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Amino Acids Derived from Titan Tholins

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An organic heteropolymer (Titan tholin) was produced by continuous dc discharge through a 0.9 N_2/0.1 CH_4 gas mixture at 0.2 mbar pressure, roughly simulating the cloudtop atmosphere of Titan. Treatment of this tholin with 6*N* HCl yielded 16 amino acids by gas chromatography after derivatization to *N*-trifluroacetyl isopropyl esters on two different capillary columns. Identifications were confirmed by GC/MS. Glycine, aspartic acid, and α- and β-alanine were produced in greatest abundance; the total yield of amino acids was $\sim 10^{-2}$, approximately equal to the yield of urea. The presence of "nonbiological" amino acids, the absence of serine, and the fact that the amino acids are racemic within experimental error together indicate that these molecules are not due to microbial or other contamination, but are derived from the tholin. In addition to the HCN, HC_2CN, and $(CN)_2$ found by Voyager, nitriles and aminonitriles should be sought in the Titanian atmosphere and, eventually, amino acids on the surface. These results suggest that episodes of liquid water in the past or future of Titan might lead to major further steps in prebiological organic chemistry on that body. © 1986 Academic Press, Inc.

INTRODUCTION

When cosmically abundant reducing gases are irradiated, a class of dark reddish-brown tarry organic solids are produced, which have been called tholins, a model-independent designation deriving from the Greek word for muddy (Sagan and Khare, 1979; Sagan *et al.*, 1984a). When nitrogen is mixed with 10% methane, or less, and irradiated at low pressures in experiments simulating conditions in the atmosphere of Titan, a category of tholin is produced that seems to resemble closely the reddish aerosol (Smith *et al.*, 1981) which is the most striking characteristic of Titan's atmosphere. The complex refractive index of Titan tholin has been measured from X-ray to microwave frequencies (Khare *et al.*, 1984), and seems able to account for Earth orbital ultraviolet and ground-based visible spectroscopy of the integrated disk of Titan (Sagan *et al.*, 1984b; 1985); Voyager measurements of limb darkening in the visible (Squyres *et al.*, 1984; Thompson *et al.*, 1984); and for the Voyager infrared continuum (Thompson and Sagan, 1984). Nine or-

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ganic molecules ranging in complexity up to butadiyne and propynenitrile have been identified in the gas phase by Voyager infrared spectroscopy (Hanel *et al.,* 1981; Maguire *et al.,* 1981; Kunde *et al.,* 1981). Many of these molecules are produced directly by the irradiation of simulated Titan atmospheres (Balestic, 1974; Toupance *et al.,* 1975; Scattergood *et al.,* 1975; Scattergood and Owen, 1977; Gupta *et al.,* 1981; Raulin *et al.,* 1982). Much more complex organic matter is to be expected in Titan tholins. The detached limb hazes seen by Voyager in the visible, and the high-altitude ultraviolet haze detected by Voyager instruments seem also to require more complex organic molecules (Sagan and Thompson, 1984).

Preliminary pyrolysis/gas chromatography/mass spectrometry (py GC/MS) of Titan tholins reveals more than 75 products, including saturated and unsaturated aliphatic hydrocarbons, substituted polycyclic aromatics, amines, pyrroles, pyrazines, pyridines, pyrimidines, and abundant nitriles (Khare *et al.*, 1985). We recognize that some products may be synthesized during pyrolysis (Irwin, 1981) in a py GC/MS analysis, but argue that many of the products formed are true fragments of the complex organic heteropolymeric material that constitutes Titan tholin (see also Khare *et al.*, 1981; Ogino and Nagy, 1981). The abundance and variety of nitriles ($C{\equiv}N$) in the pyrolysis products, the prominent 4.6-μm nitrile (or isocyanide) absorption feature in the untreated tholin (Khare *et al.*, 1984), and the strong N—H absorption near 3.0 μm in the untreated tholin (Sagan *et al.*, 1984a) naturally raise the question of whether amino acids can be produced from Titan tholin.

The mean density of Titan is 1.88 g cm^{-3}, implying—in conjunction with currently fashionable models of the origin of the solar system—that the interior of Titan contains several tens of percent of water ice (cf. Hunten *et al.*, 1984); some models of the interior structure of Titan propose water ice at the surface and layers of water-containing liquids ~100 km subsurface. Since moons in the outer solar system, including both Ganymede (of roughly the same radius and density as Titan) and the much smaller Enceladus, show clear signs of comparatively recent surface melting, it would be unwise to exclude at least episodic surface melting on Titan. High-temperature tholin–water solution reactions are expected from impact processes. At present production rates, the quantity of tholin accumulated on the surface of Titan over its history amounts to a layer ~100 m thick if only short-wavelength ultraviolet irradiation is employed in the synthetic process, and kilometers thick if longer wavelength photons can also be utilized (Sagan and Thompson, 1984). This material is denser than the putative deep hydrocarbon ocean on Titan (Lunine *et al.*, 1983), and would thus accumulate as a submarine deposit. Thus episodic melting events would subject Titan tholin to liquid water, and solid state convection on Titan may carry tholins down to liquid depths. Hydrolysis of proteins (e.g., Nagy, 1975) and other polymeric substances (e.g., Er *et al.*, 1986) can be accomplished in *either* acidic or basic media and a similar reaction is possible for the heteropolymeric tholins. Under present Titanian conditions, liquid water would form NH_4OH, in which would be dissolved a variety of other organic compounds; a subsurface liquid water–ammonia ocean is considered "conceivable" by Hunten *et al.* (1984).

Finally, somewhat similar tholins synthesized from CH_4/NH_3 gas mixtures (with a few percent H_2O) are known, in aqueous media, to be fully sufficient carbon and nitrogen sources for both aerobic and anaerobic miroorganisms (Boston *et al.*, 1986), and tholin-rich surface deposits on the primitive Earth may have provided an important environment for the origin of life. Accordingly, experiments on amino acid production by acid (or base) treatment of Titan tholin seem relevant on three independent accounts:

(1) for the light they may cast on the composition of Titan tholin;

(2) as relevant to possible episodic water-ice melting events on the surface and solid state convection in the immediate subsurface of Titan; and

(3) as possibly relevant to the primitive Earth and the origin of life in aqueous media.

Synthesis of Titan Tholin

Titan tholin was generated from a gas mixture of 0.9 N_2 and 0.1 CH_4 by volume at a total pressure of 0.2 mbar. This corresponds to a radial distance from the center of Titan of about 2825 km, just at the top of the main cloud deck viewed by Voyagers 1 and 2, and below most of the visible aerosol haze. The solar ultraviolet flux at $\lambda < 900$ Å, Saturn magnetospheric electrons and protons, solar wind electrons, and cosmic rays are all able to break N_2 chemical bonds and synthesize nitrogenous organics from N_2/CH_4 atmosphere (cf. Strobel, 1982); ultraviolet photons at $\lambda < 1450$ Å generate higher hydrocarbons, and longer wavelength photons may be involved in secondary reactions, both those including and those excluding nitrogen (Sagan and Thompson, 1984).

The experimental apparatus essentially consists of two horizontal aluminum electrodes of diameter $\simeq 7.6$ cm, separated by a vertical distance of 5.7 cm, enclosed within a vertical glass cylinder of internal diameter $\simeq 10$ cm. The 0.9 N_2/0.1 CH_4 gas mixture continuously flowed through the 1-liter chamber at a rate $\simeq 0.05$ ml/sec. A 15-mA direct current electrical discharge was maintained by a 200-V potential difference between the electrodes. The tholin products presumably form by quenching and the reaction of the ionization and dissociation products in the region of the discharge, and then diffuse outward, where they are deposited on the inner walls of the vertical glass cylinder. Further details of the experimental setup, the electrode and field configurations, and the source and purity of gases used are given elsewhere (Khare *et al.*, 1984).

Acid Treatment of Titan Tholins

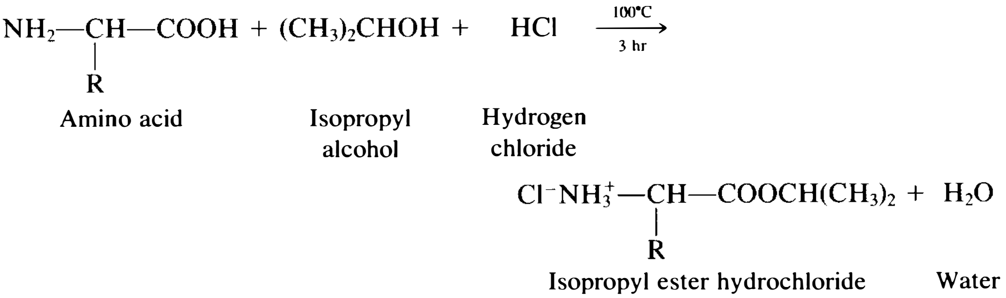
We here describe the techniques used for the acid treatment and analysis by gas chromatography/mass spectrometry (GC/MS) of Titan tholins, following the procedures of Gil-Av (1975), Engel *et al.* (1977), Zumberge *et al.* (1980), and Nagy *et al.* (1981). Tholins deposited on the glass wall of the reaction vessel were scraped off. A 3.9-mg portion of this tholin was placed into a glass tube (Pyrex, 150 mm long × 15 mm internal diameter) with 2 ml of double distilled 6*N* HCl. The glass tube was sealed under N_2 and heated to 100°C for 20 hr, after which the solution was passed through a fine frit glass filter. (All glassware was cleaned prior to use with an 85/15 mixture by volume of hot concentrated H_2SO_4 and HNO_3). Then, the filter was washed repeatedly with triple, glass-distilled H_2O and the filtrate and the washing water were combined. One quarter of this solution was used for the quantitative determination of amino acids, the remainder for the qualitative analysis. A 0.2 μl solution of the amino acid threonine of known concentration was added to the solution to serve as an internal standard for the quantitative analysis. Then the solutions, both for the quantitative and the qualitative analysis, were evaporated to dryness under a stream of N_2.

Ion-Exchange Clean-Up

Cation exchange columns were packed with 5 ml Bio-Rad AG 50W-X8, 50–100 mesh resin, a procedure commonly used to purify amino acids after hydrolysis. Before each sample application, the columns were preconditioned by washing 10 times, repeatedly and consecutively with 50 ml of water, 50 ml of 2*N* NaOH, 50 ml of water, 10 ml of 1.5*N* HCl, 50 ml of 6*N* HCl, and 50 ml of water. Next, the evaporation residues were redissolved in 1 ml of 0.06 *N* HCl and were placed on the cation exchange columns. Then, 30 ml of water, containing three drops of phenolphthalein solution, was added onto the columns. The samples were eluted with 15 ml of 2*N* NH_4OH and were collected at the NH_4OH eluent front. Again, the solutions were evaporated to dryness. The residue contains pure amino acids free from other compounds available on acid treatment of Titan tholin.

Derivatization of Amino Acids to N-Trifluoroacetyl Isopropyl Esters

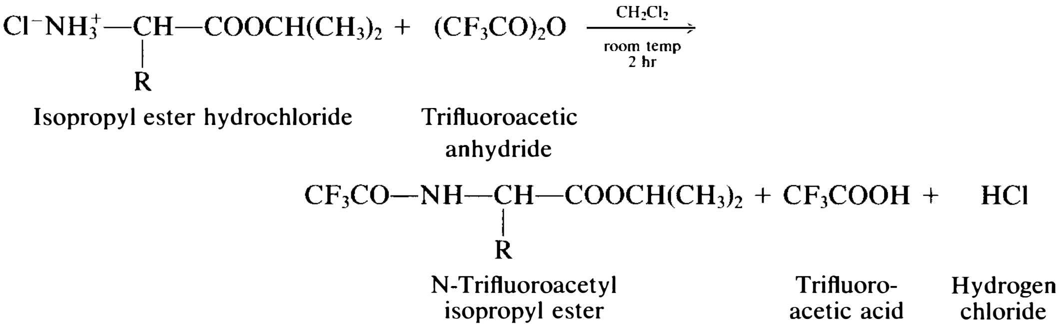
Pure amino acids are nonvolatile and therefore are not suitable for direct GC/MS analysis. Accordingly, we volatilized them by first esterifying the amino acid to isopropyl ester hydrochlorides:



$$\mathrm{NH_2{—}\underset{\substack{|\\ R}}{CH}{—}COOH + (CH_3)_2CHOH + HCl \xrightarrow[3\ hr]{100°C} Cl^-NH_3^+{—}\underset{\substack{|\\ R}}{CH}{—}COOCH(CH_3)_2 + H_2O} \qquad (1)$$

We acidified isopropyl alcohol with dry HCl gas to 3*N*, its normality determined by weight, and then added it to the vial containing dry tholin residue. After the cap on the vial was closed, the samples were heated to 100°C for 3 hr. After this esterification step, the unreacted isopropyl alcohol, hydrogen chloride, and the liberated water were evaporated under a stream of dry nitrogen leaving behind isopropyl ester hydrochloride in the vial.

The second step involved acylation of isopropyl ester hydrochloride with trifluoroacetic anhydride to form volatile *N*-trifluoroacetyl isopropyl esters suitable for GC/MS analysis:



$$\mathrm{Cl^-NH_3^+{—}\underset{\substack{|\\ R}}{CH}{—}COOCH(CH_3)_2 + (CF_3CO)_2O \xrightarrow[\substack{room\ temp\\ 2\ hr}]{CH_2Cl_2} CF_3CO{—}NH{—}\underset{\substack{|\\ R}}{CH}{—}COOCH(CH_3)_2 + CF_3COOH + HCl}$$

We added 0.2 ml of trifluoroacetic anhydride (TFAA) and 2 ml of methylene chloride (CH_2Cl_2) to the evaporated residues to allow the acylation reaction to proceed at room temperature for 2 hr after the cap on the vial was closed. Closing the vial during both esterification and acylation serves to avoid contamination by airborne contaminants and loss of reagent mixture by evaporation.

After acylation, the samples were again evaporated to dryness under nitrogen to remove excess TFAA, CH_2Cl_2, and liberated trifluoroacetic acid and hydrogen chloride, all being more volatile than the N-trifluoroacetyl isopropyl esters. Finally, the

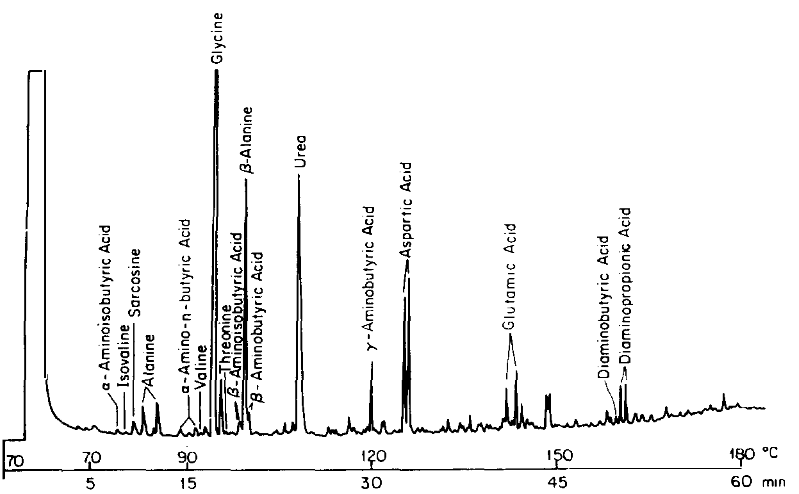


FIG. 1. Amino acids derived from Titan tholin and derivatized as their *N*-trifluoroacetyl isopropyl esters injected on Chirasil-Val 30 m × 0.2 mm i.d. fused quartz capillary column. Carrier gas is helium.

residues left as N-trifluoroacetyl isopropyl esters of amino acids were redissolved in 10–20 μl CH_2Cl_2 to be injected into the GC/MS.

Gas Chromatography/Mass Spectrometry

Initial separation and identification of the amino acids derived from Titan tholin were made using a Hewlett Packard 5880A gas chromatograph fitted with an optically active phase Chirasil-Val 30 m × 0.2 mm i.d. fused quartz capillary column. Aliquots of 0.5 μl volume were injected. Unknown samples were also run on an SP-2100, 50 m × 0.2 mm i.d. fused quartz capillary column. Retention times of the unknown on both columns were compared with standards. Finally, standards were coinjected with the unknowns to confirm the identity of the amino acids. Procedure blanks, encompassing the entire analytical scheme without samples, were handled identically to tholins and examined by quantitative and qualitative analysis.

Finally, mass spectra of the unknowns were obtained using a Varian-MAT 311A gas chromatograph/mass spectrometer under control of a Varian SS-200 data system. Operating conditions of the mass spectrometer were: ionization energy, 70 eV; source temperature, 190°C; interface temperature, 170°C; resolution, 1000; and scan speed, 2.5 sec/decade over the mass range 200–475 daltons with an interscan time of 0.5 sec.

The operating conditions of the coupled gas chromatograph using two different columns were as follows: the first column was a fused silica quartz capillary column 30 m × 0.2 mm i.d. carbowax; the second, a fused silica quartz capillary column 30 m × 0.2 mm i.d., SP-2100. The initial temperature in both cases was 100°C for 15 min followed by a programmed heating at 1°C/min to a final temperature of 190°C. The carrier gas of the column directly coupled to the mass spectrometer was helium with a flow rate maintained at 1 STP cm^3/min.

RESULTS

Figure 1 displays a chromatogram of the derivatized amino acids, obtained from the hydrolysis of Titan tholin, as the *N*-trifluoroacetyl isopropyl esters, on a Chirasil-Val column that contains an optically active phase. The most abundant products on this column as well as on the SP-2100 column are glycine, β-alanine, and aspartic acid. All identified products are tabulated in Table I, where their abundance per gram of

TABLE I

Amino Acids and Urea Identified in Acid-Treated Tholin

	mg/g
Glycine	5.30
Alanine	0.70
α-Amino-*n*-butyric acid	0.10
Valine	t
Threonine	t
Aspartic acid	1.10
Glutamic acid	0.40
β-Alanine	1.20
β-Amino-*n*-butyric acid	0.20
β-Aminoisobutyric acid	0.13
γ-Amino-*n*-butyric acid	0.30
α-Aminoisobutyric acid	0.06
α-Methyl-α-amino-*n*-butyric acid (Isovaline)	t
α,β-Diaminopropionic acid	0.10
α,γ-Diamino-*n*-butyric acid	0.02
N-Methylglycine	0.18
Urea	10.30
Amino acids	9.79
Urea	10.30

Note. t = trace amounts.

initial Titan tholin is shown. The yields by mass of all amino acids and of urea are almost the same, each approximately 10^{-2}.

The Chirasil-Val column permitted the separation of the D and L enantiomers. The D/L ratio of a few well-determined amino acids, produced from hyrolysis of the tholin, are shown in Table II. These values are racemic within experimental error. This fact, together with the presence of "nonbiological" amino acids, the clean procedure blanks, and the absence of the common contaminant serine on either column, indicates that the amino acids are not contaminants from microorganisms or from handling ("fingerprint" amino acids) during tholin synthesis and/or analysis. Threonine, another such indicator, occurred only in trace quantities, permitting the use of threonine as an internal standard for quantitative analysis.

All amino acids listed in Table I are confirmed by their mass spectra on GC/MS. The identification of aspartic and glutamic acids as examples are illustrated in Figs. 2 and 3, where they are compared with standards.

CONCLUSIONS

The tholin produced by irradiation of an N_2/CH_4 atmosphere results in an approximately 1% yield of amino acids on HCl treatment. Very crudely, the yield of amino acids, discussed in this paper, in the acid treatment of Titan tholin is an order of magnitude less than the yield of alkyl nitriles in the pyrolysis of Titan tholin (cf. Khare *et al.*, 1985). The synthesis of amino acids from Titan tholin may involve a mechanism in which some tholin moieties, such as the abundant nitriles, are attacked by free radicals and are converted to aminonitriles; for example, the nitrene radical (NH), produced by high-frequency electrical discharge through N_2 and CH_4, may be inserted into any of the C—H bonds of an alkyl chain (Gilchrist and Rees, 1969) and yield after acid treatment α, β, γ, . . . amino acids after hydrolysis. The present results seem consistent with the conclusion that the reddish Titan aerosols contain the nitrile functional group, and suggest the importance of infrared spectroscopic searches for the 4.6-μm absorption feature. Infrared properties of nitriles more complex than HCN, which are expected to exist freely in the Titanian atmosphere (Sagan and Thompson, 1984; Thompson, *et al.*, 1986)

TABLE II

Stereospecificity of Amino Acids Produced from Acid-Treated Titan Tholins

Amino acid	D/L
Alanine	0.96 ± 0.03
α-Amino-*n*-butyric acid	1.07 ± 0.06
Aspartic acid	0.95 ± 0.04
Diaminopropionic acid	1.00 ± 0.01

Note. Errors represent maximum deviations from the mean in successive trials.

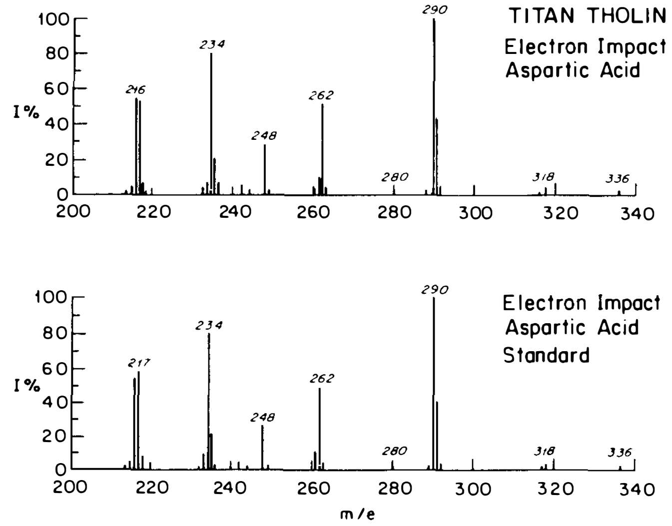


FIG. 2. Mass spectrum of a GC peak identified as the *N*-trifluoroacetyl isopropyl ester of aspartic acid. Sample injected is the derivatized amino acid from Titan tholin. The bottom spectrum is a standard, authentic aspartic acid, similarly derivatized. The ordinate is the intensity, a measure of abundance, normalized to the most prominent peak.

have been tabulated by Cerceau *et al.* (1985). Future Titan entry probes should be capable of detecting aliphatic and aromatic nitriles, including aminonitriles, preferably up to *m/e* ~ 400; landers might be equipped with specific analytic protocols for detecting surface amino acids. Exposure of tholins on the primitive Earth to treatment by acids or bases may have provided a copious source of free amino acids and their poly-

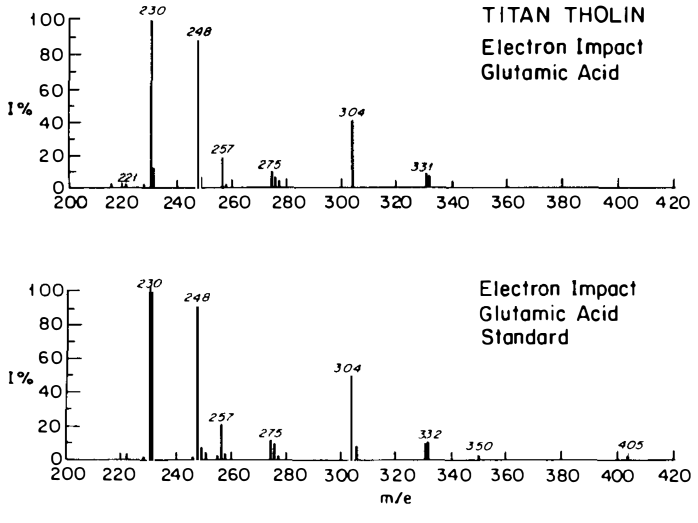


FIG. 3. Mass spectrum of a GC peak identified as the *N*-trifluoroacetyl isopropyl ester of glutamic acid. Sample injected is the derivatized amino acid from Titan tholin. The bottom spectrum is a standard, authentic glutamic acid, similarly derivatized. The ordinate is the intensity, a measure of abundance, normalized to the most prominent peak.

mers and, thereby, a significant source via an indirect route (besides direct Strecker synthesis from free aminonitriles) of building blocks for the origin of life. While life on Titan is hardly to be expected at an ambient surface temperature of 95°K, episodic melting events, endogenous or exogenous, and solid state convection may have led to important further organic synthetic steps on Titan, beyond the generation of the tholins themselves. Several times 10^9 years from now, standard theories of solar evolution predict that the Sun will enter its red giant stage, and for $\sim 10^8$ years or more the surface temperature on Titan should be above the freezing point of water. In this remote era, surface liquid water (probably containing NH_4OH) may be abundant, and chemical evolution on Titan (until now frozen at what for the Earth would be a comparatively early stage) is then likely to take further steps.

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