

Organic Solids Produced by Electrical Discharge in Reducing Atmospheres: Tholin Molecular Analysis

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Received September 5, 1979; revised August 27, 1981

The complex dark brown solid of a class called tholins, produced on passage of an electrical discharge through a roughly equimolar mixture of methane and ammonia with 2.6% water vapor, is analyzed by vacuum pyrolysis followed by gas chromatography and mass spectrometry. Pyrolyzates include a wide range of aliphatic and aromatic nitriles, alkanes, alkenes, aromatic hydrocarbons, pyrrole, and pyridine. This tholin is remarkably stable to 950°C. It and its degradation products are candidate constituents of planetary aerosols in the outer solar system and of the grains in the interstellar medium.

Voyager 1 (Hanel *et al.*, 1980) has confirmed previous inferences (Sagan, 1971; Khare and Sagan, 1973; Sagan, 1974) that the reddish clouds of Titan are composed, at least in part, of complex organic molecules. This establishes that such clouds can exist, and renews interest in the possibility that some of the chromophores in the clouds of Jupiter and Saturn are also organic (Sagan, 1961; Sagan *et al.*, 1967; Khare and Sagan, 1971; for a recent discussion, see Sagan and Salpeter, 1976). The experimental production from N₂/CH₄ atmospheres of simulated Titanian clouds, and their physical and chemical properties, are discussed elsewhere; here we treat the organic solids produced in CH₄/NH₃ atmospheres with a small admixture of water

vapor. Except for the variable H₂ abundance from object to object, such gas mixtures may be relevant to the contemporary atmospheres of the Jovian planets, to the primitive atmospheres of the terrestrial planets, including the Earth, and to Titan. (As long as significant ammonia outgassing continues, NH₃ will maintain some steady-state abundance in a reducing atmosphere despite its rapid uv photolysis.) In addition, organic solids produced from such gas mixtures may be relevant to the interstellar grains and gas (Sagan and Khare, 1979).

In Miller's (1953) original experiment on sparking reducing atmospheres simulating the primitive environment of the Earth, a brown solid was observed to collect on the tungsten electrodes. While α amino and hydroxy acids, and a range of other organic molecules, have been produced in this and similar experiments (Miller and Orgel, 1974), the brown organic residue, sometimes called "intractable polymer," has proved more difficult to analyze. We have

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reported some progress in characterizing this residue, and have proposed the generic name "tholins" (from the Greek for tar) for all such materials (e.g., Sagan and Khare, 1979). The spark tholins discussed here are produced, following Miller's original method, by electrical discharge. Somewhat similar uv-produced tholins have been described elsewhere (Khare and Sagan, 1973, 1975; Khare *et al.*, 1978). The dissociation of precursor molecules in the laboratory electrical discharge and the quenching of the products at much lower temperatures may simulate on a faster time scale a Jovian disequilibrium convection chemistry in which the energy source is not electrical discharge, but short-wavelength ultraviolet light (Sagan and Salpeter, 1976) or charged-particle leakage from the Jovian Van Allen belts. Energetic lightning discharges have been identified in the Jovian atmosphere by Voyager 1 (Smith *et al.*, 1979), providing a still more direct relevance of these experiments to the chemistry of planetary atmospheres—although the total energy avail-

able from Jovian lightning is still significantly less than is available from other sources, especially solar uv (Lewis, 1980). The $\text{CH}_4/\text{NH}_3/\text{H}_2\text{O}$ spark tholins discussed here also provide an important standard against which to compare the (presumably simpler) CH_4/N_2 spark tholins which simulate the Titanian clouds.

The experimental apparatus (Fig. 1) was used to spark, with eight pairs of tungsten electrodes, an approximately equimolar mixture of methane and ammonia with a small quantity of water vapor; presparking conditions were STP. In a typical experiment, a Pyrex flask is connected to the sparking vessel with a combined total volume of 13.326 liters and filled with methane, ammonia, and water vapor at respective volume mixing ratios of 51.5 ± 3.0 , 45.9 ± 3.6 , and $2.6 \pm 0.8\%$. The gases were transferred by a three-stage mercury diffusion pump in tandem with a mechanical pump, capable of producing a vacuum less than 10^{-6} Torr. Matheson anhydrous ammonia and research purity methane, both at

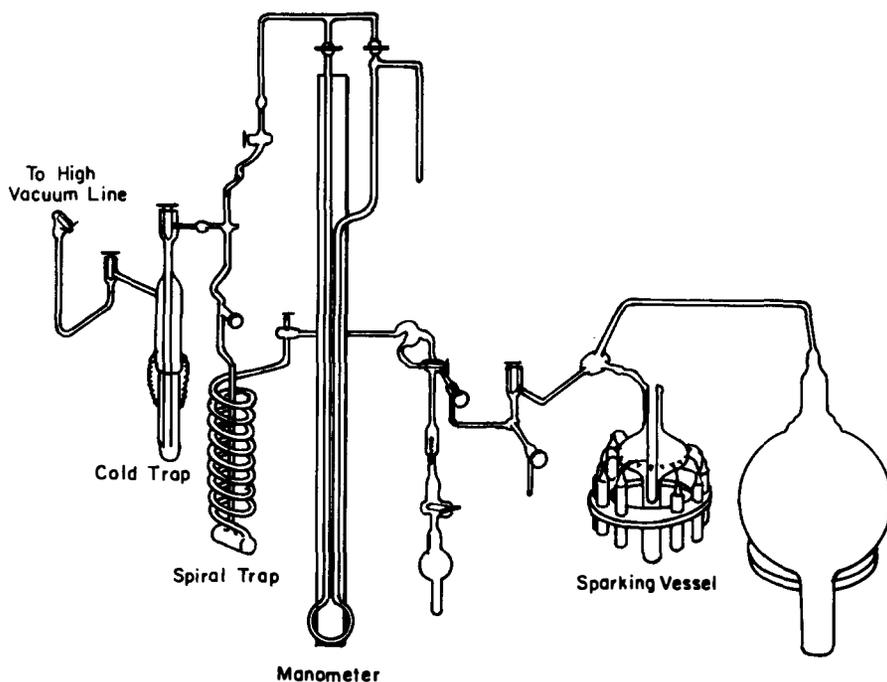


FIG. 1. Experimental apparatus.

99.99% minimum purity, were separately purified further by low-temperature vacuum distillation, down to -196°C , until they were found tensometrically homogeneous. Methane and ammonia were initially transferred into the sparking vessel through a low-temperature spiral trap. Teflon stopcocks were used. Distilled water was first boiled for 15 min. then cooled to 77°K and pumped under high vacuum (10^{-5} mm Hg). After attaining room temperature it was again cooled to 77°K and pumped. This process was repeated three times to remove

any dissolved air before the water vapor was introduced into the reaction vessel. No liquid water was introduced. The high frequency Tesla coils employed are BD-20 and BD-10, made by Electro-technic Products (Chicago), supplying approximately 50 kV at 4 to 5 MHz, and 40 to 50 kV at 3 to 4 MHz, respectively. Spark length for each of the eight pairs of electrodes was approximately 0.6 cm; they were operated according to a sequential program, no adjacent coils operating at the same time.

After several hours of sparking, the reac-

TABLE I
THOLIN PYROLYZATES FROM SPARK-DISCHARGE SYNTHESIS EXPERIMENTS (CH_4 , NH_3 , H_2O MIXTURE)^a: SEQUENTIAL PYROLYSIS AT 150, 300, 450, AND 600°C ^b

Compounds identified		Compounds identified		Mol. wt.
150°C		450°C		
Carbon dioxide	M	Carbon dioxide	M	44
Hydrogen cyanide	M	Hydrogen cyanide	M	27
Ammonia	M	Ammonia	M	17
Butadiene	m	Ethane	M	30
Acetic acid	m	Butane	m	58
Acetonitrile	M	Pentane	m	72
Acrylonitrile	M	Butene	M	56
Succinonitrile	m	Pentene	m	70
Benzonitrile	m	Toluene	m	92
		Xylene	m	106
300°C		C_3 -Alkylbenzene	m	120
Carbon dioxide	M	C_2 -Alkylindane	m, t	146
Hydrogen cyanide	M	Methylindene	m, t	130
Ammonia	M	Acetonitrile	M	41
Ethane	M	Propanenitrile	M	55
Propene	M	Pentanenitrile	m	83
Butene	m	Acrylonitrile	M	53
Acetonitrile	M	Succinonitrile	m	80
Propanenitrile	M	Benzonitrile	m	103
Acrylonitrile	m	Tolunitrile	m	117
Succinonitrile	m	Indole	m, t	117
Benzonitrile	m			
		600°C		
		Carbon dioxide	M	44
		Hydrogen cyanide	M	27
		Ammonia	M	17
		Ethane	M	30
		Acetonitrile	M	41
		Acrylonitrile	m	53
		Benzonitrile	m	103

Note. M = major component, m = minor component, t = tentative identification.

^a CH_4 = 51.5%, NH_3 = 45.9%, H_2O = 2.6%.

^b ~25 mg of tholin pyrolyzed.

tion vessel became covered with hundreds of brown spots 1 to 2 mm in diameter, with comparable interspot spacings, somewhat resembling measles. Colors were a deep, dark brown, with no hint of yellows or reds. (The visible spectrum of this tholin is displayed in Khare *et al.*, 1981). Interspot regions were initially fairly transparent; but after several weeks of sparking a uniform film of the tholin completely covered the interior walls of the sparking vessel. The discharge was terminated after 35 days, at which time the interior pressure increment was 0.3 bar larger than at 0 hr. No substantial variation in pressure occurred when cold fingers on the main flask and sparking vessel were brought to liquid N₂ tempera-

tures; this indicates evolution of such gases as H₂, N₂, and CO, all of which are indeed confirmed by high-resolution mass spectroscopy. At the end of the experiment all gases were pumped out, the reaction vessel opened and the tholin subjected to a range of analyses, including mass spectroscopy, thermogravimetric analysis, and combined vacuum pyrolysis gas chromatography/mass spectroscopy (GC/MS). High-vacuum pyrolysis was carried out on a 25-mg sample of the polymer which had been degassed at high vacuum and room temperature to remove most of the adsorbed gases. The products were trapped at liquid N₂ temperatures and then injected directly into a GC which in turn

TABLE II

THOLIN PYROLYZATES FROM SPARK-DISCHARGE SYNTHESIS EXPERIMENTS (CH₄, NH₃, H₂O MIXTURE)^a:
NONSEQUENTIAL PYROLYSIS AT 600°C^b

Compounds identified		Compounds identified		Mol. wt.
Carbon dioxide	M	<i>Nitrogenous compounds</i>		
<i>Hydrocarbons</i>		Hydrogen cyanide	M	27
Ethane	M	Ammonia	M	17
Propane	M	Acetonitrile	M	41
Butane	M	Propanenitrile	M	55
Ethene	M	2-Methylpropanenitrile	M	69
Propene	M	Butanenitrile	M	69
Butene	M	Pentanenitrile	M	83
C ₃ -Alkene	m	C ₆ -Alkyl nitrile	m, t	97
Butadiene	m	Acrylonitrile	m	53
C ₇ -Diunsaturated hydrocarbon	m	Butenenitrile or methacrylonitrile	M	67
Toluene	m	Pentenenitrile	m	81
Ethylbenzene	m	Succinonitrile	M	80
Xylene	m	Glutaronitrile	M	94
Trimethylbenzene	m	<i>N,N</i> -Dimethylamino-ethanenitrile	m	84
C ₄ -Alkylbenzene	m	Benzonitrile	m	103
Indane or methylstyrene	m	Tolunitriles	M	117
Indene	m	Pyrrole	M	67
Methylindene	m	Pyridine	m	79
Naphthalene		Methylpyridine	m	93
		C ₂ -Alkylpyridines	m	107
		Methylethylpyrazine	m, t	122

Note. M = major component, m = minor component, t = tentative identification.

^a CH₄ = 51.5%, NH₃ = 45.9%, H₂O = 2.6%.

^b 50 mg of tholin pyrolyzed.

was directly connected through a heated transfer line and a Watson-Biemann separator to a Hitachi RMU-6E medium-resolution mass spectrometer. The tholin product, now pyrolyzed at 150°C, was then returned to room temperature, heated to 300°C, its pyrolysis products trapped at liquid N₂ temperatures, and then again transferred directly to the GC/MS system. Such sequential pyrolysis was continued at 450 and 600°C; and 50 mg of sample subjected to a single high-temperature pyrolysis at 600°C as well. The analysis of the pyrolysis products was achieved using a Perkin-Elmer 226 GC equipped with a 150' × 0.02" i.d. OS 138-polyphenylether/SCOT (Support Coated Open Tubular) capillary column. The GC was programmed from 40 to 190°C at 2.5°C min⁻¹ after an initial 10-min period at 40°C. Five-second mass scans were taken of each peak as it emerged from the gas chromatograph. Details of the pyrolysis apparatus and process are described by Bandurski and Nagy (1976). The polymer was also studied less sensitively in the temperature range 22–500°C on an AEI MS-902 double-focusing MS using a direct insertion probe.

Low sensitivity direct-insertion mass spectrometry showed as principal pyrolysis products H₂, CO₂, HCN, CH₃CN, and CH₃CHO. These nitriles and aldehydes had originally been detected in the gas phase of the original experiment by Sagan and Miller (1960; see also Khare and Sagan, 1971). The pyrolytic GC/MS approach improves the detection sensitivity over direct-probe insertion by a factor of >10, and is one method of choice when, as in the present case, the material is of highly complex composition, has a very low vapor pressure, and resists standard derivatization procedures. Although the pyrolyzate was separated by GC prior to MS, analysis of individual GC peaks indicates many are mixtures of two or more compounds, as has been found for complex soluble products in previous experiments on prebiological organic chemistry. The identifications re-

ported here are based both on the principal MS peaks and on the GC retention times. There is a tendency for polar compounds to be adsorbed in the analytic system and produce spectral overlap. We have also confirmed some 75% of the pyrolysis products by the ADP mass spectra computer search system at the University of Michigan.

The compounds released at various temperatures during the sequential vacuum pyrolyses are given in Table I. This table indicates that some, if not all, of the nitrogen-containing compounds released at 150 and 300°C, such as acetonitrile, acrylonitrile, and benzonitrile, are less tightly bound in the polymer than the majority of hydrocarbons which were not released until 450°C. Also, there is a dearth of oxygen compounds, reflecting the low abundance of initial H₂O; yet CO₂ is a major product at all pyrolysis temperatures, perhaps indicative of carboxylic acids.

Results of the nonsequential pyrolysis at 600°C is given in Table II. As this pyrolysis was conducted with a larger quantity of polymer and at the maximum temperature, it confirmed the sequential pyrolysis results and helped to identify a greater and more diverse suite of components. We obtained, by both types of pyrolyses, series of homologous compounds entirely typical of abiological syntheses. The various results suggest that the spark tholin has a relatively stable matrix which consists, at least in part, of nitrogenous compounds, and probably also of hydrocarbons. Additional nitrogenous components are attached to this matrix through highly varied bonding energies.

The pyrolyzates of the uv tholin produced in CH₄/C₂H₆/NH₃/H₂O experiments with H₂S as the photon acceptor (Khare *et al.*, 1978) contain alkanes, alkenes, and alkyldisulphides up to C₇. A rather similar list of saturated and unsaturated aliphatic hydrocarbons up to C₇ emerges from the present spark discharge experiment. Simple and substituted aromatic hydrocarbons

are found in both experiments. Thiophenes, mercaptans, disulphides, and C=S compounds found in the uv tholins are, of course, not present in the sulfur-free spark tholins. The variety and nature of the nitrogenous compounds found in the spark experiments is striking.

The pyrolyzates of the spark tholin consist of at least 15 aliphatic and aromatic nitriles, pyrrole, short-chain ($\leq C_4$) aliphatic hydrocarbons, and small quantities of aromatic hydrocarbons. This suite of products can also be derived from the pyrolysis of a polymer consisting basically of amino acids and/or polypeptides (Merritt and Robinson, 1967; Simmonds *et al.*, 1969; Nagy *et al.*, 1977), and a variety of amino acids have been identified in tholins upon water or acid hydrolysis (Sagan and Khare, 1971). However, other nitrogen-containing polymers also give rise to nitriles upon pyrolysis. The spark tholin conceivably contains a heteropolypeptide formed from HCN-H₂O polymerization (Matthews *et al.*, 1977), and/or a polynitrile (Miller and Orgel, 1974), each containing hydrocarbon moieties. Simple nitriles have been detected in the atmospheres of Jupiter (Tokunaga *et al.*, 1981) and Titan (Hanel *et al.*, 1980).

The necessity to pyrolyze the tholins before GC/MS analysis raises the possibility that some products reported here were synthesized during pyrolysis, rather than being derived from an original tholin heteropolymer. However, since the effective temperatures of the corona discharge used to synthesize the spark tholin are much higher than the pyrolysis temperatures, such quenched thermodynamic equilibrium synthetic reactions have already occurred, independent of the analytic method. In addition, control experiments on the vacuum pyrolysis and subsequent GC/MS of polyethylene and polystyrene polymers show considerably fewer secondary reaction products than competing methods which utilize, e.g., flash or Curie point pyrolyses (Ogino and Nagy, 1981). In particular, vac-

uum pyrolysis at moderate temperatures and carefully selected durations is a significantly less extreme analytic procedure than flash or other pyrolyses at high temperatures. More important, microanalytic pyrolysis methods may be inapplicable to presumptive heteropolymers like tholins because of the chemical heterogeneity of the sample (*ibid.*).

Thermogravimetric analyses, performed in a nitrogen atmosphere on a Dupont Model 951 Thermogravimetric Analyzer, for both the ultraviolet sulfur-rich tholin (Khare *et al.*, 1978) and the spark sulfur-free tholin of the present experiment are shown in Fig. 2. The weight loss derivative near 200°C was so steep for the uv tholin that the experiment was terminated at that temperature for fear of contaminating the thermogravimetric analyzer. The spark tholin, on the other hand, exhibits remarkable thermal stability, being only half-dissociated at 950°C. Tholins of the sort described in this experiment, therefore, can plausibly have been ejected from high-temperature circumstellar clouds during the Hayashi phase of early stellar evolution, or after the red giant stage of late stellar evolution, and survived to interstellar space. The infrared absorption, spallation products, and other

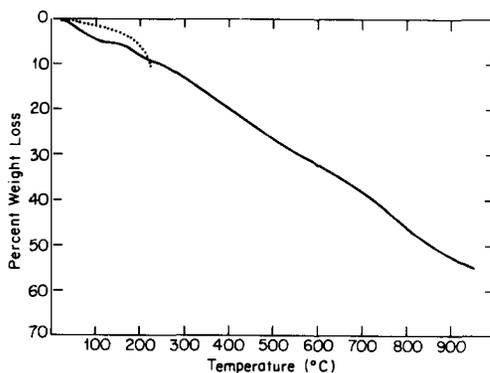


FIG. 2. Thermogravimetric analysis of (i) dark brown spark tholin produced by electric discharge through CH₄, NH₃, and H₂O (vapor)—solid line; and (ii) sulfur-free extract of brown uv tholin produced by photolysis of CH₄, C₂H₆, NH₃, H₂O, and H₂S—dotted line. The curves show weight loss of material as a function of temperature.

properties of this material seem to match astronomical observations of the interstellar medium; and we propose that the tholin described in this paper may be quite similar to a principal constituent of the interstellar grains (Sagan and Khare, 1979).

We have here reported only the tholin pyrolyzates, not the full tholin structure, which must be extremely complex. However, thermal and radiation degradation of the material is likely to make some of the molecules reported in Tables I and II accessible, both in the atmospheres of Jupiter and Saturn and in the interstellar medium, to appropriate spectral analysis. Temperatures of 950°C are reached on Jupiter at pressures of hundreds of bars; the characteristic circulation time to the 1- to 0.1-bar level, where spectroscopic observations can be made, is roughly a year (Sagan and Salpeter, 1976). If such material exists on Jupiter, produced by short solar ultraviolet radiation, Van Allen belt leakage, or electrical discharge, its high-vapor-pressure pyrolysis products should be circulated to the high atmosphere where they may be subject to spectroscopic or direct Galileo spacecraft entry probe identification. Comparable searches for these pyrolyzates in interstellar grains can be made by infrared and microwave spectroscopy of the interstellar medium.

ACKNOWLEDGMENTS

This research was supported by the Planetary Biology program of the National Aeronautics and Space Administration under Grants NGR 33-010-101 and NGR 03-002-171. We are indebted to Robert Weaver for help with the thermogravimetric analysis and to Eric L. Bandurski for assistance during the mass spectrometric scans.

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