

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23814380>

# Organic solids produced by electrical discharges in reducing atmospheres: Molecular analysis

Article · October 1978

Source: NTRS

CITATIONS

9

READS

28

5 authors, including:



[John Zumberge](#)

GeoMark Research

135 PUBLICATIONS 3,104 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



South Atlantic Margin Petroleum Systems [View project](#)



Head of Geophysics department [View project](#)

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

B. N. KHARE AND CARL SAGAN

*Laboratory for Planetary Studies, Cornell University, Ithaca, New York 14853*

AND

JOHN E. ZUMBERGE,<sup>1</sup> DEBORAH S. SKLAREW,<sup>2</sup> AND BARTHOLOMEW NAGY

*Laboratory of Organic Geochemistry, Department of Geosciences, The University of Arizona, Tucson, Arizona 85721*

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 N<sub>2</sub>/CH<sub>4</sub> atmospheres of simulated Titanian clouds, and their physical and chemical properties, are discussed elsewhere; here we treat the organic solids produced in CH<sub>4</sub>/NH<sub>3</sub> atmospheres with a small admixture of water

vapor. Except for the variable H<sub>2</sub> 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, NH<sub>3</sub> 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  $\alpha$  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

<sup>1</sup> Present address: Cities Service Co., Energy Resources Group, Exploration and Production Research, Box 50408, Tulsa, Okla. 74150.

<sup>2</sup> Present address: Battelle Pacific Northwest Laboratories, Building 329, Post Office Box 999, Richland, Wash. 99352.

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)  $\text{CH}_4/\text{N}_2$  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  $51.5 \pm 3.0$ ,  $45.9 \pm 3.6$ , 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

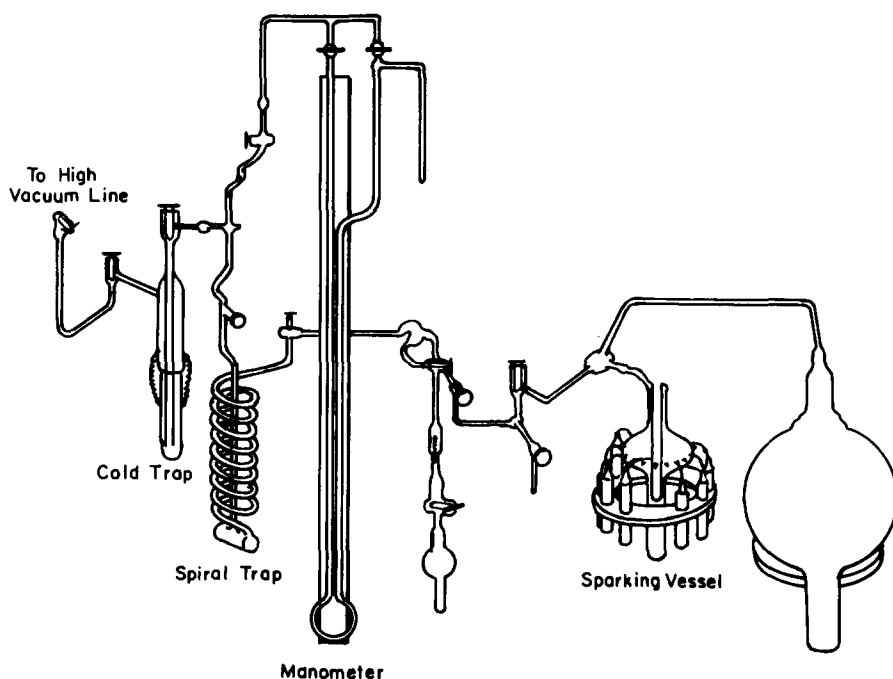


FIG. 1. Experimental apparatus.

99.99% minimum purity, were separately purified further by low-temperature vacuum distillation, down to  $-196^{\circ}\text{C}$ , 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  $77^{\circ}\text{K}$  and pumped under high vacuum ( $10^{-5}$  mm Hg). After attaining room temperature it was again cooled to  $77^{\circ}\text{K}$  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 ( $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  MIXTURE)<sup>a</sup>: SEQUENTIAL PYROLYSIS AT 150, 300, 450, AND  $600^{\circ}\text{C}$ <sup>b</sup>

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		$\text{C}_3$ -Alkylbenzene	m	120
Carbon dioxide	M	$\text{C}_2$ -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.

<sup>a</sup>  $\text{CH}_4$  = 51.5%,  $\text{NH}_3$  = 45.9%,  $\text{H}_2\text{O}$  = 2.6%.

<sup>b</sup> ~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 N<sub>2</sub> tempera-

tures; this indicates evolution of such gases as H<sub>2</sub>, N<sub>2</sub>, 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 N<sub>2</sub> temperatures and then injected directly into a GC which in turn

TABLE II

THOLIN PYROLYZATES FROM SPARK-DISCHARGE SYNTHESIS EXPERIMENTS (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O MIXTURE)<sup>a</sup>:  
NONSEQUENTIAL PYROLYSIS AT 600°C<sup>b</sup>

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

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

<sup>a</sup> CH<sub>4</sub> = 51.5%, NH<sub>3</sub> = 45.9%, H<sub>2</sub>O = 2.6%.

<sup>b</sup> 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 N<sub>2</sub> 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<sup>-1</sup> 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 H<sub>2</sub>, CO<sub>2</sub>, HCN, CH<sub>3</sub>CN, and CH<sub>3</sub>CHO. 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 H<sub>2</sub>O; yet CO<sub>2</sub> 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 CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/NH<sub>3</sub>/H<sub>2</sub>O experiments with H<sub>2</sub>S as the photon acceptor (Khare *et al.*, 1978) contain alkanes, alkenes, and alkyldisulphides up to C<sub>7</sub>. A rather similar list of saturated and unsaturated aliphatic hydrocarbons up to C<sub>7</sub> 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  $HCN-H_2O$  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  $200^\circ C$  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  $950^\circ C$ . 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

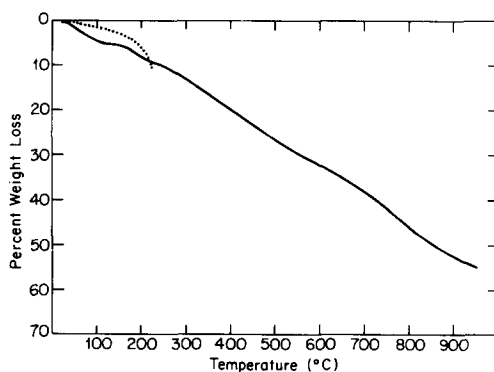


FIG. 2. Thermogravimetric analysis of (i) dark brown spark tholin produced by electric discharge through  $CH_4$ ,  $NH_3$ , and  $H_2O$  (vapor)—solid line; and (ii) sulfur-free extract of brown uv tholin produced by photolysis of  $CH_4$ ,  $C_2H_6$ ,  $NH_3$ ,  $H_2O$ , and  $H_2S$ —dotted line. The 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.

#### REFERENCES

- BANDURSKI, E. L., AND NAGY, B. (1976). The polymer-like organic material in the Orgueil Meteorite. *Geochim. Cosmochim. Acta* **40**, 1397-1406.
- HANEL, R., CONRATH, B., FLASAR, M., KUNDE, V., MAGUIRE, W., PEARL, J., PIRRAGLIA, J., SAMUELSON, R., HERATH, L., ALLISON, M., CRUIKSHANK, D., GAUTIER, D., GIERASCH, P., HORN, L., KOPPANY, R., AND PONNAMPERUMA, C. (1981). Infrared observations of the Saturnian system from Voyager 1. *Science* **212**, 192-201.
- KHARE, B. N., AND SAGAN, C. (1971). Experimental jovian photochemistry: Initial results. *Astrophys. J.* **168**, 563-570.
- KHARE, B. N., AND SAGAN, C. (1973). Red clouds in reducing atmospheres. *Icarus* **20**, 311-321.
- KHARE, B. N., AND SAGAN, C. (1975). Cyclic octatomic sulfur: A possible infrared and visible chromophore in the clouds of Jupiter. *Science* **189**, 722-723.
- KHARE, B. N., SAGAN, C., BANDURSKI, E. L., AND NAGY, B. (1978). Ultraviolet-photoproducted organic solids synthesized under simulated jovian conditions: Molecular analysis. *Science* **199**, 1199-1201.
- KHARE, B. N., SAGAN, C., AND GRADIE, J. (1981). Reflection spectra of simulated Titan organic clouds. *Bull. Amer. Astron. Soc.* **13**, 701.
- MATTHEWS, C., NELSON, J., VARMA, P., AND MINARD, R. (1977). Deuterolysis of amino acid precursors: Evidence for hydrogen cyanide polymers as protein ancestors. *Science* **198**, 622-624.
- MERRITT, C., AND ROBERTSON, D. (1967). The analysis of proteins, peptides and amino acids by pyrolysis-gas chromatography and mass spectrometry. *J. Gas Chromat.* **5**, 96-98.
- MILLER, S. L. (1953). A production of amino acids under possible primitive Earth conditions. *Science* **117**, 528-529.
- MILLER, S. L., AND ORGEL, L. E. (1974). *The Origins of Life on the Earth*. Prentice-Hall, Englewood Cliffs, N.J.
- NAGY, B., NAGY, L. A., ZUMBERGE, J. E., SKLAREW, D. S., AND ANDERSON, P. (1977). Indications of a biological and biochemical evolutionary trend during the Archean and early Proterozoic. *Precambrian Res.* **5**, 109-120.
- OGINO, H., AND NAGY, B. (1981). Pyrolysis of Transvaal kerogens. II. An evaluation of vacuum pyrolysis with polyethylene, polystyrene and their mixtures with minerals. *Precambrian Res.* **15**, 113-130.
- SAGAN, C. (1961). On the origin and planetary distribution of life. *Radiat. Res.* **15**, 174-192.
- SAGAN, C. (1971). The solar system beyond Mars: An exobiological survey. *Space Sci. Rev.* **11**, 73-112.
- SAGAN, C. (1974). Organic chemistry in the atmosphere of Titan. In *The Atmosphere of Titan* (D. Hunten, Ed.) pp. 134-142. NASA Special Publication SP-340. Washington, D.C., U.S. Gov't. Printing Office.
- SAGAN, C., AND KHARE, B. N. (1971). Long wavelength ultraviolet photoproduction of amino acids on the primitive Earth. *Science* **173**, 417-420.
- SAGAN, C., AND KHARE, B. N. (1979). Tholins: Organic chemistry of interstellar grains and gas. *Nature* **277**, 102-107.
- SAGAN, C., AND MILLER, S. L. (1960). Molecular



- synthesis in simulated reducing planetary atmospheres. *Astron. J.* **65**, 499. (Abstract)
- SAGAN, C., AND SALPETER, E. E. (1976). Particles, environments, and hypothetical ecologies in the jovian atmosphere. *Astrophys. J. Suppl.* **32**, 737-755.
- SAGAN, C., DAYHOFF, M. O., LIPPINCOTT, E. R., AND ECK, R. (1967). Organic molecules and the coloration of Jupiter. *Nature* **213**, 273-274.
- SIMMONDS, P., SCHULMAN, G., AND STEMBRIDGE, C. (1969). Organic analysis by pyrolysis-gas chromatography-mass spectrometry: A candidate experiment for the biological exploration of Mars. *J. Chromat.* **7**, 36-41.
- SMITH, B. A., SODERBLOM, L. A., JOHNSON, T. V., INGERSOLL, A. P., COLLINS, S. A., SHOEMAKER, E. M., HUNT, G. E., MASURSKY, H., CARR, M. H., DAVIES, M. E., COOK, II, A. F., BOYCE, J., DANIELSON, G. E., OWEN, T., SAGAN, C., BEEBE, R. F., VEVERKA, J., STROM, R. G., MCCAULEY, J. F., MORRISON, D., BRIGGS, G. A., SUOMI, V. E. (1979). The Jupiter system through the eyes of Voyager I. *Science* **204**, 951-972.
- TOKUNAGA, A. T., BECK, S. C., GEBALLE, T. R., LACY, J. H., AND SERABYN, E. (1981). The detection of HCN on Jupiter. *Icarus* **48**, 283-289.