

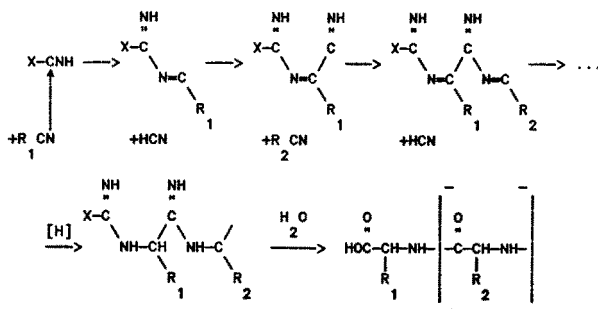
ATMOSPHERIC FORMATION OF ORGANIC HETEROPOLYMERS FROM N_2+CH_4 :
 STRUCTURAL SUGGESTIONS FOR AMINO ACID AND OLIGOMER PRECURSORS

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Amino acids formed from reducing gases in an aqueous environment by electrical discharge (Miller, 1953) or by ultraviolet light (Sagan and Khare, 1971) are usually attributed to a Strecker synthesis. However, there is another route to amino acids in reducing atmospheres: via abundant organic solids, produced both in the presence and in the absence of water vapor, for which no synthetic pathway is generally agreed upon.

The roughly 10:1 N_2+CH_4 atmosphere of Titan contains minor hydrocarbon and nitrile components in the gas phase and a solid particulate haze. We have quantitatively studied both the gaseous products and the solid organic heteropolymer (called Titan tholin) formed from a low-pressure, continuous-flow plasma discharge in 10:1 N_2+CH_4 . The optical constants of Titan tholin are in excellent agreement with those for the Titan haze (Khare *et al.*, 1984a; Sagan *et al.*, 1985), showing that the formation and properties of the tholin cannot be attributed to wall effects. Titan tholin (Khare *et al.*, 1984b) and $CH_4+NH_3+H_2O$ -derived tholin (Khare *et al.*, 1981) yield a large number of hydrocarbons, nitriles, and homo- and heterocyclic rings upon pyrolytic GC/MS. We have also shown (Khare *et al.*, 1986) that acid hydrolysis of Titan tholin produces several, racemic (primarily α - and β -) amino acids, in total yield about 1% of the solid. We therefore have a data set involving both gas phase nitriles and solid phase amino acid precursors which is constrained by (and in agreement with) observations of Titan. Consideration of fast free-radical and ion reactions in the framework set by these data suggests a formation scenario and structure for the solid which is consistent with laboratory data and organic chemical principles:

The essence, we propose, of the heteropolymer-chain buildup which results in fast, in-situ production of tholin in the excited gas lies in the ability of R-CN compounds to react rapidly with other unsaturated and radical species; the nitriles themselves form by very fast addition of CN radicals to unsaturated bonds (Lichtin and Lin, 1986). In addition to C-attack on unsaturated species, N-attack on C-radicals and ions is a likely process, analogous to the attachment of R-CN to $R-C^+=NH$ in solution reactions (March, 1964, p. 720). R-CN reaction with protonated nitriles $RCNH^+$ is especially likely; HCNH is produced from $N+CH_3$ and perhaps $N+CH_4$ collisions, and can be both a reaction site and (along with C_2H_3) a hydrogen donor. Once a chain is initiated, alternating -NC-R and -CN attachments produce a structure which can yield α -amino acids upon reduction of an imide bond followed by hydrolysis:



The CN terminus of some R-groups can be hydrolyzed to yield the acidic amino acids, or reduction by H can yield the diamino compounds found in Titan tholin hydrolysate. Similar CN addition to unsaturated side chains in a structure formed by two successive N-terminus attachments can yield β -amino acids.

All the amino acids found by Khare *et al.* (1986) can be explained by reasonable sequences of N-terminus and C-radical attachments, with partial hydrogenation of C=N bonds and addition of CN or CH₂ to multiple bonds. While the process is too complex to expect a one-to-one correspondence, the most abundant α -amino acids in tholin hydrolysate can be readily derived from the five most abundant nitriles; only aspartic acid seems to be an exception. Other than alkene/alkyne and nitrile-derived species, the allene-like CHCN radical, the NCN (carbodiimide) radical and cyanamide/formamidine-derived species may also be important for producing some structures; CHCN addition plus hydrocarbon attack can also produce β -amino acids, whereas formamidine condensations with propynenitrile could produce adenine.

We expect the heteropolymer to be very heterogeneous indeed; the sequence of C or N-attachment and identity of the R groups has a large statistical component, while the overall structure has some regularity derived from thermodynamic stability and the relative abundance of the gas-phase species. We note that α and β -amino acids result from different bonding structures, and emphasize the observation that short chains of α -amino acids (but not β -, etc.) could be formed by hydrolysis of the few segments of successive α -type linkages which are appropriately hydrogenated in the chain. The formation of certain oligomers with a few amino acid units is likely, but long stretches of substituted polyamidine are unlikely both in the gas phase and in aqueous XCN hydrolysis/radiolysis. However some amide-like links should be present (cf. Ferris *et al.*, 1981; McKay *et al.*, 1984; Niketic *et al.*, 1982). Most of the mass is a more general organic heteropolymer.

Our studies suggest mechanisms by which solid organic heteropolymer produced in auroral zones or by surface coronal discharge can yield oxygen-free heteropolymers which produce amino acids and related molecules upon hydrolysis. In quiet aqueous environments, the concentrations of organic molecules will be high near the solid surface, providing ample opportunity for reactions difficult in a dilute environment. While these results have general implications, we note that for Titan, the organic sediment should be tens of meters deep (Sagan and Thompson, 1984), and that it could be exposed to very alkaline H₂O+NH₃ solutions if Titan has or had H₂O+NH₃ volcanism (cf. Hunten *et al.*, 1984) or subduction of organic-sediment-bearing crust to a H₂O+NH₃ mantle.

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