

THE MARTIAN SURFACE:
Other Evidence Suggesting Carbon Suboxide

William T. Plummer
Polaroid Corp.
38 Henry St.
Cambridge, Mass. 02139

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News stories and journal articles about the Viking biology experiments have been carefully worded to include the possibility of explaining all the observations through "fancy chemistry". I believe that Mr. Oyama has had remarkable success in doing so.¹ Carbon suboxide, which he has invoked in explaining the results of the Pyrolytic-Release experiment, is an unusually interesting material.

SOME PROPERTIES OF CARBON SUBOXIDE

Carbon suboxide was first produced by Diels and Wolf in 1906.² They formed their sample by detaching two water molecules from the structure of the malonic acid molecule, leaving C_3O_2 . The monomer liquifies at 6.8°C and freezes at -111.3°C. The structure appears to be linear: three double-bonded carbon atoms in a row with an oxygen atom at each end.³ It is very reactive and behaves as a ketene. At room temperature it can polymerize with some violence.⁴ Polymers of $N=50$ and more have been studied.⁵ These polymers normally grow on surfaces and show increasing coloration from pale yellow, orange, reddish brown, through dark brown, to violet and nearly black as the combining molecules form a conjugated system of double carbon bonds.⁶ This polymerization can be triggered by warming above 15 C, and at higher temperatures the molecular weight is roughly proportional to temperature. It can be triggered by ultraviolet light even below 0°C.⁷ The photopolymers differ slightly in structure from the thermal polymers.⁸ Radiation and ultrasound can trigger polymerization.^{9,10} Many catalysts, particularly acids, will trigger the polymerization at low temperatures.⁶ The polymer itself is autocatalytic, particularly

when it becomes slightly carbonized by the thermal separation of a CO₂ molecule.¹¹ The monomer and low-order polymers are vigorously hygroscopic, and change color somewhat as they are dampened.⁶ Hydrated polymers slowly fade in color upon prolonged exposure to both air and room light.⁶ With some catalysts the material will alter photochemically to leave a shiny gray deposit, possibly of carbon.⁶

THE ASTRONOMICAL LITERATURE

Carbon suboxide seems to have entered the astronomical literature in 1953, in William Sinton's Dissertation.¹² His thesis advisor was Professor John Strong, who had been educated as a chemist, and the two were trying to account for a slight yellow color in the Venus clouds and some features near 11 microns in the infrared reflection spectrum.¹³

Kuiper repeated this suggestion in 1957,¹⁴ and later looked without success for the gaseous monomer in the Venus spectrum.¹⁵ Meinel and Hoxie speculated that its presence on Venus might account for the low observed water vapor quantity.¹⁶

In 1967 Moroz mentioned the possibility that carbon suboxide might be present as an intermediate in the photochemical production of molecular carbon from carbon dioxide and carbon monoxide,¹⁷ and that polymerized C₂ might account for the Martian "blue haze". He reports that the possibility of carbon suboxide has not been analyzed in detail because it "rapidly decomposes", according to Kellog and Sagan.¹⁸ But Smith reports that the polymer is "much more stable than heretofore believed."⁶

Meanwhile, Professor Strong and I had obtained some high-altitude spectra of Venus in 1964 and had identified the clouds as ice.¹⁹ In

1968 this was still a controversial matter, and I was still looking for alternate materials with a similar infrared reflection spectrum. Robert Carson and I at the University of Massachusetts decided to run some reflection spectra of carbon suboxide monomer frost, partly because he needed a project for a senior honors paper. The monomer didn't match Venus, and we published the results.²⁰

MARS SPECTRUM

Naturally, we found the polymer various places in our vacuum distillation apparatus. And of course we recorded the reflection spectra of as many samples as possible under controlled conditions. When the March 7, 1969 issue of Science came I was surprised to find one of our new spectra there, particularly since McCord and Adams had captioned it as the spectral reflectivity of Mars.²¹

We compared the spectra in greater detail and found that carbon suboxide could provide at least as good a match as limonite or oxidized basalt.⁷ We especially noted the slight decrease from 0.30 to 0.35 micron, low reflectivity for violet and blue light, the proper curvature from 0.35 to 0.8 micron, a moderate peak at 0.8 micron, a shallow minimum near 1.1 micron, and generally high reflectivity at longer wavelengths. There is a general rise in reflectivity to about 1.8 micron, followed by a decline of about 50% from 1.8 to 3.0 micron, both on Mars and in our laboratory spectra.

At that time CO₂ was known to be plentiful on Mars, so photochemical production of carbon suboxide seemed at least as likely there as on Venus.

OTHER OBSERVATIONS

Mars has always been a puzzling planet, and we tried to match up the puzzles with what we had learned about carbon suboxide. We found that Dollfus' high measurement of water vapor on Mars at 1.38 micron²² could be interpreted easily if some water were bound to carbon suboxide polymer on the Martian surface, producing an absorption band in the reflection spectrum. We fantasized that if carbon suboxide were produced fast enough by favorable photochemistry it might account for the occasional strange yellow clouds of Mars which, unlike the blue and white clouds, are most commonly found in warm areas of the planet.²³ We found some suggestion that light and dark areas of Mars might correspond to different degrees of polymerization. We reasoned that changing molecular weights or amount of hydration might account for some of the seasonal color changes, such as the "wave of darkening" which closely follows the increased humidity as a polar cap evaporates in late spring.²⁴ When we published these ideas in 1969 we knew that most of our evidence was circumstantial, that certain combinations of minerals might be contrived to fit the Mars reflection spectrum, and that the real test would come years later when some kind of apparatus actually reached the surface of Mars and started sending back inexplicable data.

In 1970 I got a phone call at Polaroid from someone at Martin-Marietta in Denver, who asked how a Viking lander might directly test the surface of Mars for carbon suboxide. I tried to refer the caller to someone better qualified in chemistry, and strongly urged that such a test be included in the experiment package. Evidently I wasn't persuasive enough!

T. A. Perls at Martin-Marietta went over some of the considerations in Icarus in 1971.²⁵ He added some more reasons for suspecting carbon suboxide on Mars. The observed wind speeds of 4 m/sec or less were lower than the 21 to 80 m/sec believed necessary to raise clouds of dust. He pointed out that the great 1956 yellow clouds formed just after an exceptional solar flare which could have hastened polymerization through radiolysis. And he suggested that carbon suboxide polymerization might help explain the "blue haze" and "blue clearings" through removal of submicron carbon particles from the atmosphere. Unfortunately, he also set up a "straw man" in the form of a requirement for radiolysis, in this case 60 Mev solar protons, to initiate and sustain the polymerization. Those who have worked with carbon suboxide know that polymerization is easier to initiate than to prevent, even at Martian temperatures, if any sort of catalyst is present.

In 1973 Perls concluded that reduced support for a correlation between solar activity and yellow clouds, coupled with a failure to find the gaseous carbon suboxide monomer in the Mariner UV spectra, was evidence against carbon suboxide polymer on Mars.²⁶ If circumstantial positive evidence is risky, circumstantial negative evidence is riskier. Monomer in equilibrium with the polymer at the Mars surface temperatures would not be detectable, and the gaseous monomer should therefore show in atmospheric spectra only if it had an extremely high formation rate.

In passing I'll note an objection to carbon suboxide made by Caldwell in 1973, who attempted to separate the ultraviolet reflectivity of Mars below 0.35 microns into atmospheric (Rayleigh scatter) and surface contributions.²⁷ Caldwell found that the atmosphere would explain the

entire upturn in reflectivity below 0.35 micron, leaving none of it to be associated with our upturning C_3O_2 polymer spectrum, unless the Martian molecular atmosphere were more than 60% CO_2 . The Viking finding of about 95% removes this objection.²⁸

When the first results of the Viking chemistry experiments were released I was most excited by the CO_2 produced in the Pyrolytic Release experiment, because CO and CO_2 are known pyrolytic products of carbon suboxide,²⁹ and even a similar exchange of carbon isotopes has been reported.^{30,31} About the middle of August I telephoned JPL and tried to reach Dr. Klein, who was in a meeting. Richard Johnson amiably hinted that others, too, had been offering their advice. It's probably quite a collection! I cited our publication in Science and left my phone number.

With new courage I've looked back over the familiar Mars observations for other suggestions of carbon suboxide. Öpik has pointed out that if the yellow clouds are believed to be dust storms, then we must explain how the dark areas regain their darkness after having been covered with dust.³³ Progressing polymerization can do the trick.

Carl Sagan has pointed out that if we had some of the "blue haze" -- whatever it is -- in a bottle, it would appear red.³² He further proposes that the observations interpreted as a "blue haze" may be explained by a purely surface effect, the similarity of reflection properties of the dark and light areas in blue and violet light. Although the available spectra represent only a skimpy sampling of the range of molecular weights, some carbon suboxide polymers⁶ do appear to have similar or slightly reversed reflectivity differences below 0.4 micron. Perhaps a "blue clearing" is merely a time when the surface composition

in the dark areas is slightly altered. In the major clearing of 1939, Hess found that during a "blue clearing" the seasonal cycle of the dark areas was halted.³⁴

Speaking of the seasonal "wave of darkening", Sagan also asserts that "no materials on Earth are known which change their darkness (or color) in the manner observed on Mars due to such a small increase in the absolute quantity of moisture."³⁵ Smith⁶, commenting on carbon suboxide, reports that "the low-temperature polymers react immediately with the water vapor in the air to give a different colored polymer."

In 1956 and 1958 Sinton found absorption bands at 3.45, 3.58, and 3.69 microns in the infrared reflection spectra of dark areas of Mars, such as Syrtis Major.³⁶ These absorptions caused some excitement because they were thought to characterize C-H bonds, suggesting the possibility of large organic molecules or life on Mars. When hydrated, carbon suboxide and its polymers contain C-H bonds. (The hydrated monomer is malonic acid, with two.) Infrared spectra of the hydrated polymers by Diallo³⁷ and by Wojtczak³⁸ show some well-defined absorptions between 2.8 and 3.7 microns, and Diallo also shows that the absorptions are not present before hydration.

NEW EVIDENCE

I'd like to suggest two new observations from the Viking mission itself which seem to support the presence of carbon suboxide. First, the Martian soil is reported to be as "cohesive as wet sand."³⁹ From experience with glassware tenaciously decorated with pretty colors I believe that similar cohesive properties can be created artificially in a test tube of clean sand or dust by polymerizing carbon suboxide on

the particles and letting in a small amount of water vapor.

Second, the strong coloration is reported not to penetrate the Mars rocks but instead to form a thin outer veneer on them, similar to "desert varnish."^{39,40} If these coatings are either limonite or oxidized basalt, then presumably they formed when the Martian atmosphere was more oxidizing than at present. On the other hand, the semicircular depressions around two rocks on Mars are presented as evidence of wind scouring.⁴⁰ In a non-oxidizing atmosphere such scouring implies a loss mechanism for the thin colored layer; thus, in turn, there must exist an efficient replacement mechanism (such as the suboxide polymerization) to maintain the vivid reddening of essentially all accessible surfaces.

If the Viking sites can be observed for an extended time, we may learn what actually happens in a "dust storm" and whether mechanical devices also accumulate "desert varnish."

If comprehensive studies continue to support the presence of carbon suboxide, perhaps we should postulate that this material was present in Earth's primordial atmosphere, as has been suggested by Raff,⁴¹ and that this reactive substance may have had a key role in assembling the first biological molecules on this planet. Perhaps Mars is merely stalled at a preliminary level of biochemical evolution.

REFERENCES

1. V. Oyama; quoted in "One Man's Mars: No Martians," *Science News* 111, 149-150(1977).
2. O. Diels & B. Wolf, *Ber. Deut. Chem. Ges.* 39, 689 (1906).
3. F. A. Miller & W. G. Fatel, "The IR Spectrum of Carbon Suboxide", *Spectrochimica Acta* 20, 253-266 (1964).
4. O. Diels & G. Meyerheim, "Über das Kohlensuboxyd (II)", *Ber. Deut. Chem. Ges.* 40, 355-363 (1907).
5. A. R. Blake, W. T. Eeles, & P. P. Jennings, "Carbon Suboxide Polymers. I. Structure of Thermal Polymers", *Trans. Faraday Soc.* 60, 691-699(1963).
6. R. N. Smith, D. A. Young, E. N. Smith, & C. C. Carter, "The Structure and Properties of Carbon Suboxide Polymer", *Inorg. Chem.* 2, 829-38(1963).
7. W. T. Plummer & R. K. Carson, "Mars: Is the Surface Colored by Carbon Suboxide," *Science* 166, 1141-2 (1969).
8. R. N. Smith, R. A. Smith, & D. A. Young, "The Photolysis of Carbon Suboxide," *Inorg. Chem.* 5, 145-8 (1966).
9. D. P. Kiryukhin, I. M. Barkalov, V. I. Gol'danskii, "Low-Temperature Radiation Polymerization of Carbon Suboxide," *Vysokomol. Soedin., Ser. A.* 18, 759-62 (1976).
10. G. Wagner, "Some Chemical Reactions in the Ultrasonic Field," *Mitt. chem. Forsch.-Inst. Ind. österr.* 3, 63-5 (1949).
11. A. R. Blake, "The Thermal Polymerisation of Carbon Suboxide," *J. Chem. Soc.* 1965, 3866-7 (1965).
12. W. M. Sinton, Dissertation, Johns Hopkins Univ., Balto. Md. (1953).
13. W. M. Sinton & J. Strong, "Radiometric Observations of Venus," *Ap. J.* 131, 470 (1960).
14. G. P. Kuiper, "The Threshold of Space," ed. M. Zelikoff (Pergamon Press, New York, 1957), p. 85.
15. G. P. Kuiper, G. T. Sill, D. P. Cruikshank, U. Fink, "Infrared Spectrum of Carbon Suboxide," *Sci. Tech. Aerosp. Rep.* 7, 566 (1969).
16. A. B. Meinel & D. T. Hoxie, "On the Spectrum of Lightning in the Atmosphere of Venus," *Comm. Lunar and Planet. Lab.* 1, 35-38 (1962).

17. V. I. Moroz, "Physics of Planets" (Nauka Press, Moscow, 1967); NASA TT F-515.
18. U. Kellogg & C. Sagan, "The Atmospheres of Mars and Venus," Natl. Acad. Sci. Natl. Res. Council, Publ. 944, Ch. IV, 37-50 (1961).
19. M. Bottema, W. Plummer, J. Strong, & R. Zander, "Composition of the Clouds of Venus," Ap. J. 140, 1640-41 (1964).
20. W. T. Plummer & R. K. Carson, "Venus Clouds: Test for Carbon Suboxide," Ap. J. 159, 159-163 (1970).
21. T. B. McCord and J. B. Adams, "Spectral Reflectivity of Mars," Science 163, 1058-60 (1969).
22. A. Dollfus, "Mesure de la vapeur d'eau dans les atmosphères de Mars et de Venus," Mem. Soc. Roy. Sci. Liège 2, 392-395 (1964).
23. E. C. Slipher, "A Photographic History of Mars, 1905-1961" (Lowell Obs., Flagstaff, Ariz., 1962).
24. P. Moore, "A Guide to the Planets" (W. W. Norton & Co., N.Y., 1954), p.99.
25. T. A. Perls, "Carbon Suboxide on Mars. A Working Hypothesis," Icarus 14, 252-64 (1971).
26. T. A. Perls, "Carbon Suboxide on Mars. Evidence Against Formation," Icarus 20, 511-512 (1973).
27. J. Caldwell, "Ultraviolet Observations of Mars Made by Orbiting Astronomical Observatory," Icarus 18, 489-496 (1973).
28. W. D. Metz, "Viking(II): Water, Ice and Argon -- Three Puzzles Resolved," Science 194, 924-927 (1976).
29. A. R. Blake & A. F. Hyde, "Carbon Suboxide Polymers. II. Pyrolysis of Thermal Polymers," Trans. Faraday Soc. 60, 1775-82 (1964).
30. M. A. Rollier, V. Maxia, & M. Secci, "Labeling of Carbon Suboxide in a Radiation Field," Radioisotopes Phys. Sci. Ind., Proc. Conf. Use, Copenhagen, 1960, 2, 465-469 (1962).
31. A. Faucitano & V. Maxia, "Possibilities of Isotopic Exchanges Between C₃O₂ and CO Labeled with C¹⁴, in Presence and in Absence of Ionizing Radiations," Ric. Sci. Rend. Sez. A 3, 131-40 (1963).
32. I. S. Shklovskii & C. Sagan, "Intelligent Life in the Universe," (Holden-Day, San Francisco, 1966), p. 266.

33. P. Moore, *op. cit.*, p. 100.
34. S. L. Hess, *Lowell Obs. Bull.* 42 (1952). Reported by F. Jackson & P. Moore, "Life on Mars" (W. W. Norton & Co., N.Y., 1965), p. 30.
35. I. S. Shklovskii & C. Sagan, *op. cit.*, p. 280.
36. W. M. Sinton, "Spectroscopic Evidence for Vegetation on Mars," *Ap. J.* 126, 214-39 (1957); "Further Evidence of Vegetation on Mars," *Science* 130, 1234-37 (1959).
37. A. O. Diallo, "Analysis by Infrared Spectroscopy of a Polymer of C_3O_2 ," *J. Chim. Phys.* 61, 1409-13 (1964).
38. J. Wojtczak, L. Weimann, & J. M. Konarski, "Einige Bemerkungen zur Struktur des Kohlensuboxidpolymeren," *Monatsh Chem.* 99, 501-8(1968).
39. J. K. Beatty, "Viking 1 Lands on a Very Red Planet," *Sky & Tel.* 52, 156-161 (1976).
40. T. A. Mutch, *et al.*, "The Surface of Mars: The View from the Viking 1 Lander," *Science* 193, 791-801 (1976).
41. R. A. Raff & G. M. Meaburn, "Photochemical Reaction Mechanism for Production of Organic Compounds in a Primitive Earth Atmosphere," *Nature* 221, 459-60 (1969).