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EXO BIOLOGY AND THE ORIGIN OF LIFE
October 1, 1977 - September 30, 1978

Principal Investigator: Professor Carl Sagan

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Carl Sagan
Principal Investigator

Appendix I

The following is a list of papers published or in press or completed since the last annual report and supported wholly or in part by NASA Grant NGR 33-010-101.

(1) "Ultraviolet-Photoproduced Organic Solids Synthesized Under Simulated Jovian Conditions: Molecular Analysis," B.N. Khare, Carl Sagan, Eric L. Bandurski, and Bartholomew Nagy, Science, 199, pp. 1199-1201 (1978).

In an earlier paper, Khare and Sagan reported the production of a brownish polymeric material from the near-ultraviolet irradiation of simulated jovian atmospheres with a low hydrogen abundance. Examination of this product indicates that hydrogen sulfide is the initial photon acceptor: the powder resulting after extraction with benzene is 84 percent sulfur, largely S₈. In results reported here, the remaining 16 percent was pyrolyzed and then examined by gas chromatography-mass spectrometry. Pyrolysis at 450°C yielded a series of alkanes, alkenes, C₃-alkylbenzenes, aromatics, thiophenes, alkylthiophenes, alkylmercaptans, alkyldisulfides, together with the nitrogenous compounds hydrogen cyanide, methyl cyanide, alkylisothiocyanates, acrylonitrile, and allylisothiocyanates. Some of these compounds might be sought on Jupiter and Saturn and their satellites by remote infrared and ultraviolet spectroscopy and directly by entry probes.

(2) "Organic Solids Produced by Electrical Discharges in Reducing Atmospheres: Molecular Analysis," B.N. Khare, Carl Sagan, John E. Zumberge, Deborah Sklarew, and Bartholomew Nagy, submitted to Science (1978).

The complex brown polymer produced on passage of an electrical discharge through a mixture of methane, ammonia, and water, is analyzed by pyrolytic GC/MS. Pyrolyzates include a wide range of alkanes, alkenes, aromatic hydrocarbons, aliphatic and aromatic nitriles, pyrroles, and pyridine. Similar pyrolyzates are obtained from polypeptides and polynucleotides with hydrocarbon moieties. This polymer is remarkably stable up to 950°C; its degradation products are candidate constituents of planetary aerosols in the outer solar system and the grains and gas in the interstellar medium.

(3) "Organic Chemistry of Interstellar Grains," Carl Sagan and B.N. Khare, submitted to Nature (1978).

A complex organic polymer produced by electrical discharge or ultraviolet irradiation in a mixture of cosmically abundant reducing gases exhibits an infrared spectrum, thermoradiation stability, and other properties characteristic of interstellar grains. Sputtering products of this polymer bear a close resemblance to the molecules found by microwave spectroscopy in the interstellar medium.

(4) "Spectra of Possible Organic Solids Present as Aerosols in Planetary Atmospheres," B.N. Khare and Carl Sagan, Icarus, to be submitted.

Ultraviolet, visible and infrared transmission spectra are presented of a variety of organic solids produced by ultraviolet irradiation or electrical discharge of gas mixtures containing some or all of the following constituents: CH_4 , C_2H_6 , NH_3 , H_2O , and H_2S . Scanning electron micrographs of these products are also presented, permitting an assessment of Mie theory scattering protocols for spherical particles used in the application of these spectra to planetary atmospheres. The general character of absorption features is remarkably independent of the energy source used to produce free radicals, and it is clear that substantial blue and ultraviolet absorption is provided by sulfur-free organic polymer.

(5) "Far Infrared Studies of Organic Polymers of Possible Astrophysical Interest," B.N. Khare and Carl Sagan, Astrophys. J., to be submitted.

Complex organic polymers produced from cosmically abundant molecules exhibit far infrared absorption features in the 45 to 90 μm range. Hexamethylenetetramine which forms stoichiometrically from formaldehyde and ammonia has such a feature at 86 μm . Orthorhombic sulfur absorbs at 52 μm . It is proposed that absorption and emission

features found in a variety of astrophysical sources at these wavelengths, and often attributed to O III, be reconsidered in the light of these findings.

(6) "Organic Dust Synthesized in Reducing Environments by Ultraviolet Radiation or Electric Discharge," B.N. Khare and Carl Sagan, Proc. Conf. on Thermodynamics of Dust in the Space Medium, Lunar and Planetary Science Institute, in press.

A dark reddish-brown high molecular weight polymer is produced by long wavelength ultraviolet irradiation of abundant gases present in reducing atmospheres, CH_4 , C_2H_6 , NH_3 , H_2O , and H_2S . The photodissociation of H_2S yields a hydrogen atom which is superthermal by several electron volts and which drives subsequent chain reactions. In a typical experiment the inner walls of the reaction vessel are characteristically coated, after a few hours of irradiation, with a brownish solid. This solid material shows some spectrometric similarity to the brown clouds observed on Jupiter, Saturn, and Titan. After a typical photolysis experiment the brown solid after extraction with benzene is 84 percent sulfur, largely S_8 . The remaining 16 percent was pyrolyzed and then examined by gas chromatography -- mass spectrometry. Pyrolysis at 450°C yields the rich array of compounds shown in Table 1.

In another experiment, similar dark brown polymeric material is produced by electric discharge through a mixture of CH_4 , NH_3 , and H_2O (vapor) which on pyrolysis at 600°C yields a similar list of compounds.

The dust produced under conditions similar to those described in these two examples may be relevant to the observed ultraviolet, visible and infrared spectroscopic characteristics of planetary atmospheres and the interstellar medium.

The synthesized polymers exhibit an impressive thermal stability. Thermogravimetric analysis shows the electrical discharge polymer in particular to be half thermally dissociated at 1000°K . Another solid material that we consider important is hexamethylenetetramine (HMTA) that is obtained stoichiometrically from ammonia and formaldehyde. HMTA on heating produces largely HCN. From the infrared spectra of this polymer after heating to 923°K , we propose that the tradition of attributing the 9 to 13 μm interstellar features to silicate dust or pure graphite should be reexamined. Our infrared study of the polymers produced both by ultraviolet light and electric discharge, their stability at high temperatures, Douglas' proposal of explaining the diffuse interstellar line at 4420 \AA and the continuum at 2200 \AA by polyatomic molecules containing carbon as C_n ($5 \leq n \leq 15$), and other arguments, suggest organic polymers as major constituents of interstellar dust.

Table 1. Polymer components from the ultraviolet synthesis experiments (the initial mixture consisted of CH₄, C₂H₄, NH₃, H₂S, and H₂O).

Compounds identified	Relative abundance*	Molecular weight	Compounds identified	Relative abundance*	Molecular weight
Hydrogen sulfide	M	34	2-Methylthiophene	M	98
Carbon dioxide	M	44	3-Methylthiophene	M	98
Carbonyl sulfide	M	60	Ethythiophenes	M	112
Hydrogen cyanide	M	27	Dimethylthiophenes	M	112
Ammonia	M	17	C ₃ -alkylthiophenes	m	126
Carbon disulfide	M	76	C ₄ -alkylthiophenes	m	140
Ethane	M	30	Methylmercaptan	M	48
Propane	M	44	Ethylmercaptan	M	62
Butane	m	58	Propylmercaptan	M	76
Ethene	M	28	CH ₃ -S-S-CH ₃	M	94
Propene	M	42	C ₂ -alkyl(-S-S-)†	M	108
Butene	M	56	C ₃ -alkyl(-S-S-)†	M	122
Pentene	m	70	C ₄ -alkyl(-S-S-) s†	M	136
Hexene	m	84	C ₅ -alkyl(-S-S-)†	M	150
Heptenes	m	98	CH ₃ -N=C=S (methyl isothiocyanate)	M	73
Butadiene	M	54	CH ₂ CH ₂ -N=C=S	M	87
Methyl cyclopentene	t	82	C ₂ -alkyl-N=C=S s	M	101
Hexadiene	t	82	C ₃ -alkyl-N=C=S	M	115
Hexyne	t	82	C ₄ -alkyl-N=C=S	m	129
Butadiyne	t	50	C ₅ -alkyl-N=C=S	m	99
Benzene	M	78	CH ₂ =CHCH ₂ -N=C=S	M	41
Toluene	M	92	CH ₃ CN	M	53
Xylene	m	106	CH ₂ =CH-CN	m	67
C ₁ -alkylbenzene	m	120	CH ₃ -CH=CH-CN	m	103
Styrene	m	104	Benzonitrile		
Thiophene	M	84			

*M, major component; m, minor component; t, tentative identification. †These compounds are alkyl disulfides (dithioalkanes): C_n-alkyl(-S-S-), for example, is either CH₃CH₂CH₂-S-S-CH₃ or CH₃CH₂-S-S-CH₂CH₃. A lowercase s after a compound indicates that two or more isomers are present.

(7) "The Diffusion of Galactic Civilizations," W.I. Newman and Carl Sagan, to be submitted to Icarus.

It has been proposed (Hart, 1975; Jones, 1976) that the apparent absence of extraterrestrials on or near the Earth shows that there are none, since a civilization moderately in advance of our own should be capable of relatively fast interstellar spaceflight, crossing the galaxy in a time much less than the age of the galaxy. Assuming that interstellar spaceflight is associated only with the wave of advance of an expanding civilization, these issues are re-examined by employing the

principles of population dynamics used in treating biological species (modified to accommodate "social" influences). The limiting velocity of an extraterrestrial colonization front is reassessed.

Population dispersal in biological problems is generally modelled after the Lotka-Volterra or semilinear diffusion equation. This equation describes in situ growth and saturation (characterized by a sigmoid curve) together with random diffusion. The solution for the population density in the Lotka-Volterra equation is characterized by a travelling wave. In this communication, the diffusion term in the equation is made population density dependent in order to reflect diffusion as a response to population pressure, a social influence generally not included in purely biological applications. Numerical studies of the modified equation reveal the existence of a travelling wave solution with a very sharp colonization front.

In terrestrial cultures, the population growth rate diminishes in response to increasing affluence, the demographic transition. Zero population growth is a concomitant of advanced technology and wealth in the terrestrial case and, it seems likely, for extraterrestrial ones. This situation may be modelled by population density dependent diffusion with no population growth mechanism. The solution for the population density in this case is asymptotically "self-similar" and has a sharp colonization front characterized by a velocity that rapidly diminishes with time.

The implications presented by these population dynamic models to the issue raised by the absence of extraterrestrials on Earth are discussed. Most significant among these is that a colonizing civilization that practices zero population growth would expand only over a small fraction of the galactic disc in the age of the galaxy.

(8) "Eavesdropping on Galactic Civilizations," Carl Sagan, Science, in press.

The anthropogenic radio flux of the Earth is likely to be a delta function centered around the present implying that there is no civilization in the entire Milky Way Galaxy which should be preferentially detectable through radio eavesdropping.

(9) "Lander Imaging as a Detector of Life on Mars," Elliot, C. Levinthal, Kenneth L. Jones, Paul Fox and Carl Sagan, Journal of Geophys. Res., 82, pp. 4468-4478, 1977.

Biological goals were among the important science objectives of the Viking lander camera. The camera performance characteristics relevant to these goals are discussed. They include the ability to observe (1) morphological detail, (2) color and reflectance spectra, and (3) motion and change. The scenes obtained by the cameras were scrutinized in many ways; monoscopically, stereoscopically, in color, and by computerized differencing of camera events. At the lander

sites and during the times that observations were carried out on the surface of Mars, no evidence, direct or indirect, has been obtained for macroscopic biology on Mars. No obvious examples of geometric distortion that might have been motion induced have been observed. Using the repeated line scanning mode of the camera has revealed no changes or motion suggesting life. These negative results may be due to limitations in sampling, in camera design, or in our understanding of Martian biology, but they are certainly consistent with the hypothesis that macroscopic life is absent on Mars.

(10) "Continuing Puzzles About Mars," Carl Sagan, N. Horowitz and B. Murray, Bulletin American Academy of Arts and Sciences, 30, (7), pp. 21-30, April (1977).

The following paper was written in part when one of its co-authors, Professor Blackburn, was in residence at the Laboratory for Planetary Studies and partially supported by this Grant.

(11) "X-ray Photoelectron Spectrometric and Gas Exchange Evidence for Surface Oxidation of Martian Regolith Analogues After Ultraviolet Irradiation," H.D. Holland and T.R. Blackburn, Presented XXI COSPAR Meeting, Innsbruck (1978); to be published Life Sciences and Space Research 17.

Ultraviolet irradiation of pyrolusite ($\beta\text{-MnO}_2$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) in a humid, oxygen-rich Mars atmosphere produced changes in

the oxygen (1s) and manganese (3p) binding energies as measured by x-ray photoelectron (ESCA) spectroscopy. The changes on MnO_2 are consistent with the formation of a surface layer of an oxide of Mn(V) or (VI) which, by reference to the properties of the bulk materials, would be highly oxidizing. The change in the O(1s) spectrum of $\alpha-Fe_2O_3$ is not as easily interpreted; chemisorbed O may account for it. A gas exchange experiment on UV-irradiated MnO_2 powder results in oxygen evolution on exposure to water vapor. Thus transition metal surface chemistry may play an indicator role in the explication of extraterrestrial regolith chemistry.

In addition, following are a few additional publications which, while not supported by this grant, are nevertheless directly relevant to its objectives.

(12) "The Quest for Intelligent Life in Space is Just Beginning," Smithsonian Magazine, 9, pp. 38-47 (1978); reprinted in Cosmic Search, Volume 1, Number 1, January 1979, and in Reader's Digest (Canada), in press.

(13) "Other Civilizations in Space," Encyclopaedia Britannica Yearbook of Science and the Future, 1978, 112-125.

(14) "The Search for Extraterrestrial Intelligence," (with P. Morrison and 14 others), NASA Special Publication SP-419 (Washington: U.S. Government Printing Office), 1978.