

Croconic Acid: An Absorber in the Venus Clouds?

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Croconic acid, a polymer of carbon monoxide, exhibits very strong absorption in the blue and near ultraviolet. We propose that this material, as a minor contaminant of the sulfuric acid cloud droplets, may represent the absorber responsible for the ultraviolet cloud features and the pale yellow color of the Venus clouds. The results of measurements of the absorption coefficients for a dilute solution of croconic acid in sulfuric acid are presented and used in models of the scattering by the clouds to show that the observed behavior of the planetary albedo in the blue and near ultraviolet can be qualitatively reproduced. We also propose a possible mechanism for the production of croconic acid in the cloudtop region on Venus. © 1989 Academic Press, Inc.

I. INTRODUCTION

To the naked eye the thick cloud layer on Venus exhibits a pale yellow color, while at shorter wavelengths in the near ultraviolet we encounter horizontal variations in the absorption which are responsible for the so-called UV cloud features. The identification of the principal cloud constituent as concentrated sulfuric acid droplets (cf. Sill, 1972; Young, 1973) did little to address the issue of the absorber(s) in the blue and near ultraviolet because sulfuric acid is transparent in that wavelength region. Over time quite a number of candidate absorbers have been proposed, e.g., carbon suboxide (Sinton, 1953; Kuiper, 1957; Shimizu, 1977), hydrated ferrous chloride (Kuiper, 1969), sulfur (Hapke and Nelson, 1975; Young, 1977; Toon *et al.*, 1982), hydrobromic acid (Sill, 1975), sulfur dioxide (Pollack *et al.*, 1979), and chlorine (Pollack *et al.*, 1980). The presence of sulfur dioxide in the cloud-

top region has in fact been unambiguously established from ground-based spectra (Barker, 1979) and from Pioneer Venus ultraviolet spectrometer observations (Esposito *et al.*, 1979). However, it is now obvious that while sulfur dioxide is an important absorber shortward of approximately 320 nm, it cannot be responsible for the absorption apparent at the longer wavelengths (cf. Esposito, 1980; Pollack *et al.*, 1980).

At present, elemental sulfur seems to be the favored candidate for explaining the requisite absorption longward of the sulfur dioxide bands (cf. Toon *et al.*, 1982). However, that thesis is still based on inferential evidence and depends sensitively on an appropriate admixture of the metastable allotropes S_3 and S_4 with the normal orthorhombic sulfur S_8 . The optical constants of the various sulfur forms are not well known, so the spectral behavior of such a model is qualitative.

We propose that croconic acid, $C_5O_5H_2$, as a contaminant dissolved in the concentrated sulfuric acid droplets of the Venus clouds represents an interesting alternative candidate absorber. Several strong and rel-

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atively broad absorption bands in the blue and near ultraviolet impart an intense yellow color to croconic acid and croconate solutions. Although it is a somewhat more complex molecule than might ordinarily be expected to be present, we propose a possible mechanism for producing croconic acid in the cloudtop region of the Venus atmosphere through an acid-catalyzed polymerization of carbon monoxide. We report here the results of our measurements of the absorption coefficients for croconic acid dissolved in concentrated sulfuric acid. These optical properties are then employed in detailed scattering models for the clouds which show that a modest degree of contamination by croconic acid is in fact capable of producing the basic features of the planetary albedo in the blue and near ultraviolet.

II. MEASUREMENTS

Potassium croconate was prepared using the method described by Carlqvist and Dyrssen (1962). Specifically, 16.8 g (0.285 mole) of potassium hydroxide was added to 330 ml of deionized water with stirring, followed by the addition of 15 g (0.061 mole) of rhodizonic acid dipotassium salt. This solution was heated to 55°C with magnetic stirring, and air was bubbled through until the solution changed color (approximately 15 min). The temperature of the solution was increased to 100°C and maintained until the volume was reduced to about 50 ml. The solution was then cooled in ice and produced orange needles of the hydrated potassium croconate crystals, which were collected under suction and dried in a desiccator for approximately 24 h. Elemental analysis gave C 27.26%, H <0.01%, K 35.2%, and O 37.5% compared with the theoretical values C 27.52%, H 0.00%, K 35.8%, and O 36.7%.

Crystals of potassium croconate were dissolved in 84% (by weight) concentrated sulfuric acid to prepare a dilute solution of 2×10^{-5} mole of croconic acid per liter of

sulfuric acid. The 84% sulfuric acid concentration was selected based upon the determination by Pollack *et al.* (1978) that the best fit to the near-infrared spectrum for Venus is achieved for cloud droplets of that concentration. A sample of the croconic acid-contaminated sulfuric acid solution was placed in the 1-cm cell of a Perkin-Elmer Lambda 3B UV spectrometer, which was used to determine the absorption coefficient in the near ultraviolet and blue as shown in Fig. 1. Although the solution appears to exhibit its peak absorption near 300 nm, we note substantial absorption well into the blue portion of the spectrum. The specific values for the absorption coefficients represented in Fig. 1 of course apply only for the concentration of 2×10^{-5} mole croconic acid per liter of sulfuric acid, or a molar mixing ratio of 6.48×10^{-7} . However, since the absorption is due solely to the croconic acid and involves no reaction between it and the sulfuric acid, the absorption coefficient at a particular wavelength for a different concentration is just that shown in Fig. 1 scaled by the ratio of concentrations.

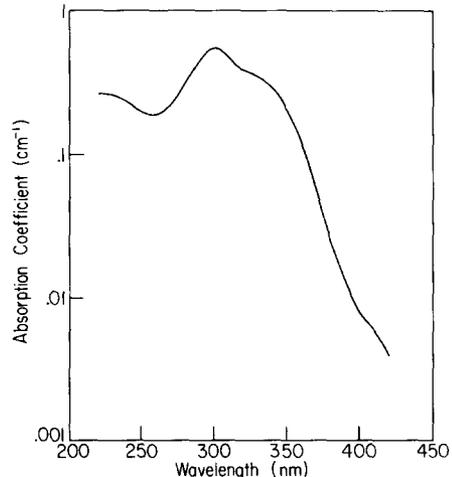


FIG. 1. Absorption coefficient for a dilute solution of $20 \mu\text{mole}$ of croconic acid per liter of concentrated sulfuric acid.

III. PLANETARY ALBEDO

We now turn to the examination of theoretical models of the scattering of sunlight by the clouds on Venus under the assumption that some portion of the cloud system consists of concentrated sulfuric acid droplets contaminated by croconic acid. The degree of concentration of the contaminant is the primary free parameter which we adjust within reasonable limits to determine if absorption by the croconic acid is capable of producing the essential features of the planetary albedo in the near-ultraviolet and blue portion of the spectrum. For a specific concentration of croconic acid, the absorption coefficients scaled from the results shown in Fig. 1 are used in Mie scattering computations which provide the single scattering albedo and scattering phase function for the cloud particles. This in turn serves as input for multiple scattering computations for the entire cloud system, providing the theoretical spherical albedo for the model at a selected set of wavelengths.

Previous analysis and interpretation of Pioneer Venus observations strongly suggest that the unidentified absorber must be located vertically in the lower portion of the so-called upper cloud (cf. Tomasko *et al.*, 1980; Pollack *et al.*, 1980). Vertical variation in cloud properties observed at the Pioneer Venus Large Probe location led to the characterization of the cloud system in terms of three regions of distinct cloud structure and particle populations (cf. Knollenberg and Hunten, 1980). The upper cloud above the altitude of 56.2 km (411-mb pressure level) has a particle distribution that is bimodal: mode 1 particles with an effective radius of order 0.15–0.3 μm , and mode 2 particles of about 1.0- μm radius. Mode 2 particles are responsible for about two-thirds of the extinction optical thickness of the upper cloud at visible wavelengths. In the middle cloud region from 49.7 to 56.2 km (1.044 to 0.411 bars), a third particle population with a radius of order 3.2 μm is apparent in the data from the

cloud particle spectrometer (LCPS) on the Pioneer Venus Large Probe (Knollenberg and Hunten, 1980), and it contributes approximately one-half of the total optical thickness for that cloud region. A lower cloud, in which mode 3 particles are dominant with respect to cloud extinction, is found in the altitude range 47.7 to 49.7 km (1.34 to 1.044 bars). By adopting this cloud structure and placing the croconic acid contaminant in the lower portion of the upper cloud, the free parameters for our model are the concentration of croconic acid in the sulfuric acid cloud droplets and the location of the top of the absorbing layer.

With the basic cloud structure as described above, the spherical albedo for Venus over visible wavelengths longward of about 330 nm would be well in excess of 90% if there were no absorption other than that due to sulfur dioxide and pure concentrated sulfuric acid. The addition of an absorbing contaminant to the sulfuric acid droplets decreases the single scattering albedo for the particles with the consequence that each scattering event for a photon results in further light being absorbed, thus producing a lower overall spherical albedo. Our preliminary model calculations showed that if the top of the absorbing layer is placed too high, a croconic acid concentration sufficient to produce an appropriate spherical albedo at 420 nm yields an albedo much too low at shorter wavelengths owing to the strong wavelength dependence of the croconic acid absorption. Rather, we require a nearly nonabsorbing top layer of optical thickness on the order of 3 or 4, which produces a spherical albedo of order 0.4 irrespective of how absorbing (and hence, intrinsically dark) the layers below may be. This is qualitatively consistent with the inference that the absorber must be located somewhat below the cloud tops to produce the decrease in contrast of the UV features observed at increasing phase angles in Venera photometry (Ksanfomaliti *et al.*, 1976) and in Pioneer Venus images (Travis *et al.*, 1979; Esposito, 1980; Pollack

et al., 1980). Young (1977) earlier concluded that a strongly absorbing layer must lie below optical depth 4 to produce the reflectance on the order of 0.5 observed in the ultraviolet.

For the sake of simplicity and without evidence to the contrary, we assume that particles of both modes 1 and 2 are contaminated by the same percentage concentration of croconic acid in the absorbing cloud layer. That degree of concentration and the location of the top of the absorbing layer were adjusted to achieve the best overall fit between the observed spherical albedo over the wavelength range 330–420 nm and those values calculated for our model. For an upper boundary of the absorbing layer placed at the 98-mb level and a 2.5% concentration of croconic acid, we find a spherical albedo of 0.74 at 420 nm decreasing to 0.54 at 330 nm. The wavelength-dependent albedo corresponding to this best fit is indicated by the solid line in Fig. 2. Open circles represent observed spherical

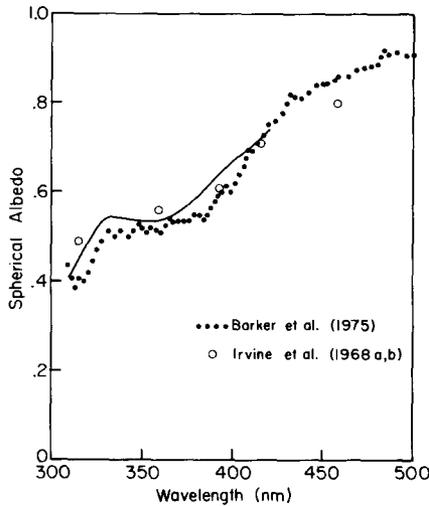


FIG. 2. Theoretical spherical albedo (solid line curve) for the cloud model compared to the wavelength-dependent albedo derived from observations of Venus by Barker *et al.* (1975) and Irvine *et al.* (1968a, b). The cloud model has an absorbing layer located between 98 and 411 mb in which the sulfuric acid cloud droplets are contaminated by a 2.5% concentration of croconic acid.

TABLE I
SUMMARY OF CLOUD MODEL STRUCTURE

Region	Altitude (km)	Pressure (mb)	Optical depth ^a	Single scattering albedo ^a
Upper cloud				
Top portion	>64.3	<98	4.67	0.9995
Absorbing layer	56.2–64.3	98–411	7.04	0.7315
Middle cloud	49.7–56.2	411–1044	7.38	0.9995
Lower cloud	47.7–49.7	1044–1340	7.35	0.9995

^a At a wavelength of 360 nm.

albedo values at 314.7, 359.0, 392.6, 415.5, and 457.3 nm based upon cloud scattering model fits (Travis, 1975) to multicolor photometry over phase angles from 36.5° to 158.7° by Irvine *et al.* (1968a, b). The dots in Fig. 2 correspond to Venus spectrophotometry by Barker *et al.* (1975) for phase angles near 76°, normalized to the albedo at 626.4 nm from the Irvine *et al.* data.

Table I provides a summary of the gross structure of the cloud model which yields the best fit albedo curve shown in Fig. 2. Optical depth and single scattering albedo values tabulated for each layer are for a wavelength of 360 nm. For each of the layers other than the absorbing layer, we assume a single scattering albedo of 0.9995, independent of wavelength. This assumption of a nearly conservative scattering behavior for these layers thus corresponds to the vertical distribution of the UV absorption implied by the analysis described by Tomasko *et al.* (1980). Locations of the boundaries for the lower and middle cloud layers and the particle distributions in each are those specified by Knollenberg and Hunten (1980) from analysis of the LCPS data. However, we have reduced their number densities for mode 3 particles by 41% in the middle cloud and 23% in the lower cloud as suggested by Tomasko *et al.* in order to be consistent with the *in situ* solar flux measurements. Mie scattering computations provide the phase functions and extinction coefficients for each of the particle modes.

For the upper cloud, the *in situ* LCPS

data on particle size distributions are restricted to altitudes below about 66 km. However, model inversions of narrow-band flux data at 630 nm from the solar flux radiometer (LSFR) on the Pioneer Venus Large Probe indicate that the cloud optical thickness above the 64-km level at which LSFR measurements began must be on the order of 4 (Tomasko *et al.*, 1980). Analyses of remote sensing observations of the polarization of sunlight reflected from the clouds indicate the presence of both mode 1 and 2 particles at the 30-mb (71 km) level, with mode 1 contributing about 6.5% of the opacity at 935 nm (Kawabata *et al.*, 1980). This implies a number density of mode 1 particles 8.2 times that of mode 2, which is in reasonable agreement with the 10.1 ratio in the LCPS data for the altitude range 62.5 to 66.1 km. Accordingly, we adopt a number density ratio of 8.2 and use the mode 1 and 2 particle size distribution parameters given by Kawabata *et al.* throughout the region above 64.3 km. The total optical thickness of 4.17 for 630 nm from Table 6 of Tomasko *et al.* thus corresponds to 4.57 at 360 nm.

Table II summarizes the optical depths at 360 nm for each particle mode within the layers of our cloud model. The total optical depth listed in Table I is just the sum for the three modes plus the contribution due to Rayleigh scattering. There is a modest wavelength dependence of the optical thicknesses for the cloud particle modes which is specified through the Mie scattering computations, and the Rayleigh scattering of course follows the approximate λ^{-4}

variation. In addition, for wavelengths shortward of 330 nm, we include the contribution by sulfur dioxide absorption to the total extinction optical depth. The sulfur dioxide mixing ratio is set at 1×10^{-7} at the 40-mb level and is presumed to vary with a scale height of 1 km as inferred from the measurements of the ultraviolet spectrometer on the Pioneer Venus Orbiter (Esposito *et al.*, 1979). Following Pollack *et al.* (1980), we fix the mixing ratio at a constant value of 5×10^{-6} for altitudes below the point at which the scale height of 1 km would otherwise imply higher values. The sulfur dioxide absorption cross sections measured by McGee and Burris (1987) are used for wavelengths below 320 nm and those of Wu and Judge (1981) for 320–330 nm.

For all cloud layers other than the absorbing layer, the particle refractive index is assumed to be that for pure 84% concentrated sulfuric acid (Palmer and Williams, 1975). The imaginary part of the refractive index, n_i , for the particles within the absorbing layer is specified by $n_i(\lambda) = \lambda \alpha(\lambda) / (4\pi)$, where the wavelength-dependent absorption coefficient, $\alpha(\lambda)$, is scaled from that shown in Fig. 1 to correspond to the 2.5% concentration of croconic acid. The real part of the refractive index, n_r , is specified using $n_i(\lambda)$ in a subtractive Kramers–Kronig analysis (cf. Ahrenkiel, 1971) in which we choose a reference wavelength sufficiently far from the absorption bands of croconic acid so that the refractive index is just that of sulfuric acid, viz., $n_r = 1.427$ at 700 nm. Table III summarizes the resulting refractive indices and the corresponding single scattering albedos for the mode 1 and 2 cloud particles.

Spherical albedos corresponding to the cloud models are calculated using the doubling/adding technique (cf. Hansen and Travis, 1974) to account for multiple scattering within each cloud layer and to determine the reflection for the combined set of layers. Each layer is assumed to be homogeneous; i.e., the single scattering albedo

TABLE II

CLOUD MODEL OPTICAL DEPTHS AT 360 nm

Region	Mode 1	Mode 2	Mode 3	Rayleigh scattering
Upper cloud				
Top portion	1.16	3.41	—	0.10
Absorbing layer	2.46	4.25	—	0.33
Middle cloud	0.37	3.35	3.02	0.64
Lower cloud	0.49	1.72	4.83	0.31

TABLE III

OPTICAL PROPERTIES OF SULFURIC ACID DROPLETS
CONTAMINATED WITH CROCONIC ACID

Wavelength (nm)	n_r	n_i	Single scattering albedo	
			Mode 1	Mode 2
310	1.481	4.47×10^{-2}	0.6166	0.5287
320	1.482	3.83	0.6399	0.5361
330	1.484	3.52	0.6549	0.5422
340	1.487	3.01	0.6802	0.5557
350	1.489	2.20	0.7283	0.5919
360	1.486	1.32	0.8011	0.6706
370	1.480	0.648	0.8823	0.7879
380	1.474	0.297	0.9395	0.8854
390	1.469	0.158	0.9666	0.9349
400	1.465	0.0994	0.9788	0.9581
410	1.462	0.0761	0.9839	0.9677
420	1.459	0.0520	0.9891	0.9776

and phase function are independent of height within the layer. However, for wavelengths where sulfur dioxide absorption is important, we split the topmost layer into two regions, 0–40 and 40–98 mb, to better represent the vertical distribution corresponding to the small scale height for the sulfur dioxide mixing ratio.

IV. MECHANISM OF PRODUCTION OF CROCONIC ACID

The proposed polymerization of carbon monoxide shown schematically in Fig. 3 involves the reversible cationic addition of successive carbon monoxide units until a five-carbon chain is formed. The chain undergoes ring closure, losing an oxygen molecule in the process and producing croconic acid (7 in Fig. 3). This set of reactions will occur in the liquid phase as neither the initiating species, H^+ , nor the product acids, **1C** through **5C**, are particularly volatile.

The initiation step is the attack of a hydrogen ion (from the abundant sulfuric acid in the atmosphere) at one of the oxygens of a carbon dioxide molecule to form the protonated species **1A**. In the most favored resonance form, the positive charge is centered on the carbon, and the cation formed is reasonably stable (Yu *et al.*, 1986); it will

certainly have an appreciable lifetime at the low temperatures and pressures associated with the upper cloud layer. This cation then begins adding carbon monoxide to form **2A** through **5A**, with the formal positive charge transferring to the carbon at the growing end of the polymer with each successive addition. These carbon monoxide insertion reactions are almost identical with the Koch reaction in organic chemistry (cf. March, 1985). Structure **2A** is able to stabilize the positive charge by delocalization across two of the carbonyl groups compared to **1A**, but no further benefit is gained by successive carbonyl additions. Thus, structures **2A** to **5A** are similar in energy and, discounting entropic effects, the rates of forward and reverse reactions between the species will be approximately equal. The equilibrium constants will be on the order of 1.0 for these reactions. The slowest step of the process will be the first addition step, the conversion of **1A** to **2A**.

During this reaction set, water may add to and be eliminated from the growing cation a number of times, forming the nB and nC species. This will not affect the primary reaction path from **1A** to **5A**; it will simply provide a reservoir of additional precursors for each of the carbonium ions. For n of 4 or less, this diacid is a stable species and will not decompose except by the dehydration route shown. When n is 5, however, the diacid can undergo photochemical ring closure: **5C** to **5D** to **6** to form the bicyclic dioxetane. Loss of oxygen from this species will then produce the five-membered oxocarbon, croconic acid (7). The ring closure step is a 2+2 photochemical reaction and, as such, is stereospecific. That is, the two carbonyl groups involved will rotate toward each other; either both up above the future plane of the ring or both down below the plane, bringing the oxygens together in a one-step process (Woodward and Hoffman, 1971). Oxygen loss from this bicyclic intermediate will be rapid.

Should the cation add another carbon monoxide before ring closure occurs, the

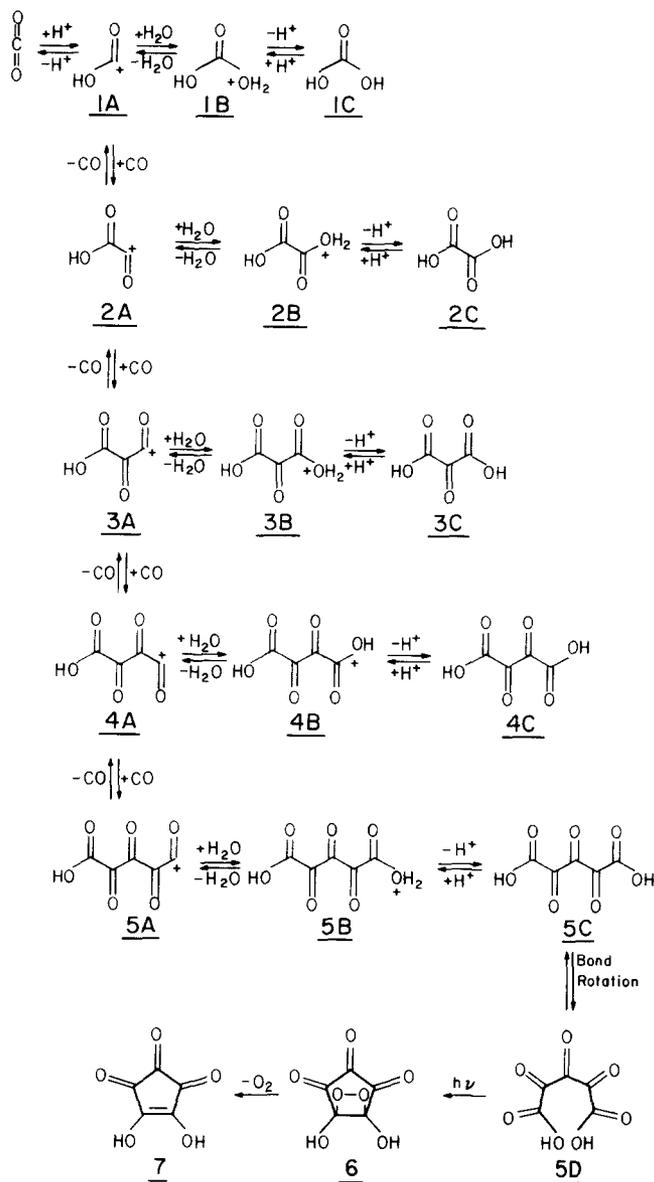


FIG. 3. Reaction path for the synthesis of croconic acid from carbon monoxide.

six-membered oxocarbon, rhodizonic acid, will be formed. This is an unstable species at low pH, and is quickly destroyed under the conditions expected in the upper cloud layer. Even if the reaction of 5C to produce croconic acid is inefficient, the process is essentially irreversible. Thus, a significant concentration of croconic acid can be built

up given the fact that the main reaction path 1A to 5A consists of equilibria with constants on the order of unity.

Once the croconic acid is produced, its stable nature then raises the question of how those sulfuric acid droplets so contaminated are confined to the lower portion of the upper cloud as indicated by the *in situ*

probe observations. Even assuming that the upper cloud is the production region for croconic acid, we would expect that normal sedimentation would result in contaminated droplets eventually populating the middle and lower cloud layers as well. There is no obvious chemical loss mechanism for croconic acid under this range of conditions; it is expected to be stable for temperatures throughout the cloud system. Absent a likely decomposition mechanism, it may well be that the answer lies with the as yet unknown process responsible for the observed cloud layering. The characterization of distinct upper and middle cloud layers was based on Pioneer Venus LCPS data (Knollenberg and Hunten, 1980) which showed a transition region of approximately 1-km thickness within which there was a sharp decrease in particle number density. There is also the appearance of mode 3 particles in the middle cloud, while such particles are absent above this transition region. It would thus appear that some process creates an effective separation between upper and middle cloud layers; whether it can also constrain the location of the contaminated sulfuric acid droplets is presently unknown.

V. SUMMARY

We find that croconic acid exhibits sufficient absorption in the blue and near ultraviolet so that a 2.5% contamination of the sulfuric acid droplets over the 56.2 to 64.3-km altitude range of the Venus cloud system is capable of producing a wavelength-dependent spherical albedo in good agreement with observations as illustrated in Fig. 2. Total cloud columnar mass within the absorbing layer is approximately 8×10^{-4} g cm⁻², corresponding to a volume mixing ratio for sulfuric acid of about 8×10^{-7} for that region of the atmosphere. The 2.5% croconic acid concentration required by our model thus represents a mixing ratio of only 2×10^{-8} . While we cannot demonstrate the actual existence of croconic acid

in the cloudtop region of Venus, it seems plausible that the suggested mechanism for its production may be operative and capable of yielding the relatively small amounts required.

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REFERENCES

- AHRENKIEL, R. K. 1971. Modified Kramers-Kronig analysis of optical spectra. *J. Opt. Soc. Amer.* **61**, 1651-1655.
- BARKER, E. S. 1979. Detection of SO₂ in the UV spectrum of Venus. *Geophys. Res. Lett.* **6**, 117-120.
- BARKER, E. S., J. H. WOODMAN, AND M. A. PERRY 1975. Relative spectrophotometry of Venus from 3067 to 5960 Å. *J. Atmos. Sci.* **32**, 1205-1211.
- CARLQVIST, B., AND D. DYRSSEN 1962. Studies of metal complexes of radiobiological interest. I. The acidity constants of croconic acid. *Acta Chem. Scand.* **16**, 94-104.
- ESPOSITO, L. W. 1980. Ultraviolet contrasts and the absorbers near the Venus cloud tops. *J. Geophys. Res.* **85**, 8151-8157.
- ESPOSITO, L. W., J. R. WINICK, AND A. I. STEWART 1979. Sulfur dioxide in the Venus atmosphere: Distribution and implications. *Geophys. Res. Lett.* **6**, 601-604.
- HANSEN, J. E., AND L. D. TRAVIS 1974. Light scattering in planetary atmospheres. *Space Sci. Rev.* **16**, 527-610.
- HAPKE, B., AND R. NELSON 1975. Evidence for an elemental sulfur component of the clouds from Venus spectrophotometry. *J. Atmos. Sci.* **32**, 1212-1218.
- IRVINE, W. M., T. SIMON, D. H. MENZEL, J. CHARON, G. LECOMTE, P. GRIBOVAL, AND A. T. YOUNG 1968a. Multicolor photoelectric photometry of the brighter planets. II. Observations from Le Houga Observatory. *Astron. J.* **73**, 251-264.
- IRVINE, W. M., T. SIMON, D. H. MENZEL, C. PIKOOS, AND A. T. YOUNG 1968b. Multicolor photoelectric photometry of the brighter planets. III. Observations from Boyden Observatory. *Astron. J.* **73**, 807-828.
- KAWABATA, K., D. COFFEEN, J. HANSEN, W. LANE, M. SATO, AND L. TRAVIS 1980. Cloud and haze properties from Pioneer Venus polarimetry. *J. Geophys. Res.* **85**, 8129-8140.

- KNOLLENBERG, R. G., AND D. M. HUNTEN 1980. The microphysics of the clouds of Venus: Results of the Pioneer Venus particle size spectrometer experiment. *J. Geophys. Res.* **85**, 8039–8058.
- KSANFOMALITI, L. V., YE. V. DEDOVA, V. G. ZOLO-TUKHIN, G. N. KRASOVSKY, AND V. M. FILIMONOVA 1976. Ultraviolet photometry of Venus. A scattering layer above absorbing clouds. *Kosm. Issled.* **14**, 776–788.
- KUIPER, G. P. 1957. The atmosphere and cloud layer of Venus. In *Threshold of Space* (M. Zelikoff, Ed.). Pergamon Press, New York.
- KUIPER, G. P. 1969. Identification of the Venus cloud layers. *Commun. Lunar Planet. Lab. No. 101*, 1–21.
- MARCH, J. 1985. *Advanced Organic Chemistry*. Wiley, New York.
- MCGEE, T. J., AND J. BURRIS JR. 1987. SO₂ absorption cross sections in the near u.v. *J. Quant. Spectrosc. Radiat. Transfer* **37**, 165–182.
- PALMER, K. F., AND D. WILLIAMS 1975. Optical constants of sulfuric acid: Application to the clouds of Venus? *Appl. Opt.* **14**, 208–219.
- POLLACK, J. B., B. RAGENT, R. BOESE, M. TOMASKO, J. BLAMONT, R. KNOLLENBERG, L. ESPOSITO, A. I. STEWART, AND L. TRAVIS 1979. Nature of the ultraviolet absorber in the Venus clouds: Inferences based on Pioneer Venus data. *Science* **205**, 76–79.
- POLLACK, J. B., D. W. STRECKER, F. C. WITTEBORN, E. F. ERICKSON, AND B. J. BALDWIN 1978. Properties of the clouds of Venus as inferred from airborne observations of its near-infrared reflectivity spectrum. *Icarus* **34**, 28–45.
- POLLACK, J. B., O. B. TOON, R. WHITTEN, R. BOESE, B. RAGENT, M. TOMASKO, L. ESPOSITO, L. TRAVIS, AND D. WIEDMAN 1980. Distribution and source of the UV absorption in Venus' atmosphere. *J. Geophys. Res.* **85**, 8141–8150.
- SHIMIZU, M. 1977. Ultraviolet absorbers in the Venus clouds. *Astrophys. Space Sci.* **51**, 497–499.
- SILL, G. T. 1972. Sulfuric acid in the Venus clouds. *Commun. Lunar Planet. Lab. No. 171*, 191–198.
- SILL, G. T. 1975. The composition of the ultraviolet dark markings on Venus. *J. Atmos. Sci.* **32**, 1201–1204.
- SINTON, W. M. 1953. Ph.D. thesis, Johns Hopkins University.
- TOMASKO, M. G., L. R. DOOSE, P. H. SMITH, AND A. P. ODELL 1980. Measurements of the flux of sunlight in the atmosphere of Venus. *J. Geophys. Res.* **85**, 8167–8186.
- TOON, O. B., R. P. TURCO, AND J. B. POLLACK 1982. The ultraviolet absorber on Venus: Amorphous sulfur. *Icarus* **51**, 358–373.
- TRAVIS, L. D. 1975. On the origin of ultraviolet contrasts on Venus. *J. Atmos. Sci.* **32**, 1190–1200.
- TRAVIS, L., D. COFFEEN, J. HANSEN, K. KAWABATA, A. LACIS, W. LANE, S. LIMAYE, AND P. STONE 1979. Orbiter cloud photopolarimeter investigation. *Science* **203**, 781–785.
- WOODWARD, R. B., AND R. HOFFMAN 1971. *The Conservation of Orbital Symmetry*. Verlag Chemie/Academic Press, Weinheim/Bergstrasse.
- WU, C. Y. R., AND D. L. JUDGE 1981. SO₂ and CS₂ cross section data in the ultraviolet region. *Geophys. Res. Lett.* **8**, 769–771.
- YOUNG, A. T. 1973. Are the clouds of Venus sulfuric acid? *Icarus* **18**, 564–582.
- YOUNG, A. T. 1977. An improved Venus cloud model. *Icarus* **32**, 1–26.
- YU, J. G., X. Y. FU, R. Z. LIU, K. YAMASHITA, N. KOGA, AND K. MOROKUMA 1986. Theoretical study of structures and energies of [HCOO]⁺ and [COOH]⁺ and their rearrangement. *Chem. Phys. Lett.* **125**, 438–442.