quake strikes, in complete agreement with my observations. Whitcomb *et al.* (*12*) have examined the relationship between the precursor time interval and the magnitude of earthquakes; their results indicate a precursor time interval of about 25 days for an $M = 4$ event. This value agrees fairly well with the duration of the premonitory episode seen in Fig. 3A. After the earthquake, the stress drop will cause the cracks to close and fluids to migrate outward. This process is likely to be relatively slow and could account for the slow return of Δt to its normal value.

A few seismologists have expressed the view that the observed phenomenon may be an artifact of variations in the spatial location of seismic events rather than of changes in the stress field. This possibiity perhaps cannot be ruled out completely, although it is not easy to conceive a geometry giving rise to a large-amplitude SV type phase arriving a fraction of a second later than the S_g phase.

The differential stress responsible for a shallow earthquake may induce measurable pre-earthquake velocity anisotropy of the shear wave. The observed premonitory results for two earthquakes in Nevada are consistent with the elastic rebound theory and can be explained on the basis of the dilatancy–fluid saturation hypothesis. Systematic observations of the parameter Δt may be used to monitor stress changes, and its leveling off at a high value may signal an impending earthquake. In principle, one can monitor a given area by means of a single three-component seismograph, and the observed results are almost independent of local effects. I believe that this method has the potential for being one of the simplest ways of predicting earthquakes.

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Venus: Composition and Structure of the Visible Clouds

Abstract. *It is proposed that the visible cloud deck on Venus is composed of droplets of sulfuric acid. These are formed by the very rapid photooxidation of carbonyl sulfide in the upper atmosphere. The clouds are best described as an extensive haze since the predicted particulate scale height probably exceeds the gas scale height within the layer. The predicted mixing ratio for water is* 10^{-6} *(lower limit), and for both carbonyl sulfide and sulfur dioxide it is* 10^{-7} *(upper limit); these are in good agreement with observations. Gaps in the layer are not possible unless the planetary scale dynamics produce cloud turnover times of less than a few days. Under these conditions the water mixing ratio could approach* 10^{-4} *and the formation of a thin hydrochloric acid haze at high altitude above the main cloud is possible.*

Venus is the closest planet to the earth in the solar system, and in view of the substantial literature in the field of planetary atmospheres it is surprising that there is as yet no definitive evidence on the chemical composition of the clouds which completely shroud the planet. Visual observations, together with the uniformity of the infrared emission temperatures (*1*), imply that there are few gaps (if any) in this cloud layer. The analysis of gaseous absorption bands (*2*) implies temperatures around 250°K and pressures around 200 mbar within these visible clouds. A cloud top might also be inferred around 200 mbar (altitude approximately 63 km) from the abrupt change from an adiabatic to a subadiabatic lapse rate detected at this level by Mariner 5 (*3*). However, a cloud top as such is apparently difficult to define. Analyses of the degree of polarization of sunlight reflected from the planet (*4*) imply the existence of spherical droplets of radius about 1.1 μm and refractive index 1.44 at the 50-mbar level, while the tenuous intermittent haze layers observed in ultraviolet photographs (*5*) probably lie at pressures near 10 mbar.

In view of the observation of both HCl and H_2O gases on the planet, it has been suggested (*6*) that an upper haze layer composed of droplets of concentrated hydrochloric acid solution might be formed at temperatures around 198°K, corresponding to pressures around 20 mbar. The H_2O number mixing ratio was assumed to be 10^{-4} at the cloud-top level (*2*). However, recent observations by Fink *et al.*

Table 1. Possible reaction sequence leading to the production of H_2SO_4 aerosols in the upper atmosphere of Venus. The constant J_1 is obtained by convolving the solar ultraviolet spectrum at Venus with the COS absorption spectrum of Sidhu *et al.* (*28*) between 2200 and 2700 Å and dividing by 4 for a planetary average. In reactions 1 and 2, $S(^1D)$ is an excited state of sulfur.

Reaction	Rate constant	Reference
1. $COS \rightarrow CO + S(^1D)$	$J_1 = 10^{-5}$ sec^{-1}	
2. $S(^1D) + CO_2 \rightarrow S + CO_2$	$k_2 > 1.66 \times 10^{-11}$ cm^3 sec^{-1}	(*29*)
3. $S + O_2 \rightarrow SO + O$	$k_3 = 2 \times 10^{-12}$ cm^3 sec^{-1}	(*30*)
4. $SO + OH \rightarrow SO_2 + H$	$k_4 = 1.17 \times 10^{-10}$ cm^3 sec^{-1}	(*30*)
5. $SO_2 + HO_2 \rightarrow SO_3 + OH$	$k_5 = 3 \times 10^{-16}$ cm^3 sec^{-1}	(*31*)
6. $SO_3 + H_2O + CO_2 \rightarrow H_2SO_4 + CO_2$		

(*7*) imply that the H_2O mixing ratio is perhaps as low as 10^{-6} within the main cloud deck. For this low mixing ratio and the Mariner 5 temperature profile we expect HCl and H_2O to condense only above about 88 km (1 mbar, 160°K); the stable condensed phases are ice crystals and solid $HCl \cdot 3H_2O$. If the H_2O mixing ratio in fact varies between 10^{-4} and 10^{-6}, then thin, tenuous hazes of condensed phases of H_2O and HCl will occur. However, these are strictly high altitude layers since H_2O mixing ratios of about 10^{-2} are required to saturate HCl and H_2O in the region of the visible cloud deck.

The observation of very low H_2O mixing ratios implies either that such ratios exist throughout the entire atmosphere or that some very hygroscopic cloud material limits the H_2O abundance in the visible atmosphere. Young and Young (*8*) have noted that droplets of sulfuric acid (75 percent by weight) have a refractive index of about 1.44 and appear to satisfy the observed infrared spectrum of Venus. The vapor pressure of H_2O over these droplets is small enough to reduce the H_2O mixing ratio to 10^{-6} at the temperatures and pressures in the visible clouds. Although these workers did not suggest any feasible source for the sulfuric acid, we argue here that the production of this acid in the upper atmosphere by photochemical reactions is an extremely facile process.

A surprising aspect of spectroscopic studies of Venus has been the apparent failure to detect any sulfur-bearing gases in the visible atmosphere. The upper limits on mixing ratios of COS, SO_2, and H_2S implied from observations are 10^{-6} (*9*), 3.5×10^{-8} (*10*), and 3×10^{-7} (*11*), respectively. From thermodynamic equilibrium studies of the very hot surface, Lewis (*12*) has computed mixing ratios for COS, SO_2, and H_2S of 5×10^{-5}, 3×10^{-7}, and 5×10^{-6}, respectively, and these are well above the limits of observation. Even if Venus received very little FeS during accretion from the primitive solar nebula (*13*), or if a considerable amount of FeS lies in the core (*14*), only extremely small quantities of sulfur are required to saturate the atmosphere. The element is of sufficiently high cosmic abundance that cometary impact alone could provide all that is necessary. In order to explain the nonobservation of these gases it has been suggested (*15*) that condensation of HgS clouds occurs deep in the atmosphere. However, the formation of these and other condensates containing Hg requires amounts of Hg in the atmosphere equivalent to complete degassing of a chondritic Venus model. Considerably less Hg is expected, and quantitative removal of S by HgS precipitation is then not possible. With this caveat we can discuss how photochemical destruction of sulfur-bearing gases in the upper atmosphere can reduce their concentrations to negligible levels in this region and lead to the production of sulfuric acid particles.

Certain aspects of the photodissociation of COS and H_2S on Venus have already been discussed (*16*). Dissociation of both gases is due mainly to ultraviolet radiation between 2200 and 2700 Å, and the upper atmosphere is optically thin in this wavelength region. Dissociation lifetimes of these molecules are essentially constant above the clouds and are very short (between 10^3 and 10^5 seconds). A partial list of the more important reactions for the most abundant gas, COS, is given in Table 1. Reformation of COS by the slow spin-forbidden reaction of S with CO cannot compete with reaction 3 (Table 1) at the 100-mbar level provided the O_2 mixing ratio exceeds about 10^{-8}, which agrees with present observations (*17*). Thus, COS is essentially irreversibly destroyed upon photodissociation. The "odd hydrogen" (OH and HO_2) required in reactions 4 and 5 is produced mainly from HCl photodissociation (*18*). Reaction 5 is the slowest reaction in the sequence, but further oxidants such as ClOO, ClO, and OH (*16, 19*) may considerably accelerate the SO_2 oxidation rate. The pertinent rate constants are at present unavailable. It should be emphasized that sulfuric acid provides a condensed form of oxygen, and this may help to explain the very low abundance of gaseous oxygen in the upper atmosphere relative to CO. This point will be discussed elsewhere (*20*).

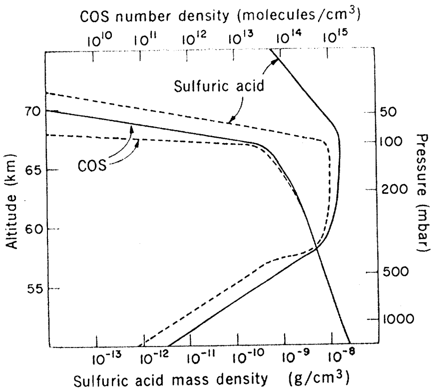

Fig. 1. Average distributions over the planet of COS gas and sulfuric acid aerosol in our model for the Venus clouds. We assume that the planetary scale motions (especially the high altitude 4-day zonal circulation) provide sufficient transport of particles from the daylight to the dark hemisphere, and of COS gas in the opposite direction, to make this average realistic. Otherwise, somewhat higher particle densities (but less than four times those indicated) and somewhat lower COS gas densities will occur on the day side, with correspondingly lower particle densities and higher COS densities on the dark side. The following values (in square centimeters per second) of the vertical turbulent eddy diffusion coefficient are assumed: 10^5 below 57 km; 5×10^4 (solid lines) or 10^4 (dashed lines) between 57 and 67 km; and 10^4 (solid lines) or 10^3 (dashed lines) above 67 km. The COS and H_2SO_4 densities given here are both directly proportional to the COS mixing ratio at the surface (in this case taken as 5×10^{-5}).

Experiments involving the photooxidation of SO_2 in the presence of O_2 and small amounts of H_2O with the resultant production of sulfuric acid aerosols have been reported by Friend *et al.* (*21*). They suggest that reaction 6 is followed by condensation of H_2SO_4 and H_2O molecules to form very small nuclei and rapid coagulation of these nuclei to yield the larger particles. Reaction schemes similar to those in Table 1 involve the conversion of H_2S or SO_2 entering the upper atmosphere into sulfuric acid particles with time constants of about 10^5 seconds or less in the daylight hemisphere.

These chemical lifetimes can be compared to typical transport times in the upper atmosphere. The observed 4-day circulation of the upper levels (*22*) implies that COS gas rising on the dark side has a maximum lifetime of 1.7×10^5 seconds before reaching the day side, where it is dissociated. Thus, the maximum lifetime of any COS molecule in the atmosphere on the day or night side is approximately 10^5 seconds. In contrast, vertical transport times are at least 10^7 seconds. Thus, gases containing sulfur will be severely depleted in the visible atmosphere through irreversible conversion to sulfuric acid. With this in mind, we have developed a model to describe COS number densities and H_2SO_4 aerosol mass densities as a function of altitude on Venus for comparison with observations.

Vertical transport of COS is assumed to be dominated by small-scale turbulence, and vertical transport of the sulfuric acid particles by both small-scale turbulence and gravitational sedimentation. The turbulent eddy diffusion coefficient is taken as $\geqslant 10^3$

$cm^2\ sec^{-1}$ in the subadiabatic region above 67 km, increasing to $10^5\ cm^2\ sec^{-1}$ in the adiabatic region below 57 km. The mass-weighted mean terminal velocity of particles (3×10^{-2} cm sec^{-1}) was computed by using an assumed particle radius of 1.1 μm, together with the kinematic viscosity of pure CO_2 at 254°K and the density of 75 percent (by weight) H_2SO_4 solution. We can identify an "aerosol production" region as lying above the level defined by the effective optical depth *(23)* for the absorption of photons at the wavelength of the COS absorption peak (about 2220 Å). From albedos of Venus measured in the ultraviolet *(11)*, this is roughly at 67 km. We assume that J_1 is constant above this level and zero below it because of absorption by cloud particles or reflection of the appropriate ultraviolet photons. The main haze layer will lie between 67 km and the level where significant destruction of the H_2SO_4 particles begins. From vapor pressure data *(24)* for 75 percent H_2SO_4 solutions, the vapor pressure of H_2O over particles of radius 1.1 μm exceeds the background H_2O pressure for a mixing ratio of 10^{-4} at the 57-km level (460 mbar, 293°K). We identify this level as the bottom of the haze layer. We assume that the H_2O mixing ratio is 10^{-4} below this level. Finally, in the "aerosol destruction" region the H_2SO_4 particles evaporate to yield H_2SO_4 molecules, followed by the thermochemical reactions

$$H_2SO_4 \rightarrow H_2O + SO_3$$
$$SO_3 + 4CO \rightarrow COS + 3CO_2$$

We have roughly described this destruction process by assuming that the lifetime of H_2SO_4 is 10^5 seconds below 57 km. Since the CO_2 produced here can be dissociated in the upper atmosphere to yield the O_2 required for oxidation of COS, there is no total production or loss of any species in the model. Alternatively, the CO_2 could be removed at the surface by reaction with minerals such as olivine to produce CO. In a steady state model the total rate of this crustal oxidation must equal the H_2 escape rate from the top of the atmosphere.

We have conveniently chosen the element S as a tracer in the atmosphere and demanded that in a steady state model the net flux of S (in COS gas or H_2SO_4 particles) through any horizontal surface is zero. A system of coupled differential equations is obtained from considerations of continuity and flux, and explicit solutions may be derived to describe both the number density of COS molecules and the total mass of sulfuric acid particles (75 percent by weight) per unit gas volume. We assume a constant atmospheric scale height in the haze layer region and demand that the COS concentration approach zero at high altitudes, the sulfuric acid concentration approach zero at low altitudes, and the COS mixing ratio be 5×10^{-5} at the surface. The results are shown in Fig. 1. The mixing ratio of COS above the haze layer is about 10^{-7} or less, and the SO_2 mixing ratio obtained from

$$[SO_2] = \frac{J_1[COS]}{k_5[HO_2]}$$

implies similar values for SO_2 (the square brackets enclosing a species denote the number concentration of that species). Both of these predicted values are in good agreement with observation.

The extinction optical depth of the haze layer (assuming that the appropriate radius for computing the effective particle cross section is 1.1 μm) is about 100. The particulate scale height in the visible upper part of the haze (50 to 200 mbar) often exceeds the atmospheric scale height. This is in remarkable agreement with the result inferred from spectrographic constraints by Gierasch and Goody *(25)*, which they could not reconcile with feasible cloud types. This increase in particle mixing ratio with altitude is due primarily to the aerosols being produced at the top of the layer in thick photochemical hazes, rather than in condensing clouds or dust clouds, where the particulate source is near or at the bottom of the layer. In this respect we recall the conclusion of Gierasch and Goody *(25)* that neither dust clouds nor condensing clouds could exist in a radiative-convective model for the Venus clouds. They argued that if such clouds existed they would require large-scale dynamics to support them. The new cloud type presented here places no such demands on the dynamics. The requirements on vertical transport of the precursor gas, COS, are very modest. Breaks in the cloud layer are unlikely as they require cloud removal times to exceed the COS destruction times (2 days on the dark side, 0.3 day on the day side). Under such conditions of strong circulation we would expect a temporary increase in the H_2O mixing ratio to values approaching 10^{-4} since the removal of H_2O by H_2SO_4 would be inhibited. In this case a high altitude hydrochloric acid haze becomes possible. However, the rapid 4-day circulation probably prevents any correlation between regions covered by the high altitude haze and regions of enhanced H_2O mixing ratio. Variations of an order of magnitude in this ratio have been observed, and no apparent correlation exists *(26)*. The surface COS mixing ratio used here (5×10^{-5}) results in almost precisely enough sulfuric acid to decrease the H_2O mixing ratio from 10^{-4} below the haze to 10^{-6} above it and thus provides a simple answer to the observed H_2O variability.

Finally, we emphasize that once the sulfuric acid droplets are formed in the atmosphere, dissolution of such species as HCl, Cl_2, HF, and NH_3 in them may alter their composition and optical properties somewhat. In addition, the oxidation of SO_2 by O_2 could be very rapid within the droplets themselves because of catalysis by dissolved NH_4^+ ions. The Russian entry probe Venera 8 has tentatively detected NH_3 in the lower atmosphere, and values of the NH_3 mixing ratio around 10^{-5} to 10^{-6} are predicted *(27)* in the region of the visible clouds (if NH_3 does not dissolve in particulates). This catalytic mechanism sharply accelerates the rate of production of the large droplets, and Friend *et al.* *(21)* have proposed that the large ammonium sulfate haze particles in the terrestrial stratosphere are produced by this mechanism. The particle distribution in the earth's stratosphere has a strong peak at a particle radius of about 1 μm, which is remarkably similar to what is inferred on Venus *(4)*.

We have demonstrated that the rapid photochemical production of sulfuric acid (and perhaps ammonium sulfate) particulates in the upper atmosphere of Venus is very probable. Since such particulates are compatible with observations of a variable H_2O mixing ratio, the particle size and refractive index, the particulate density, and the infrared spectrum, they are the most plausible candidate to date for the visible cloud deck on Venus. Although an unambiguous chemical identification of H_2SO_4 by a Pioneer entry probe would be difficult, the presence of sulfur in the cloud particles could easily be verified by using an x-ray fluorescence detector mounted externally on the probe.

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Bicyclic Phosphorus Esters: High Toxicity without Cholinesterase Inhibition

Abstract. *4-Isopropyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane 1-oxide has a mouse intraperitoneal lethal dose, 50 percent effective, of 0.18 milligram per kilogram of body weight. Related compounds used by many chemical researchers are also highly toxic. Brain acetylcholinesterase inhibition is not involved in their mode of action. The structural similarity of these compounds to adenosine 3′,5′-monophosphate (cyclic AMP) is of interest.*

4-Alkyl derivatives of 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane are extensively used for spectroscopic studies and are candidates for use as flame retardants, vinyl resin stabilizers, and antioxidants (*1*). The commercially available (*2*) 4-ethyl phosphite derivative forms a relatively stable ozone adduct useful as a convenient singlet oxygen source (*3*). Thus many investigators have studied and continue to study the chemistry of these compounds without an awareness of any unusual hazard. Our findings indicate that these bicyclic phosphorus compounds should be handled with great care because of their high toxicity to mammals.

The bicyclic compounds were prepared by modifications of published procedures (*1, 4*). Their toxicity was tested by injecting them intraperitoneally into male Swiss Webster mice (18 to 20 g), with LD_{50} (lethal dose, 50 percent effective) determinations being made after 24 hours. The administration vehicle was methoxytriglycol unless indicated otherwise.

The toxic 4-alkyl bicyclic phosphorus esters shown in Table 1 each produce convulsive seizures and death in mice within a few minutes. The bicyclic phosphites (P), phosphates [P(O)], and thionophosphates [P(S)] with the same 4-alkyl substituents are of similar toxicity, but the potency is greatly dependent on the nature of the 4-alkyl substituent with a maximum toxicity for compounds with the isopropyl group. Phosphates of the 4-isopropyl or 4-*n*-propyl compounds are slightly more toxic than the phosphites or thionophosphates. Bicyclic phosphites and thionophosphates undergo rapid and almost quantitative oxidation to the corresponding phosphates on treatment with *m*-chloroperoxybenzoic acid, as expected from earlier studies (*1, 4*). Comparable oxidation reactions occur with many other thionophosphates, including parathion, in living mammals (*5*). Accordingly, it is likely that the bicyclic phosphites and thionophosphates are oxidized in vivo prior to exerting their poisoning action.

The mode of action of toxic phosphorus esters has been extensively studied because of their importance as insecticides and chemical warfare agents, exemplified by parathion and diisopropyl fluorophosphate (DFP), respectively. Their toxicity is generally attributed to inhibition of acetylcholinesterase (AChE) in the nervous system (*5*). The toxic signs produced by 4-alkyl bicyclic phosphorus esters in mice and rats do not, however, resemble the characteristic manifestations of poisoning by anticholinesterase agents, that is, there is no indication of excessive parasympathetic stimulation, twitching of the muscles, paralysis, or clonic convulsions. Rats treated intraperitoneally with the isopropyl bicyclic phosphate at 0.3 mg/kg die in 20 to 30 minutes without inhibition of the AChE activity in the whole brain or blood (*6*). Even when the concentration of the isopropyl bicyclic phosphate is 3 mg/kg, which produces death within 5 minutes, the brain AChE activity is not at all inhibited. For comparison, rats 1 hour after treatment with a nonlethal dose

Table 1. Intraperitoneal toxicity to mice of bicyclic phosphorus esters in comparison with parathion and DFP; P, phosphite; P(O), phosphate; P(S), thionophosphate.

Type structure	LD_{50} (mg/kg)		
	X = P	X = P(O)	X = P(S)
		Bicyclic phosphorus esters	
$NO_2C(CH_2O)_3X$		9.5	
$HOCH_2C(CH_2O)_3X$	> 500*	> 500†	> 500*
$CH_3C(CH_2S)_3X$			95*‡
$CH_3C(CH_2O)_3X$		32	34
$CH_3CH_2C(CH_2O)_3X$	1.1§	1.0	1.1
$CH_3(CH_2)_2C(CH_2O)_3X$	0.39	0.38	0.79
$(CH_3)_2CHC(CH_2O)_3X$	0.22	0.18‖	0.26
$(O)P(CH_2O)_3X$	174*‡	189*‡	
		Parathion and DFP	
$4\text{-}NO_2\text{-}\O OX(OCH_2CH_3)_2$			5.9
$FX[OCH(CH_3)_2]_2$		6.0	

* Dimethyl sulfoxide was used as the vehicle. † Water was used as the vehicle. ‡ Samples were provided by Professor J. G. Verkade, Department of Chemistry, Iowa State University, Ames. § Other mouse LD_{50} values are 4 mg/kg dermally, with 10 μl of dimethyl sulfoxide as vehicle per mouse for treatment on the back; 7 mg/kg, orally, with 50 μl of methoxytriglycol for administration by stomach tube. ‖ This is the 4-isopropyl bicyclic phosphate (see structure).