—NH_2		0.4				
O ‖ C=C—C—NH_2						2.2
CH_3OH	0.3					
CH_3CHO		<0.1				
C—C—CHO | C			1.9			
C—C—C—CHO | C				<0.1		
C—C—C—CHO | C					0.7	
C=C—COOH						17.8
C—C=N—C—C		3.4				
C—C—C=N—C—C—C | C			13.8			
C—C—C—C=N—C—C—C—C | C				7.8		
C—C—C—C=N—C—C—C—C | C					11.8	
CH_4	0.6	0.8	0.2	0.4	0.3	<0.1
C=C	<0.1	0.3	<0.1	<0.1	1.0	<0.1
C—C	<0.1	0.2	<0.1	<0.1	2.3	<0.1
C—C=C		<0.1	0.6	0.4	0.6	<0.1
C—C—C		<0.1	0.5	0.2	<0.1	<0.1

(Continued)

Table I. (*Continued*)

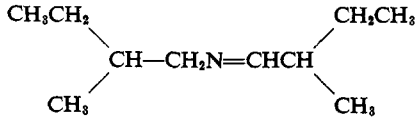
Product	Glycine	Alanine	Valine	Leucine	Isoleucine	β-Alanine
C–C=C			0.6	0.5		
C–C–C			<0.1	0.3		
C–C=C–C					0.7	
C–C–C=C					1.0	
C–C–C–C					0.3	
C–C–C=C				0.4		
C–C–C=C					0.9	
C–C–C–C				<0.1	<0.1	
C–C–C	<0.1	<0.1	<0.1			
C–C–C–C			0.2			



(* REACTIONS FAVORED BY ZWITTERION FORM)
R'H DENOTES ANY SOURCE FOR HYDROGEN ABSTRACTION

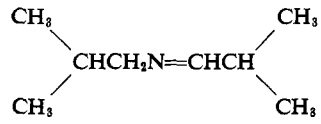
Figure 1. Tentative thermal decomposition pathways of aliphatic monoamino monocarboxylic acids

Table II. Mass Spectral and NMR Data for *N*-Alkyl Aldimines



A

NMR[e] 7.6[a] (1.0)[b] (N=CH—)[c] m[d]
3.25 (2.0) (C—CH_2—N) d(complex)
[f] 1.2–2.5 (2.2) (>CH—C—N— and =C—CH<) m(complex)
0.8–1.2 (17) (alkyl, methyl, and ethyl) m(complex)



B

7.6 (1.0) (N=CH—) m
3.18 (2.0) (C—CH_2—N) d(complex)
[f] 1.2–2.7 (1.9) (>CH—C—N and =C—CH<) m(complex)
0.8–1.2 (13) (alkyl, methyl) m(complex)

Mass spectra *m/e*	Normalized abundance A	B	Mass spectra *m/e*	Normalized abundance A	B
26		0.96	71	33.20	0.56
27	8.22	10.70	72	2.30	2.5
29	16.30	18.00	73		0.79
30	17.80	9.25	77	0.99	
31	0.41		78	4.28	
38		1.01	79	0.41	
39	8.08	10.00	80	0.49	
40	1.32	1.12	81	0.82	
41	29.00	34.40	82	1.48	2.24
42	21.70	8.71	83	0.66	0.39
43	44.60	16.30	84	13.00	100.00
44	5.52	0.22	85	1.32	7.85
50	0.66		98	100.00	1.12
51	1.15		99	8.58	
52	0.99		112	5.18	4.50
53	2.07	1.40	113	7.40	
54	1.64	1.68	114	0.66	
55	7.41	22.70	126	3.61	1.24
56	10.83	11.20	127	15.60	3.70(mol ion)
57	7.75	78.00	128	1.48	
58		4.50	140	7.00	
67	1.23	1.85	141	0.82	
68	3.87	2.81	154	0.91	
69	19.80	1.12	155	0.66(mol ion)	
70	40.20	6.74	156	0.25	

[a] Chemical shift in ppm relative to TMS
[b] Area under peak.
[c] Assignment.
[d] Description of peak; s-singlet, d-doublet, m-multiplet.
[e] Solvent CCl_4.
[f] The area from 1.2 to 2.5 in very complex, representing alkyl protons with only small chemical shift differences.

Methane was also observed in the pyrolysis of all amino acids (yield invariably <1%) and most probably arises from the abstraction of hydrogen by methyl radicals.

Deamination would appear to be a third mode of decomposition, presumably through rupture of the carbon–nitrogen bond to yield an amino radical. However, as will be seen later, ammonia may also be produced as a result of secondary reactions, and its formation as part of a primary decomposition may therefore be less important.

Similarly a fourth mode of thermal decomposition would involve a loss of water, but condensation reactions such as the formation of a dipeptide or diketopiperazine would also release water. Nevertheless, loss of water is primarily a consequence of pyrolysis and not from water of crystallization. Only in the case of β-alanine was there substantial water of crystallization (approximately 2.5%). For all other amino acids, it was less than 0.3%.

While the major products from the pyrolysis of the aliphatic amino acids are amines, these may continue to fragment and react as evident from the presence of secondary reaction products. Each amine therefore decomposes by the loss of two molecules of hydrogen to yield the corresponding nitrile. Previous work (*6*, *19*) suggests that this decomposition proceeds through an imine intermediate, as shown below.

$$RCH_2CH_2NH_2 \rightarrow [RCH_2CH{=}NH] \rightarrow RCH_2CN$$

Interestingly, almost all of the amino acids give *N*-alkyl aldimines as significant pyrolysis products, thus providing convincing evidence for the presence of an imine precursor that is apparently trapped by a condensation reaction.

The structure of the *N*-alkyl aldimines was confirmed by syntheses involving condensation of the amines with the corresponding aldehyde to form a Schiff's base. Relevant NMR and mass spectral data are listed in Table II. The mass spectra of each synthesized *N*-alkyl aldimine was identical to the mass spectrum of the corresponding imine formed from the pyrolysis of individual amino acids; and the mass spectral fragmentation patterns were consistent with the reported spectra of related imines (*20*).

(19) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, N.Y., 1929, p 290.
(20) M. Fischer and C. Djerassi, *Chem. Ber.*, **99**, 1541 (1966).

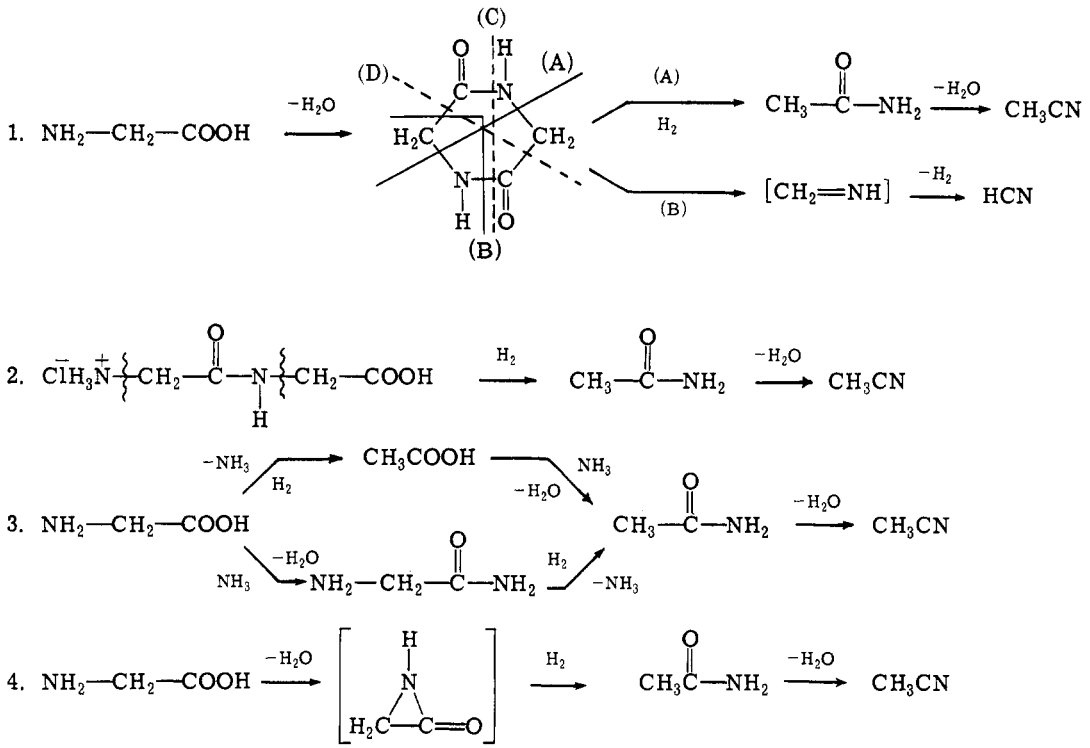
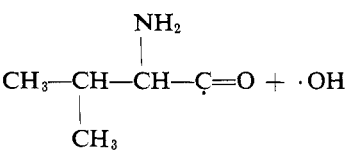


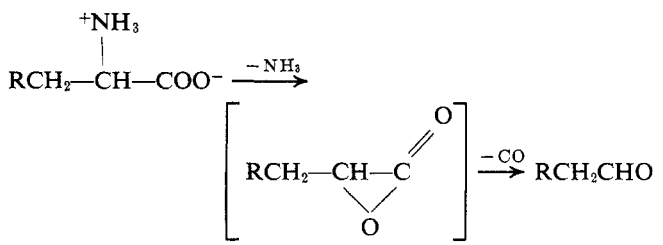
Figure 2. Possible routes for formation of ethanenitrile from glycine

Reactions which might lead to the formation of the *N*-alkyl aldimines are postulated in Figure 1. Thus, loss of hydrogen from the primary amine yields an imine intermediate which can either react with the amine itself by a transalkylidenation reaction (*21*) or with water to form an aldehyde, which subsequently undergoes a condensation reaction with the amine. The latter of these possibilities is less acceptable since both a hydrolysis and a condensation reaction are required. Not only are the conditions unfavorable for hydrolysis, but the final *N*-alkyl aldimine product would require four separate reactions for its formation from the amino acid.

Aldehydes and also ketones have been reported previously as products from the pyrolysis of amino acids (*6*, *22*). However, in the present experiments, aldehydes and ketones were observed only as relatively minor products. Their formation is at best obscure, although a simple explanation would be to invoke the presence of an acyl radical as the intermediate. Pyrolysis of carboxylic acids is reported to yield aldehydes and ketones (*23*). Also the formation of ketones from the decomposition of carboxylic acid salts appears to proceed by an acyl radical mechanism (*24*). The presence of carbon monoxide in all of the pyrolysates also lends some support to the transitory existence of an acyl radical. Unfortunately, the acyl radical which would, for example, result from homolytic scission of the carboxylic group of valine, is not in fact the radical which would lead to 2-methyl propionaldehyde, the only aldehyde observed from the pyrolysis of valine.



An alternative explanation, but one which is at present speculative is expressed below:



This mechanism also accounts for the presence of carbon monoxide and furthermore suggests a route to ammonia via a primary decomposition which does not involve the amino radical.

Unfortunately, it is not possible at present to determine if any aldehyde resulting from pyrolysis, subsequently condensed with the amine formed in the primary decarboxylation reaction.

In addition to the formation of nitriles with one carbon atom less than the parent amino acids (*vide supra*) other nitriles are also formed during pyrolysis. As previously reported (*6*, *22*) all amino acids gave ethanenitrile and propanenitrile. Acrylonitrile was observed as a very minor product in most amino acids but was not detected from the pyrolysis of either glycine or valine. Of special interest is the presence of nitriles of chain length equivalent to the parent amino acid; certainly these cannot be formed after decarboxylation has occurred. More likely they are formed by loss of water from the appropriate amide. The presence of acetamide and propionamide in the pyrolysates of glycine and alanine, respec-

(21) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. I., W. A. Benjamin, New York, N.Y., 1954, p 301.
(22) C. Merritt, Jr., and D. H. Robertson, *J. Gas Chromatogr.*, **5**, 96 (1967).
(23) T. Wolf, Ph.D. Thesis, University of Rhode Island, Kingston, R.I., 1966.
(24) R. Hites and K. Biemann, *J. Amer. Chem. Soc.*, **94**, 5772 (1972).

tively, supports this hypothesis. The corresponding amides of the higher amino acids (*i.e.*, valine, leucine, and isoleucine) were not observed, although it is doubtful that they would be eluted from the chromatograph under the conditions employed, particularly since the shortest elution time of propionamide on the columns used was 75 minutes and then only as a broad peak. Their presence is nevertheless inferred by the formation of 3-methyl butyronitrile (0.9%) from valine, 4-methyl valeronitrile (0.8%) from leucine, and 3-methyl valeronitrile (1.7%) from isoleucine. These nitriles represent the dehydration products from the amides of interest.

There are several possible routes for formation of the amides as shown in Figure 2 using glycine as an example. A most likely pathway (Equation 1) is via decomposition of the diketopiperazine through the points bissected by A. Pyrolysis of the diketopiperazines of glycine and valine both yielded the expected nitriles containing the same number of carbon atoms as the parent amino acids. In addition, acetamide was observed in the pyrolysate of glycine diketopiperazine. Cleavage of the diketopiperazine through B followed by dehydrogenation would lead to the formation of another observed product, HCN. An alternative route (Equation 2) would be through the dipeptide. Pyrolysis of glycyl-glycine hydrochloride yielded both the expected acetamide and ethanenitrile and a small quantity of HCN. A third possibility (Equation 3) involving addition and subtraction of ammonia is considered unlikely for two reasons. First, the acid intermediate was not detected and second, longer chain amides would be predicted as a result of condensation between other amines and the acid intermediate. A fourth mechanism (Equation 4) would involve a unimolecular decomposition via a cyclic α-lactam intermediate. Although α-lactams are highly labile they have been suggested as intermediates in several reactions (*25–27*) and a substituted aziridinone (α-lactam) has been isolated by Baumgarten *et al.* (*28*).

Both the α-lactam (Equation 4) and the diketopiperazine (Equation 1) might simultaneously be involved. Decomposition of the diketopiperazine through the bonds bissected by A (Equation 1) would formally produce a diradical species which upon ring closure would result in the same α-lactam as that produced by the dehydration reaction of Equation 4. Alternatively, a concerted decomposition of the diketopiperazine could yield the intermediate α-lactam directly with no need for invoking the diradical species. Cleavage through the bonds bissected by A represents only one of three alternatives for the formation of the α-lactam from a diketopiperazine. Cleavage through bonds bissected by C and D with concomitant ring closure (or concerted ring formation) would also produce the α-lactam. For a symmetrical diketopiperazine, the products are identical and only labeling experiments would provide the answer, although the path through C seems least likely since cleavage through an amide bond is necessary. The α-lactam once formed could then undergo reductive ring opening to yield the amide and therefore the nitrile. Alternatively, loss of CO would give HCN via the imine intermediate.

A particularly interesting comparison in the present work is provided by the pyrolysis of β-alanine in which the amino function is β to the carboxyl group. By contrast to the α-amino acids, the primary decomposition pathway for β-alanine is one of deamination to yield acrylic acid as a major pyrolysis product (~18%). As might be expected, acrylamide and acrylonitrile are also significant products. The low yield of carbon dioxide is particularly interesting since decarboxylation is such a predominent reaction for α-amino acids. Furthermore, the presence of only a trace of ethylene, suggests that acrylic acid does not decarboxylate to any great extent as would have been predicted for an unsaturated carboxylic acid and particularly those of greater chain length (*29*). Since acrylic acid is not found as a product from the pyrolysis of α-alanine, one must conclude that deamination to yield unsaturated carboxylic acids is not an important decomposition pathway for α-amino acids. This is particularly true for valine where simple deamination should produce β,β-dimethyl acrylic acid which is known to resist decarboxylation at least to a temperature of 300 °C (*30*).

If ammonia is to be lost as a result of a primary decomposition, one must invoke either the formation of an amino radical or a unimolecular deamination, presumably via some type of cyclic intermediate. Certainly much of the ammonia which is observed can be accounted for by secondary reactions; *e.g.*, as a by-product of the transalkylidenation reaction or by deamination of amines. Similar arguments must be used to account for the formation of water. Homolysis of the carboxylic acid group to a hydroxyl radical, or formation of a cyclic α-lactam (see Equation 4, Figure 2) would both release water in a primary decomposition step. However, secondary decomposition such as the dehydration of amides must also be considered as a source of water.

Although the α-amino acids apparently decompose by a common fragmentation pathway, glycine is in some respects anomalous. Fragmentation to small molecules is more severe and inorganic gases such as CO_2, NH_3, and H_2O account for the majority of the pyrolysate. The yield of methyl amine is also surprisingly low, but even more anomolous is the presence of approximately 1% propanenitrile. No other α-amino acid produced a nitrile with a longer carbon chain than the parent amino acid under the same pyrolysis conditions. Gas chromatographic analysis of the starting material as the trimethylsilyl-*n*-butylester established that the glycine was not contaminated with alanine or other amino acids. However, pyrolysis of glycine 2-^{13}C showed clearly that the propanenitrile formed in the pyrolysis was doubly labeled with ^{13}C. This suggests that methyl radicals may be generated when glycine is thermally decomposed.

Previous attempts (*23*) to distinguish between a radical or a unimolecular decomposition mechanism for the thermal fragmentation of simple organic molecules have been generally inconclusive. Based on the present information, it appears likely that both mechanisms are operative in the pyrolysis of amino acids.

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