Reports

Ultraviolet-Photoproduced Organic Solids Synthesized Under Simulated Jovian Conditions: Molecular Analysis

Abstract. *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* S_8. *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,* C_3*-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.*

The contemporary atmospheres of the jovian planets and of Titan, a satellite of Saturn and the largest moon in the solar system, are strongly reducing. The primitive atmospheres of Earth and the other terrestrial planets were probably at least weakly reducing, a condition thought to be a prerequisite for the origin of life on Earth. The chemistry of such atmospheres, containing CH_4, NH_3, H_2O, and other gases, is therefore of interest in a range of disciplines from planetary astronomy to biology. With the development of flyby and orbital infrared and ultraviolet spectroscopy, and entry gas chromatography and mass spectrometry, organic chemistry of the outer solar system is about to enter a rigorous experimental stage.

The simplest hydrocarbons—ethane, ethylene, and acetylene—have been identified in the atmospheres of Jupiter, Saturn, and Titan (*1*), as had been predicted from experiments (*2*) on electrical discharges through simulated jovian atmospheres in an excess of H_2 and related calculations on quenched thermodynamic equilibrium (*3*). Although H_2S has not yet been identified in the atmospheres of the jovian planets, it is the thermodynamically stable form of cosmically abundant sulfur and is widely anticipated to be present. By far the most readily available energy source for organic synthesis in the Jupiter and Saturn systems is near-ultraviolet sunlight, and a wide range of products are generated in simulated jovian atmospheres which contain H_2S; the photodissociation of H_2S yields a hydrogen atom which is superthermal by several electron volts and which drives subsequent chain reactions (*4, 5*). In typical experiments which include an aqueous NH_3 solution, organic products are found in the gas, liquid, and solid phases, including upon hydrolysis more than 40 amino acids, among them cystine (*4*). The inner walls of the reaction vessel are characteristically coated, after a few hours of irradiation, with a brownish solid sometimes described as an "intractable polymer." This material shows some spectrometric similarity to the brown clouds observed on Jupiter, Saturn, and Titan (*6*), and it has been speculated (*7*) that the molecular constitutions of the two products are similar. The eddy diffusion coefficients on Jupiter and Saturn are sufficiently high that the steady-state abundance of any complex molecules will be powerfully limited by convection to pyrolytic depths; nevertheless, there are circumstances in which the ultraviolet quantum yield is sufficiently high for the observed optical depth of the chromophore to be maintained in the steady state (*8*). These limitations do not apply to Titan, which very likely does not have a high-temperature surface.

After a typical photolysis experiment (*9*), we carried out an atomic analysis of the solid residue which remained after hydrolysis with 6*N* HCl. This analysis revealed that the solid residue is about 95 percent sulfur (mainly S_8) and about 5 percent complex organics (*10*). We present here the results of a study of the organic polymer left after removal of elemental sulfur from the raw brown solid.

At the end of the ultraviolet irradiation, the 12.7-liter bulb was broken and the brown solid product was scraped from a fragment with an area of about 100 cm^2 (the spatula used had been cleaned with freshly distilled solvent, and the material was collected in an acid-cleaned vial). Sulfur was removed from the solid by extraction with distilled benzene under ultrasonication. Between extractions the solvent and dispersed polymer were centrifuged and the solvent was decanted. Results consistent with the quantitative removal of elemental sulfur from the organic solid were obtained in a separate experiment with a mass spectrometer (MS) in which direct probe insertion was used. A portion of the same polymeric material was extracted with benzene according to the same procedure and then tested in the solid inlet system of the MS at sequential temperatures of 70°, 90°, 120°, 150°, 200°, 250°, and 300°C at a pressure of 6×10^{-7} torr; no elemental sulfur was detected.

The polymer after extraction with benzene had the consistency of sticky paste and would not dry readily. We therefore smeared it on the bottom of a pyrolysis chamber (Vycor), using an acid-cleaned glass rod, and degassed it under high vacuum at room temperature to remove most of the adsorbed benzene. This sticky paste is 16 percent by weight of the raw brown solid. The remaining 84 percent is mainly S_8. The raw brown solid contains at least 16 percent organics, because some organics may be soluble in benzene. This figure is larger than the 5 percent organics after HCl hydrolysis reported in (*10*) because (i), as we show below, the organics themselves are sulfur-rich and (ii) benzene extraction does not destroy organics as HCl hydrolysis does. Pyrolysis was then carried out under a high vacuum at 450°C; all products were trapped with liquid nitrogen and then injected directly into a gas chromatograph (GC), which in turn was directly connected through a heated transfer line to the MS system (*11*). It is widely recognized (*12*) that pyrolysis at a pressure under or near 1 bar may lead to inter- and intramolecular rearrangement of the breakdown products; vacuum pyrolysis at more moderate temperatures (near 450°C) minimizes such rearrangements.

The richness of the polymeric breakdown products is evident from the GC results; this richness was also apparent in an earlier study (*6*) in which a sulfur-free extract was pyrolyzed at 175°C and examined in a MS by direct probe insertion techniques. Although the pyroly-

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zate was separated by gas chromatography prior to mass spectrometry, analysis of individual GC peaks indicated that many are mixtures of two or more compounds, as has been found for complex soluble products in previous experiments on prebiological organic chemistry. As a result, some of the identifications given here, particularly for very minor products, must be treated with caution. Nevertheless, this work is, so far as we know, the first systematic analysis of the insoluble products in such experiments.

Identifications are based both on the principal mass spectral peaks and the GC retention times. There is a tendency for polar compounds to be adsorbed in the analytical system and to produce spectral overlap. In principle, it is possible to unravel the mass spectrum of a complex mixture, for example, by finding a peak specific to each compound and then subtracting spectra one at a time from the mixture (*13*). However, for our case, with over 200 mass spectra, such a task would have been overly time-consuming in the absence of a fully computerized subtraction technique. But we were able roughly to approximate the method and unravel a number of complex spectra by a manual subtraction method. The majority of the heavier components in the pyrolyzate have not yet been identified. We attempted to identify unknown mass spectra by using the computer library search routines called PBM (Probability Based Matching System) and STIRS (Self-Training Interpretive Retrieval System) at Cornell. These attempts were unsuccessful despite the 41,366 mass spectra listed in the computer library. Despite these difficulties, the resolution, particularly for compounds of lower molecular weight, was sufficient to allow the identification of many compounds on the basis of their characteristic mass spectral fragmentation patterns. We used the GC retention times in certain cases to distinguish between isomers (for example, the methyl thiophenes).

The principal compounds identified are listed in Table 1. Major polymer fragments include alkanes, alkenes, substituted aromatics, thiophenes (five-membered heterocyclic compounds containing one sulfur atom in the ring), alkylmercaptans, alkyldisulfides (up to hexyldisulfide), isothiocyanates, and nitriles. The expected nonselective synthesis during this simulation experiment is consistent with the production of homolog and isomer series of heteroatomic compounds from the polymer. The high sulfur abundance in these compounds is an additional confirmation that they are synthesized from our original mixture and are not contaminants. The efficiency of the sulfur-extraction technique is such, as verified by infrared and mass spectroscopy, that we do not believe that sulfur-containing organics could have been synthesized at a significant concentration from elemental sulfur during pyrolysis. There is a conspicuous absence of oxygen atoms in any but the simplest of the polymer fragments. A large abundance of CO_2 and COS suggests decarboxylation of larger moieties. Water is not detectable in such an analysis, but an earlier low-temperature mass spectral analysis (*6*) showed MS peaks attributable to water and consistent with dehydration reactions. Nitriles are the Strecker synthesis hydrolysis precursors of amino acids as well as the pyrolytic products of amino acids, peptides, nucleosides, and other nitrogenous compounds. Their presence is consistent with our earlier identification (*6*) of a wide range of amino acids in the hydrolyzate of the brown solid. The aromatic compounds found suggest the cracking of a condensed aromatic polymer; however, toluene, styrene, and C_3-alkylbenzene are also among the pyrolytic fragments of the amino acid phenylalanine (*14*). Methylthiophene can be formed by the cyclization of cystine (*15*), which we know to be present in the brown solid. Our earlier conclusion (*6*) that the component of the brown solid free of elemental sulfur "is composed in significant part of straight chain alkyl groups with amino groups present" is consistent with these findings, as was our earlier suggestion of the presence of alkenes. The infrared transition probabilities of aromatics are sufficiently low that there is no contradiction between our present findings of aromatics and our prior inability to detect such compounds with infrared spectroscopy.

Table 1. Polymer components from the ultraviolet synthesis experiments (the initial mixture consisted of CH_4, C_2H_6, NH_3, H_2S, and H_2O).

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	Ethylthiophenes	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_3-alkyl($-S-S-$)†	M	108
Butene	M	56	C_4-alkyl($-S-S-$)†	M	122
Pentene	M	70	C_5-alkyl($-S-S-$) s†	M	136
Hexene	m	84	C_6-alkyl($-S-S-$)†	M	150
Heptenes	m	98	$CH_3-N=C=S$ (methyl isothiocyanate)	M	73
Butadiene	M	54			
Methyl cyclopentene	t	82	$CH_3CH_2-N=C=S$	M	87
Hexadiene	t	82	C_3-alkyl$-N=C=S$ s	M	101
Hexyne	t	82	C_4-alkyl$-N=C=S$	M	115
Butadiyne	t	50	C_5-alkyl$-N=C=S$	m	129
Benzene	M	78	$CH_2=CHCH_2-N=C=S$	m	99
Toluene	M	92	CH_3CN	M	41
Xylene	m	106	$CH_2=CH-CN$	M	53
C_3-alkylbenzene	m	120	$CH_3-CH=CH-CN$	m	67
Styrene	m	104	Benzonitrile	m	103
Thiophene	M	84			

*M, major component; m, minor component; t, tentative identification. †These compounds are alkyl disulfides (dithioalkanes); C_4-alkyl($-S-S-$), for example, is either $CH_3CH_2CH_3-S-S-CH_3$ or $CH_3CH_2-S-S-CH_2CH_3$. A lowercase s after a compound indicates that two or more isomers are present.

Our results suggest that, because of the great efficiency of H_2S in initiating photochemistry in reducing atmospheres, sulfur-rich organic compounds may be significant constituents of reducing planetary atmospheres and in prebiological organic chemistry. This tentative conclusion should be retested under more realistic jovian simulations with high H_2 dilutions. Alkanes, aromatics, and amino acids are also common constituents of carbonaceous chondrites, but the sulfur abundance in meteoritic polymeric material is usually not nearly so high (*11, 16*) as it is in our material. This high sulfur content suggests that, whether the organics in carbonaceous meteorites are made according to Fischer-Tropsch (*17*) or Miller-Urey (*18*) processes, H_2S photolysis was not the initial step. We have produced in other experiments a brownish polymer from sulfur-free reducing atmospheres; this result demonstrates that sulfur compounds are not essential for the optical absorption in such products.

Some of the compounds found in our ultraviolet syntheses are coal tar derivatives. Many have impressive thermal stabilities (for example, thiophene can be maintained at 850°C for substantial periods without decomposition). We stress that in our analysis we have not necessarily identified the organics in the brown solid but only some of the pyrolysis products of this solid. However, because of the deep circulation in Jupiter and Saturn, pyrolysis must occur there at depth. Our pyrolysis temperature of 450°C is achieved at a pressure of about 100 bars on Jupiter (*8*) at high H_2 dilutions. Pyrolysis products are probably circulated to high altitudes on Jupiter where they may be observed and identified. As analytical techniques improve, those products (Table 1) which may form and persist at high H_2 abundances should be sought in investigations of the atmospheres in the outer solar system. The promising candidates for this search would be aliphatic and aromatic hydrocarbons, thiophenes, and to a lesser degree organic sulfides.

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9. In a typical experiment, a spherical reaction vessel (12.7 liters) is filled with 3350 cm^3 of CH_4, 3437 cm^3 of NH_3, and 2862 cm^3 of H_2S; the gases are irradiated with the resonance emission lines of mercury from a 450-W high-pressure quartz (Hanovia) lamp radiating 5.8 W at 2537 Å. The gases, along with the photolytic products, are recycled by a greaseless solenoid pump [J. S. Watson, *Can. J. Technol.* **34**, 373 (1956)] out from and back into the reaction vessel. As the photolysis continues, the interior wall of the reaction vessel accumulates an orange-brown solid. After 12 hours and 40 minutes of photolysis, 3521 cm^3 of C_2H_6 and an additional 850 cm^3 of H_2S are introduced. After 29 hours of further photolysis, a seal is magnetically broken on a tube containing 50 ml of distilled water; thereupon, the pump can circulate gases and reaction products over an NH_4OH bath. After another 6 days and 19 hours, 1150 cm^3 of H_2S are introduced. The experiment is terminated after an additional 8 days and 22 hours. The visual appearance of the brownish solid did not change after the first few hours of photolysis. The NH_4OH bath, which was not exposed to ultraviolet radiation, also acquired a distinct brownish coloration after the reaction products acquired access to it. Gases were transferred to the reaction vessel through a coiled glass diffusion trap maintained at −78°C, as a precaution against the introduction of mercury vapor and other impurities into the reaction vessel.
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11. The pyrolysis products were analyzed with a GC (Perkin-Elmer model 226) equipped with an OS 138 (polyphenylether) SCOT capillary column (45 m long and 0.05 cm in inside diameter). The GC was programmed from 40° to 190°C at 2.5°C min^{-1} after an initial 10-minute period at 40°C. The GC was interfaced to a medium-resolution MS (Hitachi RMU-6E) through a Watson-Biemann molecular separator. Mass scans, each 5 seconds, were taken of each peak as it emerged from the GC. Further details of the pyrolysis apparatus can be found in E. L. Bandurski and B. Nagy, *Geochim. Cosmochim. Acta* **40**, 1397 (1976).
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Phobos Transit of Mars as Viewed by the Viking Cameras

Abstract. *A Viking orbiting spacecraft successfully obtained pictures of the martian satellite Phobos with Mars in the background. This is the first time that a single picture was obtained from a spacecraft which contained both a planet and a moon and had significant surface detail visible on both. The region of Mars below Phobos included volcanoes in the Tharsis Montes region. These pictures showed Phobos to be smaller than previously thought. The image of Phobos can be used as a control point to determine the map coordinates of surface features on Mars.*

On 23 June 1977, the Viking Orbiter 2 (VO-2) spacecraft imaged Phobos as the martian satellite was in transit across Mars. The spacecraft camera viewed Phobos against the volcanoes in the Tharsis Montes region. Four television sequences were designed to obtain a photomosaic covering Olympus Mons, Ascraeus Mons, and Pavonis Mons as background to three separate views of Phobos. Olympus Mons was beyond the pointing limits of the camera when the

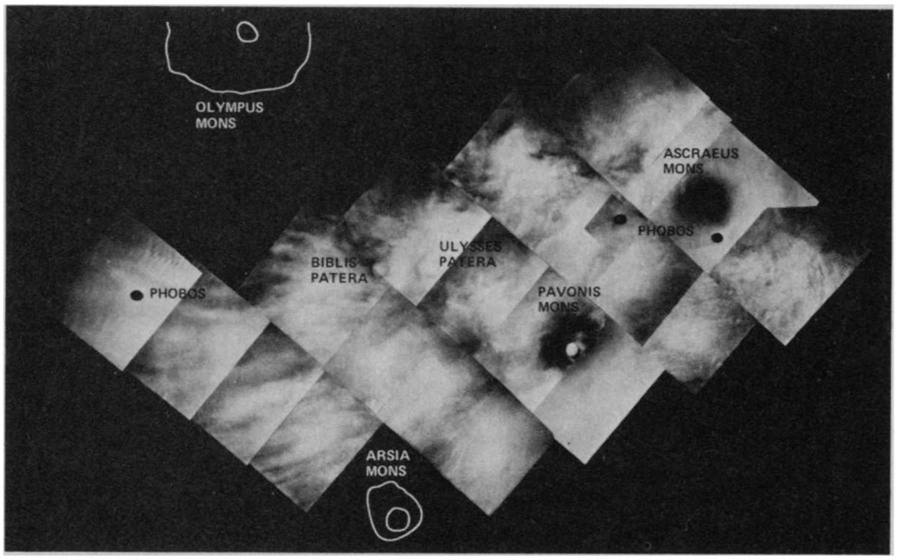

Fig. 1. A mosaic of 20 VO-2 television pictures (pictures 304B51–89) taken within a 5-minute period showing the Tharsis Montes region of Mars with Phobos in transit across Mars. The exposures of these pictures were set for the brightness of Mars, making the much darker Phobos appear as dark areas in the mosaic. This is the first time that a picture of any moon against its primary planet has been obtained where the surfaces of both bodies were readily visible.