Thermal Decomposition of Aromatic and Heteroaromatic Amino-acids†

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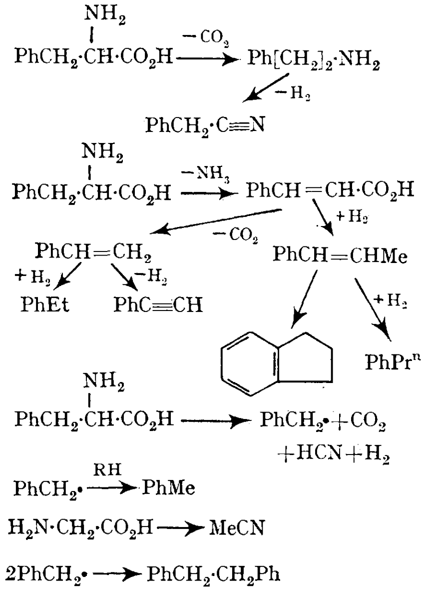
RECENTLY, investigations of the pyrolysis of amino-acids[1,2] or their sodium salts[3] have been reported. The method is potentially useful for rapid identification of amino-acid constituents of peptides or proteins. It was apparent that either the analytical techniques (gas chromatography and mass spectroscopy) were inadequate to detect all the products, or that markedly different reaction schemes applied to the closely related amino-acids phenylalanine, tyrosine, tryptophan, and histidine. We have now characterized the volatile products obtained from pyrolysis of these amino-acids, and conclude that there is no significant variation in the mode of decomposition.

A complete gas chromatographic analysis of the phenylalanine pyrolysate is shown in the Figure. The magnitude of quantitative variations (Table) resulting from changes in construction materials are also typical of those obtained by varying pyrolysis temperature from 400 to 600° or pyrolysis time from 4 sec. to 1 min. It is obvious from the products that suitable conditions for oxidation–reduction reactions are established during pyrolysis. Products can be explained as resulting from the following reaction sequences:



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Analytical data from pyrolysis of amino-acids, $RCH_2{\cdot}CH(NH_2){\cdot}CO_2H$

R	G.c. column	Pyrolysis temp.	Chamber material	Relative percentage of									
				CO_2[a]	H_2O	CH_3CN	RH	RMe	REt	$RCH{=}CH_2$	RCH_2CN	$RCH_2CH_2NH_2$	RCH_2CH_2R
Ph	A[b]	500°	Stainless	Qualitative analysis									
	B[c]	400	Stainless	d	d	—	—	28	0·74	0·95	8·2	49	6·9
	B	500	Stainless	d	d	—	—	30	0·79	1·1	8·6	53	6·2
	B	600	Stainless	d	d	—	—	24	0·47	0·91	6·2	64	5·2
	B	500	Stainless	27	20	1·0	2·7	14	0·6	0·6	5·1	26	1·5
	B	500	Quartz	29	24	0·8	1·4	28	0·8	1·2	2·5	10	0·5
	B	500	Pyrex	28	19	0·8	1·6	19	0·5	0·4	5·0	21	2·0
	B	500	Pyrex[e]	d	d	—	—	44	1·9	4·9	8·2	30	4·3
	C[f]	500	Stainless	Qualitative analysis									
p-$C_6H_4{\cdot}OH$	A	500	Stainless	Qualitative analysis									
	B	500	Stainless	52	30	1·0	9	6	2				
Indol-3-yl	C	500	Stainless	22	12	0·7	27	33					
Imidazolyl	D[g]	500	Stainless	Qualitative analysis									

[a] Including CH_4 and other hydrocarbons.

[b] Squalane—50 ft. of 0·02 i.d. support coated open tubular column programmed 50 to 125° at 6° min.$^{-1}$ then maintained at 125°.

[c] Carbowax 20M—200 ft. of 0·02 i.d. stainless steel capillary coated with 10% solution, programmed 50 to 200° at 6° min.$^{-1}$, then maintained at 200°.

[d] Not determined (flame ionization detector).

[e] Sealed tube—1 min. pyrolysis.

[f] Silicon oil—300 ft. of 0·2 i.d. stainless steel capillary coated with DC200–Igepal 880/20 : 1, programmed 50 to 200° at 4° min., then maintained at 200°.

[g] Ethylene glycol adipate—6 ft. of 4 mm. i.d. glass tubing containing 10% EGA on 80—100 mesh Gas-Chrom Q support.

An amide formed by condensation of two amino-acids is a likely, though unproven, intermediate in the pyrolysis of amine to olefin. Each of the products indicated was identified by comparison of its mass spectrum with published spectra.[4]

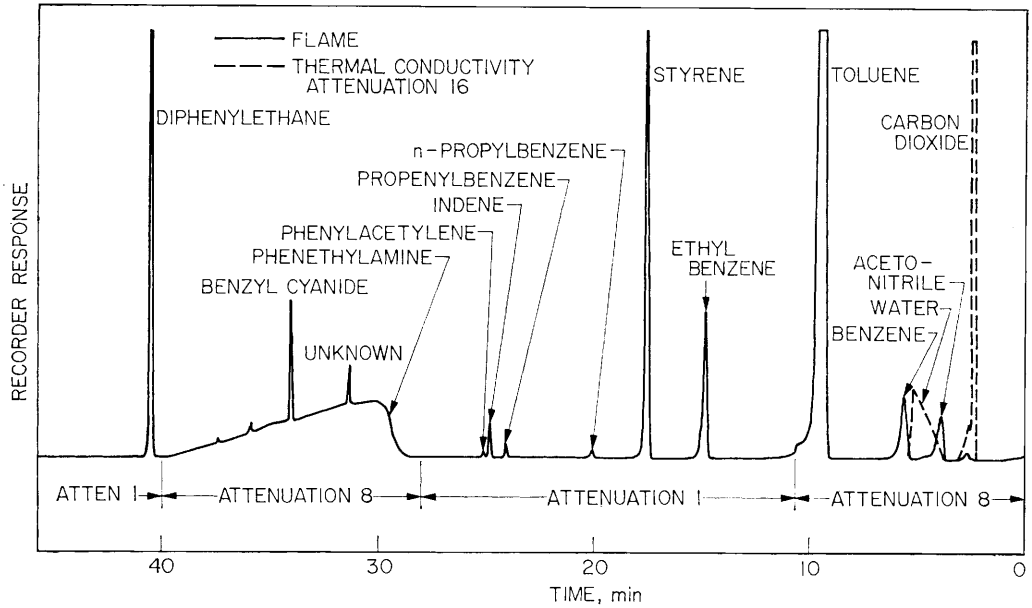

FIGURE. *Gas chromatogram of phenylalanine pyrolysate on DC200 silicone oil.*

Pyrolysis of tyrosine under comparable conditions (4 sec. at 500°), gave the expected products phenol, *p*-cresol, and *p*-ethylphenol (corresponding to benzene, toluene, and ethylbenzene from phenylalanine). Also formed were the previously reported methane,[3] water,[3] carbon dioxide,[3] and toluene,[1] methyl cyanide, and rearrangement products *o*- or *m*-cresol, xylenol, and *o*- or *m*-ethylphenol. Similarly, tryptophan gave indole, 3-methylindole, and vinylindole. Histidine would be expected to form imidazole and imidazole derivatives on pyrolysis. An established gas chromatographic method[5] for these was used, but under operating conditions compatible with the mass spectrometer inlet, clearly defined peaks were not obtained. A broad background spectrum of imidazole was obtained (*m/e* 68, 41, and 40).

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