Geochimica et Cosmochimica Acta

Volume 28, Issue 2, February 1964, Pages 157-188

Biogeochemistry of organic matterâ€”II Thermal reaction kinetics and transformation products of amino compounds

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https://doi.org/10.1016/0016-7037(64)90147-4

Abstract

The following ninhydrin-reactive products were identified in 0.01 M solutions of single amino acids pyrolysed in the absence of oxygen: gamma-aminobutyric acid from glutamic acid; methylamine from glycine; ethylamine from alanine; glycine, alanine and ethanolamine from serine; glycine from threonine; phenethylamine and benzylamine (?) from phenylalanine; glycine and alanine from methionine; and proline from arginine. R_f values are listed for unidentified ninhydrin-reactive products that arose from pyrolysed solutions of leucine, isoleucine, valine, histidine, tyrosine and lysine. Aspartic acid yielded only malic acid and ammonia on pyrolysis and neither proline nor hydroxyproline yielded ninhydrin-reactive products. In terms of increasing order of relative thermal stability at temperatures between 216 and 280Â°C the amino acids studied fell into the following four groups: (1) aspartic acid, cystine, threonine, serine, arginine-HCl; (2) lysine-HCl,

histidine-HCl, methionine; (3) tyrosine, glycine, valine, leucine, isoleucine; (4) alanine, proline, hydroxyproline (?), glutamic acid. It is suggested that part of the glycine, proline and alanine in fossil materials may bo diagenetic and not original.

Pyrolytic experiments on equimolar mixtures of amino acids in aqueous solution showed the relative stability order predicted on the basis of experiments with single amino acids to remain unchanged; however, glycine,alanine and phenylalanine were observed to decompose more rapidly in mixtures than when present alone. Alanine was shown to be much more liable during pyrolysis in the presence of glucose than in its absence, the kinetics increasing with the concentration of glucose.

Arrhenius equations describing the reaction rates of four amino acids present singly in 0.01 M solutions were found to be: pyroglutamic acid,
$k = 2$ Ã— $10^{9} e^{â^'35,800RT}$; phenylalanine,
$k = 2$ Ã— $10^{8} e^{â^'30,800/RT}$; threonine,
$k = 2$ Ã— $10^{12} e^{â^'35,800/RT}$ and serine,
$k = 4$ Ã— 10^{9} $â^'29,350/RT$. Using these equations and old data obtained for alanine by Abelson (1954), a table was constructed showing the predicted amounts of each amino acid remaining after the application of time temperature combinations between 0.1 million years at 10Â°C and 5000 million years at 100Â°C. Applications of the data to geothermometry are illustrated and a case is made for the possible development of a new method in geothermometry based on selective destruction of certain amino acids.

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