

Red Clouds in Reducing Atmospheres

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A dark reddish-brown high-molecular-weight polymer is produced by long wavelength ultraviolet irradiation of abundant gases in reducing planetary atmospheres. The polymer is examined by paper chromatography, mass spectrometry, and infrared, visible, and ultraviolet spectroscopy. High carbon-number straight-chain alkanes with NH_2 and, probably, OH and C=O groups are identified, along with the previously reported amino acids. There are chemical similarities between this polymer and organic compounds recovered from carbonaceous chondrites and precambrian sediments. The visible and near-ultraviolet transmission spectrum of the polymer shows its absorption optical depth to be redder than λ^{-2} and perhaps similar in coloration to the clouds of Jupiter, Saturn, and Titan. The near-ultraviolet absorption coefficient is $\sim 10^3 \text{ cm}^{-1}$, and typical grain sizes $\sim 30 \mu\text{m}$. The nitrile content is small, and the polymer should be semitransparent in the $5 \mu\text{m}$ atmospheric window. Such polymers may be a common constituent of clouds in the outer solar system and on the early Earth.

INTRODUCTION

The outer solar system is remarkably red. The visible and near-ultraviolet reflection spectra of the Galilean satellites, the rings of Saturn, and the atmospheres of Jupiter, Saturn, and Titan all show a marked decrease in reflectivity from long to short visible wavelength. However, the red coloration of these objects can be divided into two different groups (see, e.g., Johnson and McCord, 1971; McCord, Johnson, and Elias, 1971): the Galilean satellites and the rings of Saturn, on the one hand, and Jupiter, Saturn and Titan, on the other. This is a division into objects without and objects with atmospheres.

The decrease in redness of the Galilean satellites with increasing distance from the primary, and the absence of extensive atmospheres on these satellites, suggests that their reddish coloration is due to F centers in the surface ice crystal lattices in these objects produced by the Jovian radiation belts (Sagan, 1970; Veverka, 1970; Sagan, 1971a). Io, the reddest of the Galilean satellites, lives almost within the measured interferometric contours of the

Jovian radiation belt (Sagan, 1971a). Jupiter 5 lives very near the middle of the belt but, because of its low mass, it may not have outgassed sufficient volatiles to have produced extensive ice F centers. The color of Jupiter 5 may be representative of that produced by high-energy charged-particle bombardment of silicates. There is a substantial difference in the $5 \mu\text{m}$ region between Io and Titan (Joyce, Knacke, and Owen, 1973); the visual albedo of Titan is also much less than that of Io (Harris, 1961).

The similarity in coloration of the rings of Saturn to the Galilean satellites suggests a similar explanation there, but seems to require the existence of a Saturnian radiation belt as well. Synchrotron radiation physics and the observed microwave spectrum do not exclude such a belt (Luthey, 1973), and the high temperature of the C ring (Murphy, 1973) may be due to an interaction between the outer parts of the rings of Saturn and such Saturnian radiation belts. It is apparent that trapped charged particles intersecting the ring plane once each passage from magneto-

spheric mirror point to mirror point will very efficiently be swept up. But particles exterior to the rings may have much longer lifetimes. To check this hypothesis, it would be useful to search for color differences among the A, B, and C rings of Saturn—and, eventually, to examine Saturn directly for a radiation belt.

This paper is, however, primarily concerned with the other class of red objects in the outer solar system, those with atmospheres. The pale variegated and time-dependent colors of the belts, bands, and Great Red Spot of Jupiter are well known, as is the somewhat less vivid coloration of the equatorial regions of Saturn. What is not quite so generally appreciated is that the largest Saturnian satellite, Titan, is an extremely red object with a very low albedo in the blue, violet, and ultraviolet. Moreover, there is evidence, directly from polarimetric observations (Veverka, 1973; Zellner, 1973) and indirectly from requirements for a Titanian greenhouse effect (Sagan and Mullen, 1972; Sagan, 1973; Pollack, 1973) that, in the visible and ultraviolet, we are observing an almost completely cloud-covered satellite. The predominant cloud color of material on Jupiter and Saturn is also red. It is, therefore, apparent that some molecular species which is very dark and very red is preferentially produced in the reducing atmospheres of the Jovian planets.

Since the Great Red Spot is viewed at high altitudes on Jupiter and since there is no likely mechanism for the preferential external production of red material at that xenographic position, it is likely that red material is preferentially produced at depth in the Jovian atmosphere and surfaces to view in locales such as the Great Red Spot (Sagan, 1971b).

While at one time places on Jupiter of high infrared brightness temperature, such as the North Equatorial Belt, were simultaneously colored red (Westphal, 1969), there now appear to be cases in which the high temperatures are correlated with blue coloration (Low, 1973). Typical cloud pressures on Jupiter are of the order of a few bars. We know from Apollo color photography of the Earth

that the planet is almost uniformly blue due to Rayleigh scattering at ~ 1 bar pressure. Therefore, in clear regions and substantial pressures in the Jovian atmosphere a blue coloration is not unexpected; and it is possible that deep hot regions are sometimes red and sometimes blue depending upon the occurrence and time-dependence of red chromophores. The observations seem to require the production of these chromophores at depth.

In the case of Titan, the temperatures of the portion of the atmosphere which we view are too low for there to be any significant quantities of ammonia, water, or H_2S . The only compounds that should be present in any abundance above the Titanian clouds are methane and hydrogen, and these are precisely the materials observed (Trafton, 1972). Were the red coloring material in the Titanian clouds produced only from these precursors, the identity of the material as hydrocarbons would immediately be established. This is to some extent a tempting conclusion because, in computer quenched thermodynamic equilibrium experiments at low H/C ratios in simulated Jovian atmospheres, Sagan *et al.* (1967) found that high molecular-weight polycyclic aromatic hydrocarbons should be produced; these experiments also predicted the preferential formation of just the smaller organic molecules found in comparable laboratory experiments (Sagan and Miller, 1960). However, it is possible that substantially higher temperatures prevail below the visible Titanian clouds and that ammonia or even water vapor may be present there.

Early suggestions on the coloration of Jupiter in terms of solutions of sodium in ammonia (Wildt, 1939) and free radical chemistry (Rice, 1956) are not widely accepted (see, e.g., Sagan, 1971b). The two most prominently advertised current views are that the coloring material is a combination of ammonium sulfide and ammonium hydrosulfide (Lewis, 1969; Owen and Mason, 1969) or is one of various possible organic compounds (Urey, 1959; Sagan, 1962; Sagan *et al.*, 1967; Woeller and Ponnampuruma, 1969; Sagan, 1971a;

Sagan and Khare, 1971a). Woeller and Ponnampertuma produced a reddish polymer after subjecting a mixture of methane and ammonia or HCN and ammonia to electrical discharge; while Sagan and Khare (1971a, 1971b; Sagan, 1971a) also produced reddish-brown polymeric material upon subjecting a mixture of CH_4 , C_2H_6 , NH_3 , and H_2O to long wavelength ultraviolet light with H_2S as the primary photon acceptor. In the present paper, we discuss the preliminary chemical and optical properties of the polymer produced in this latter set of experiments.

EXPERIMENTAL

From the known reducing character of the atmosphere of Jupiter and the high cosmic abundance of sulfur, we expect H_2S in the lower clouds of the Jovian planets. Prinn (1970) has calculated the ultraviolet radiative transfer at $\lambda \leq 2700 \text{ \AA}$ for the Jupiter atmosphere and concluded that photolysis of H_2S occurs in the lower NH_4SH clouds proposed by Lewis (1969). H_2S absorbs where the solar energy is abundant at long ultraviolet wavelengths. It has a broad absorption continuum starting at 2700 \AA and continuing down to vacuum ultraviolet (Schultz *et al.*, 1973). The dissociation energy of the H-SH bond is 85–95 kcal/mole (Gann and Dubrin, 1967). Ninety-seven percent of the excess energy of photodissociation of the H-SH bond by 2537 \AA radiation is carried away as translational kinetic energy of the H atom. This excess energy of 17.5–27.2 kcal/mole is more than the activation energy required in reactions with such molecules as CH_4 , NH_3 , and H_2O .

Because of the chain reactions induced in this manner by hot hydrogen atoms, the subsequent chemistry, particularly of the high molecular-weight species, may not be extremely different from that produced by other energy sources. Electrical discharges can reasonably be expected in the lower aqueous clouds of Jupiter and the production of a variety of organic compounds by silent discharge in reducing atmospheres (see, e.g., Miller and Orgel, 1973)

and hypervelocity shocks (“thunder”: Bar-Nun *et al.*, 1970) are well known. Likewise we suspect that the end product of our experiments is not greatly dependent upon the presence of ethane; but beginning with a two-carbon atom molecule increases greatly the rate of reaction. Accordingly the results described in this paper may also be applicable to other energy sources and to other mixtures of reduced gases.

In a typical experiment a spherical reaction vessel of 12.7-liter capacity was filled with 3350, 3521, 3437, and 2862 cc of CH_4 , C_2H_6 , NH_3 , and H_2S , respectively, along with 50 cc of liquid water, and the gases irradiated with the resonance emission lines of mercury from a 450-W Hanovia High Pressure Quartz Mercury Lamp, radiating 5.8 W at 2537 \AA . The gases, along with the photolytic product, were recycled over the NH_4OH bath by a Watson greaseless solenoid pump (Watson, 1956) and back to the reaction vessel (Fig. 1). The gases were transferred in the reaction vessel through a coiled glass trap kept at -78°C to insure the trapping out of impurities and any mercury vapor from the vacuum system. The photolysis was first performed only with CH_4 , NH_3 , and H_2S . No liquid water was introduced. As the photolysis proceeded, the reaction vessel appeared cloudy, changing later to an orange-brown color. After 12 hr 40 min of photolysis, gas samples were withdrawn from the reaction vessel for analysis of vapor-phase products. At the same time 3521 cc C_2H_6 and 850 cc of additional H_2S were introduced into the reaction vessel. After 29 hr of further photolysis, gaseous samples were again withdrawn. After withdrawing the sample the seal for liquid water (Fig. 1) was broken. The ampule containing water was kept warm in order to facilitate its transfer into the reaction vessel. After another 6 days 19 hr, 1150 cc H_2S was further added to the reaction vessel. The experiment was terminated after another 8 days and 22 hr.

A variety of other experiments with different relative proportions of gases and time histories produced similar orange-brown coating of the reaction vessel walls (see, e.g., Sagan and Khare, 1971b). In

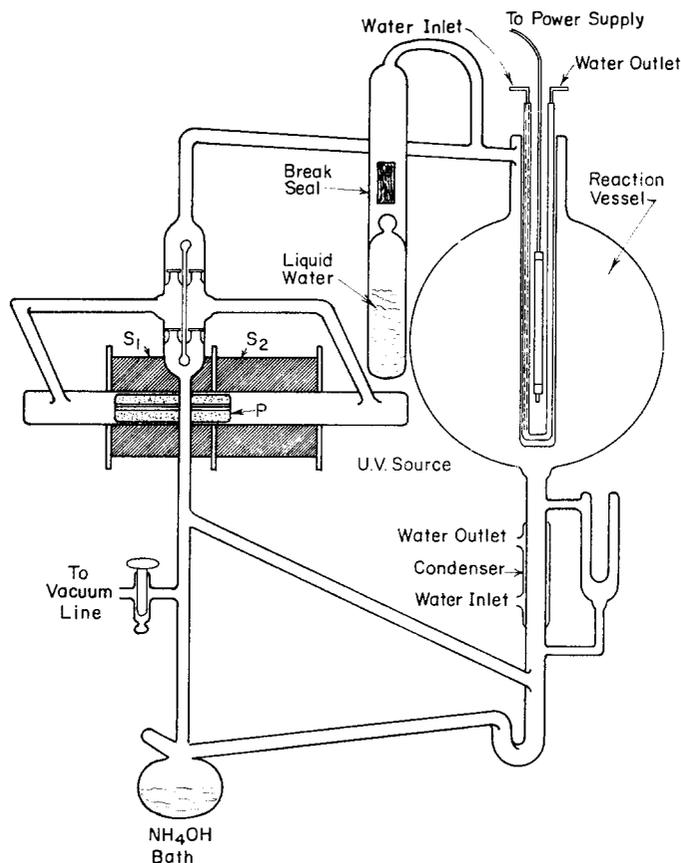


FIG. 1. Experimental apparatus for simulations of Jovian photochemistry. The Hg-discharge lamp irradiates initial reactants in the reaction vessel, which are circulated through the simulated ammonium hydroxide clouds (lower left) by the Watson pump (upper left).

addition, the bath of NH_4OH which was not directly exposed to ultraviolet irradiation also acquired a distinct brownish-yellow coloration. Preliminary results on the identification of gas phase and liquid phase products from such experiments have been reported (Sagan and Khare, 1971a; 1971b; Khare and Sagan, 1971). The present paper is restricted to an analysis of the solid powdery orange-brown polymer which coated the interior of the reaction vessel at the conclusion of these experiments. A color photograph of this polymer has been published (Sagan, 1971a). It bears a superficial resemblance to the coloration of the Jovian Great Red Spot and the occasional appearance of reddish-brown areas on Jupiter such as the North Equatorial Belt.

We have already reported (Sagan and Khare, 1971b) the production in such experiments of amino acids in very high yield, upon acid hydrolysis of the polymer as well as the liquid aqueous phase. In addition, mass spectrometric evidence of polymeric sulfur from S_1 to S_8 was secured for an evaporated aliquot of the aqueous solution. As we report below, no evidence of polymeric sulfur is present in the yellow component of the brown polymer discussed in the present paper.

Two-dimensional paper chromatography was performed on Whatman No. 1 paper. The first solvent used was *n*-propanol, concentrated NH_4OH , and water (deionized) in a 6:3:1 ratio. The second solvent was isobutyric acid, 1*N* ammonium hydroxide, and water (deionized) in a

100:60:1.6 ratio. Both solvents were run generally for 17–20 hr each. Prior to development of the chromatograms, the chromatocab was saturated with the appropriate solvent for 3 hr. The methanol extract of the polymeric material, or of the yellow material eluted from two-dimensional chromatograms of the methanol extract, were first evaporated on an Irtran-2 Window, and then scanned on a Perkin-Elmer 621 infrared grating double-beam spectrophotometer. The resolution was of the order of 1 cm^{-1} for the region $4000\text{--}700\text{ cm}^{-1}$. Visible and near-ultraviolet transmission spectroscopy were performed on a Cary 14 double-beam spectrophotometer with an effective resolution of the order of 50 \AA . Mass spectra of the yellow material were obtained on MS-9 and LKB-9000 mass spectrometers under various conditions of temperature and ionizing voltage, by direct insertion of the probe carrying the material.

CHEMICAL RESULTS

Two-dimensional chromatography of the methanol extract of the photoproduced polymer revealed yellow material at the solvent front. The yellow material was eluted off the paper chromatogram. A similar yellow material was also obtained when the methanol extract of the brown polymeric material was eluted off Dowex 50H^+ resin by 3N HCl . We also found an insoluble yellow residue on dissolving the brown polymer in 1.5N HCl .

The paper chromatographic properties of the yellow residue were compared with a large number of sulfur compounds; poly-

cyclic aromatic hydrocarbons; nitrogenous bases; and aromatic amino acids. The chromatographic position of the yellow compound synthesized in our experiment did not coincide with any of the compounds, essentially because the yellow material ran with the solvent front. We can reasonably infer that the yellow material consists of high molecular-weight polymeric material.

Accordingly the parent brown polymer must be of even higher molecular weight, and is probably a mixture of a large number of components. Similar material produced in such experiments is often described as "intractable," the organic chemists' way of saying that we have no idea of what it is. Our attempts in the present paper are only a small step toward the characterization of this complex collection of high molecular-weight molecules.

We note that the presence of —NH_2 is likely in the yellow polymer, since in running it on a Dowex 50 or CG-120 cation-exchange column and eluting with $4\text{N NH}_4\text{OH}$, the yellow material remained on the columns until eluted by 4N HCl . This is usually a good indication of the basic nature of the yellow material.

Figure 2 is the infrared spectrum of the methanol extract of the polymeric material without purification. This spectrum was compared with the infrared spectra of several mixtures of compounds listed below.

1. Sixteen amino acids (gly, α -ala, val, leu, isoleu, lys, arg, his, tyr, ϕ -ala, threo, ser, glu, asp, met, cys).

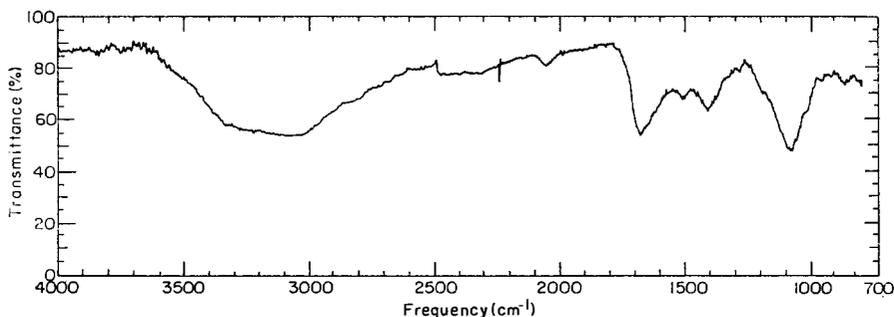


FIG. 2. Infrared spectrum of the methanol extract of brown polymeric material.

2. 2,6-Dipicolnic acid, anthranilic acid, naphthalene, anthracene, dithiouracil.
3. 2,6-Dipicolnic acid, anthranilic acid, dithiouracil.
4. 2,6-Dithiouracil, adenine, guanine, 8-aza 2,6-diaminopurine sulfate, hypoxanthine, 6-azathymine, dithiothymine, dihydrothymine.
5. Adenosine, cytidine.
6. Rhamnose, ribose, glucose, naphthalene.
7. Thiourea, urea.
8. 1,2-Benzanthracene, anthracene, naphthalene, norborane, δ^4 -cholestene-3-one, adamantane, cholesterol.
9. Methylamino-acetonitrile hydrochloride, methylene-aminoacetonitrile.
10. 5,5'-Dithiobis (2-nitro-benzoic acid), glutathione (oxidized), glycine methyl ester HCl, cystine ethyl ester HCl.
11. Rhombic sulfur in carbon disulfide.

No close correspondence could be found between the methanol extract and any of the compounds indicated above. A comparison of the spectra was also made with the brown polymeric material produced by Woeller and Ponnampuruma (1969) in their discharge experiment using CH_4 and NH_3 . No correspondence in the spectrum is indicated there either.

However, a comparison of the spectrum with the literature indicates a resemblance between the extracts of terrestrial sediments and the 2-Murray and 1-Orgueil meteorites (Meinschein *et al.*, 1963) with the infrared spectrum of the purified yellow material of our polymer as shown in Fig. 3.

Resemblance is due to coincidence of the following infrared absorptions:

Vibrations	Frequency region
O-H and N-H	3448-3226 cm^{-1}
C-H	3030-2778
C-O	1786-1667 and 1250-1111
C=C	1650-1600
Other bands	1000-714

The 1613 to 1409- cm^{-1} region of our spectrum is not comparable with Meinschein *et al.*'s because of CS_2 absorption in their published data. (The similarity of our abiogenic product with carbonaceous chondrite material is entirely consistent with the view that indigenous meteoritic organics are not of biological origin.) We compared our infrared spectra also with that of sulfur (Meyer, 1965) and found no resemblance.

Finally, mass spectrometry was used to help identify the yellow purified material. Figure 4 is the mass spectrum taken at 310°C on the MS-9. Similar spectra with high sensitivity at about 175°C on an LKB 9000 mass spectrometer show peaks up to $m/e \geq 679$ (Fig. 5). Some lines may be the result of recombination of ionic fragments. As we find a systematic loss of 14 mass units particularly in the five- to seven-hundred mass number region (Fig. 5), we could expect molecular ions successively with fewer CH_2 group and a parent molecule with a molecular weight higher than 679.

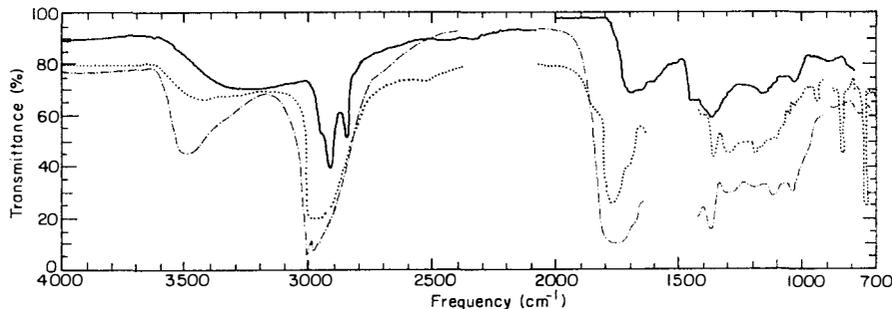


FIG. 3. The unbroken line shows the ir spectrum of the yellow constituent separated from the brown polymeric material by two-dimensional paper chromatography. The alternating dashes and dots show 2-Murray, 6hr extract. The dotted line shows 1-Orgueil, 6hr extract. The last two curves are taken from Meinschein *et al.* (1963).

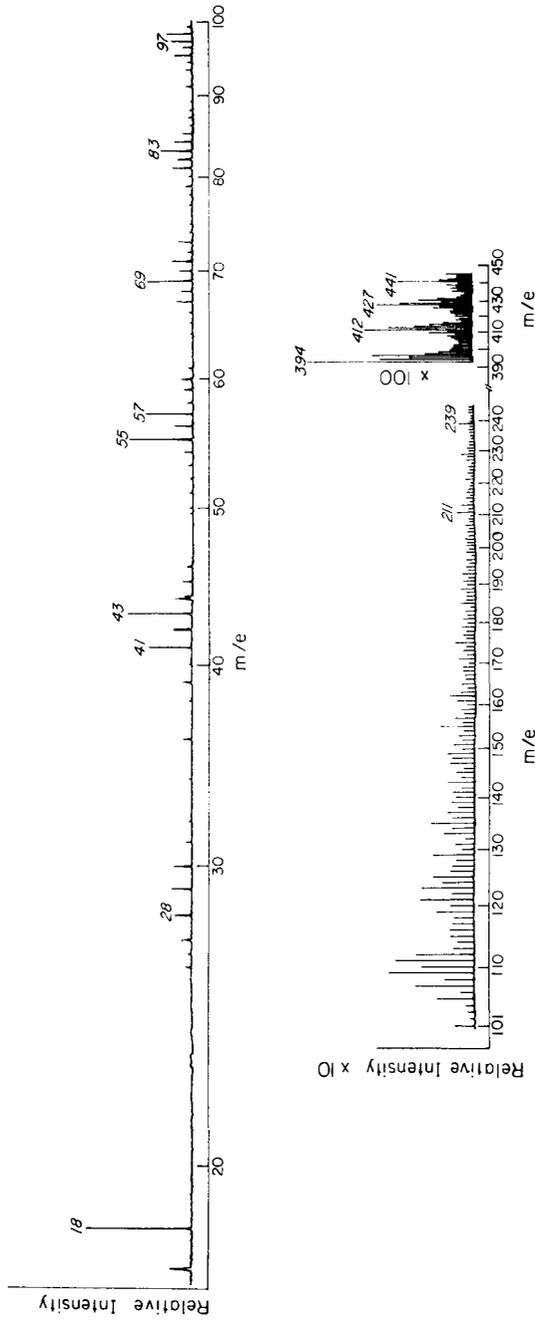


FIG. 4. Mass spectra of purified yellow material in CH_4 , NH_3 , H_2O , C_2H_6 , and H_2S photolysis experiment. The spectra is taken on MS-9 at 310°C by direct probe-insertion techniques.

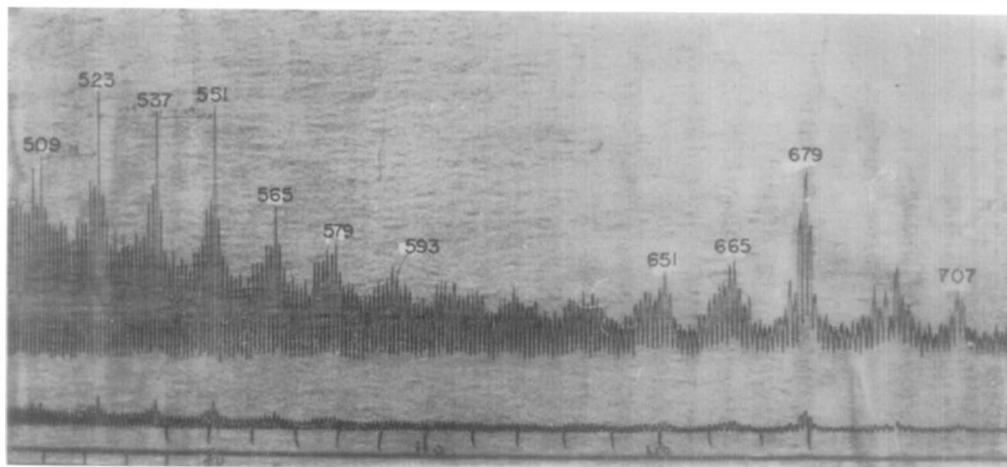


FIG. 5. Mass spectra of yellow component of the brown polymeric material taken at 175°C on an LKB 9000 mass spectrometer by direct probe-insertion technique. The spectra are displayed for high mass numbers only.

The spectrum does not show the presence of S as we do not find a substantial peak at $m/e = 32, 64, 96, \dots$ (Fig. 4). Thus, the purified yellow material does not contain appreciable elemental sulfur although the aqueous fraction does (Sagan and Khare, 1971b). An examination of the spectrum (Fig. 6) between mass numbers 25 and 33 reveals the presence of the $-\text{NH}_2$ group predicted earlier by ion-exchange chromatography and substantiated by infrared spectra (Fig. 3). We find the isotopic peaks

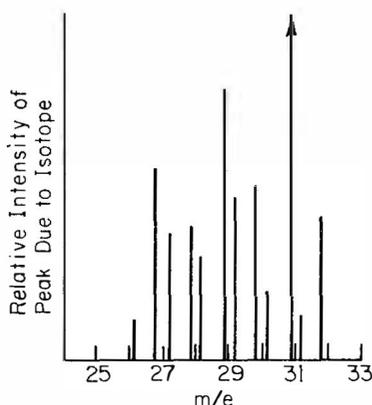


FIG. 6. Isotopic peaks of CH_3NH_2 and C_2H_6 in the mass spectra of yellow component of the brown polymeric material taken at 175°C on an LKB 9000 mass spectrometer by direct probe-insertion techniques.

of CH_3NH_2 and C_2H_6 and their fragments. $\text{C}^{13}\text{N}^{14}$ and $\text{C}^{12}\text{N}^{15}$ in CH_3NH_2 are so close in mass that we cannot with this instrument resolve these two species. The isotopic peaks due to $\text{C}^{13}\text{N}^{14}$ or $\text{C}^{12}\text{N}^{15}$ and $\text{C}^{13}\text{C}^{12}$ lay on the correct side of the principal peak with their intensity in good harmony with the isotopic abundances.

There are three striking peaks at $m/e = 394, 412, \text{ and } 430$ (Fig. 4) with a mass difference of 18, suggesting the loss of H_2O from the ion. The proportional intensity of m/e 18 and 17 is consistent with loss of H_2O through dehydration of the parent molecules.

The peaks at 55, 69, 83, 97, etc. (Fig. 4) show consecutive loss of $m/e = 14$ and are consistent with an alkene (and simple alicyclic hydrocarbon) structure. Further evidence for straight-chain hydrocarbon substructure is shown by the loss of 14 mass numbers by the large molecular ions of mass number 495, 509, 523, ..., 565, 579 and again 651, 665, 679. It appears that a significant portion of the parent molecule(s) is composed of one or more hydrocarbon chains. Similar results follow from the infrared spectra (Fig. 3) showing strong peaks at 2920 and 1455 cm^{-1} typical of long-chain alkanes, and the 1650 to 1600- cm^{-1} feature attributed to $\text{C}=\text{C}$ stretching vibrations. There is no feature

in the infrared that could be associated with aromatic compounds. Thus, our conclusion, based on infrared and mass-spectrometric studies, is that the yellow material is composed in significant part of straight-chain alkyl groups with amino groups present and probably carboxyl and hydroxyl groups as well. Such alkanes are, however, colorless. Dr. R. Hayatsu has suggested to us that the yellow coloration is due to conjugated polyenes. For example $\text{H}(\text{CH}=\text{CH})_n\text{H}$ is colorless for $n = 3$, but yellow-orange for $n = 8$ (Sondheimer *et al.*, 1961). The brownish polymer probably contains, as well, nitriles, which are the precursors in the Strecker synthesis for the amino acids we find on acid hydrolysis. Polypeptides may also be present. Further investigations of the brown polymer are in progress.

OPTICAL RESULTS AND CONCLUSIONS

The ultraviolet transmission spectrum through the brown polymer in these experiments was obtained between 2750 Å and 8000 Å on a Cary 14 double-beam spectrophotometer. First, two Pyrex pieces from two nearly identical fragments of a 12-liter Pyrex bulb were run against each other to provide a baseline. Then one of these pieces was replaced by a similarly sized and shaped fragment from the 12-

liter Pyrex globe used in the actual experiment and to which the brown polymer adhered. The difference between the results of these two double-beam experiments is shown in Fig. 7. The estimated errors in the measurements are the sizes of the points shown. These transmission measurements confirm that the polymer is very red. If we consider the steepest portion of the curve between about 3000 Å and about 5200 Å we find a transmissivity decline of somewhat over an order of magnitude, which corresponds to a wavelength dependence of absorption optical depth $\sim\lambda^{-2}$. A still redder material which goes as λ^{-4} in a planetary atmosphere can dominate the color effects due to Rayleigh scattering. Thus, an atmosphere with a large abundance of such polymer can have its geometric albedo decline monotonically with decreasing wavelength; while another atmosphere with a low abundance of such polymeric material can have the effects of Rayleigh scattering dominate and have, after an initial decline of reflectivity with decreasing wavelength, a gradual turnout at the shortest wavelengths. If we compare visible and near-ultraviolet observations for the clouds of the outer solar system, we find both effects present. Our polymer is quite red, but not this red.

The thickness of the thin layer of

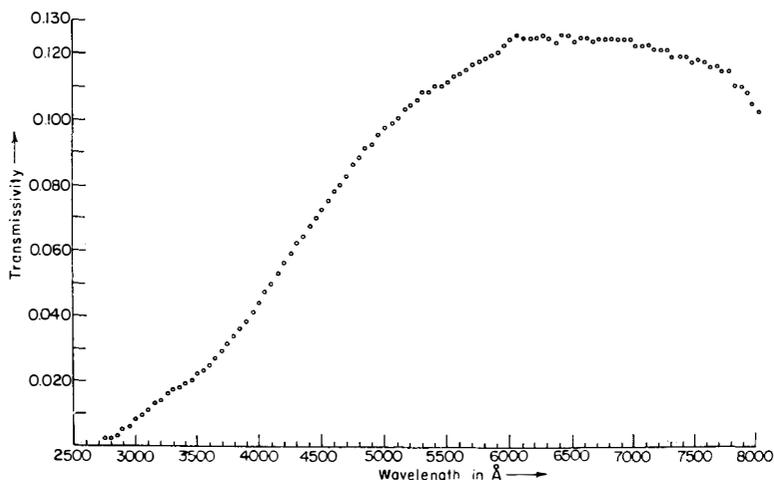


FIG. 7. Ultraviolet and visible transmittance spectrum of brown polymeric material taken on Cary-14 spectrophotometer. Path length estimated is 0.03 ± 0.02 mm.

reddish-brown polymer produced on our Pyrex vessel is not trivial to measure. Microscopic examination shows fine granular material deposited with some larger crystals, of various shapes and sizes. The thickness of the granular material was examined by a traveling stage microscope and also by a spectrum-measuring magnifier with built-in scale. In addition, measurements were made on a Gaertner linear comparator, commonly used for measurements on spectrographic or X-ray diffraction plates. The average thickness of the film giving the transmissivity shown in Fig. 7 is 0.03 ± 0.02 mm. The largest crystals, however, were found to be as large as 0.15 mm. From the transmissivities in Fig. 7 this thickness of film implies an absorption coefficient $k_v \sim 10^3$ cm^{-1} . As an example purely of heuristic interest, if each monomer in our polymer had a molecular weight ~ 1000 , the corresponding absorption coefficient would be $\sim 10^{-18}$ cm^2 per monomer.

The substantial similarity of our laboratory curves with the appropriate transmissivity deduced for the outer planets, as well as the similar visual color impression, lends some credence to the idea that the brown polymer reported here is similar in composition to the clouds of Jupiter, Saturn, and Titan. However, this is clearly a preliminary conclusion and further observations are needed. Mariner Jupiter/Saturn ultraviolet, visible, and infrared observations will be very useful. The predominance of aliphatic hydrocarbons in our sample at high C numbers resembles the organic chemistry of both carbonaceous chondrites (see, e.g., Anders *et al.*, 1973) and of terrestrial precambrian sediments (see, e.g., Kvenvolden, 1972). However, aromatics dominate in the meteorites and alkanes in the sediments. Amino acids are also recovered from both sets of samples. The infrared spectra are similar to our polymer spectra.

Our infrared spectra show only a small 2050-cm^{-1} nitrile absorption (Fig. 2), compared with a much more striking 2050-cm^{-1} feature in the HCN-NH₃ condensation of Woeller and Ponnampuruma (1969, their Fig. 8). Thus, polymers which

are not synthesized in an excess of nitriles may be transparent in the 4- to 5- μm gas window of reducing planetary atmospheres and observations to great depths may, despite multiple scattering, be feasible in this window.

It is clear that much closer study, particularly by gas chromatography, of our polymer and other polymers produced under similar conditions is warranted. But it appears possible that ultraviolet synthetic processes—as well as Fischer-Tropsch processes (Anders *et al.*, 1973)—contributed to the prebiological organics in meteorite parent bodies and especially on the early Earth as well as to the chromophores of the outer solar system.

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