

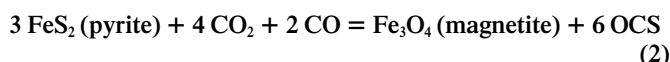
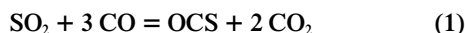
Formation of Carbonyl Sulfide (OCS) from Carbon Monoxide and Sulfur Vapor and Applications to Venus

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We use gas chromatography to identify and measure the amounts of carbonyl sulfide (OCS) formed in a gas-flow system via the net thermochemical reactions



at temperatures of 470–612°C and ambient atmospheric pressure. The goal of our work is to evaluate the importance of reactions (1) to (3), which have been proposed as potential sources of OCS in Venus' lower atmosphere. Our results show OCS formation by reaction (3), but not by reactions (1) or (2) under our experimental conditions. Based on our results, experimental data from the literature, and theoretical models in the literature, we conclude that (1) the reaction of S₂ and CO is an important source of OCS in Venus' lower atmosphere, and (2) probably neither reaction (1) nor reaction (2) is an important source of OCS on Venus. Finally, we use thermodynamic data for reaction (3) and Venera spacecraft observations of CO and sulfur vapor at 0–12-km altitude to calculate an OCS equilibrium abundance of 1–14 ppmv, with a nominal value of 5 ppmv, for reaction (3) near Venus' surface. © 1997

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Key Words: Venus; atmospheric chemistry; pyrite; carbonyl sulfide; sulfur; pyrrhotite

INTRODUCTION

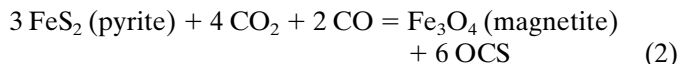
Carbonyl sulfide (OCS) is the dominant reduced sulfur gas and is the second most abundant sulfur gas, after SO₂, observed below Venus' clouds. The chemical reactions responsible for the formation and destruction of OCS are important for the oxidation state of the lower atmosphere, for sulfur geochemistry on Venus, and for maintenance of the global sulfuric acid clouds.

Carbonyl sulfide has been included in models of atmospheric chemistry and atmosphere–lithosphere interactions since the work of Lewis (1970) and Prinn (1973). However, it was very difficult to confirm the presence of OCS on Venus. Earth-based IR observations of Venus' atmosphere above the clouds gave an OCS upper limit of <1 ppmv (part per million by volume) (Cruikshank 1967). Below the clouds, the Pioneer Venus mass spectrometer and gas chromatograph experiments suggested an upper limit of <(2–3) ppmv above 22 km altitude (Von Zahn *et al.* 1983). Mukhin *et al.* (1983) claimed the detection of 40 ± 20 ppmv OCS and 80 ± 40 ppmv H₂S by the Venera 13/14 gas chromatograph experiment in the 29–37 km altitude region. However, the Venera 13/14 “detections” are generally discounted because instrumental malfunctions caused problems with peak identifications for many compounds (Krasnopolsky 1986).

Carbonyl sulfide was first definitively observed on Venus by Bézard *et al.* (1990). Subsequently, Pollack *et al.* (1993) made a detailed analysis of Earth-based IR spectra of Venus' nightside. At 33 km altitude, they found an OCS mixing ratio of 4.4 ± 1.0 ppmv and a positive gradient of +1.58 ± 0.30 ppmv/km toward Venus' surface. By 26 km OCS has increased to about 10 ppmv, but Pollack *et al.* (1993) note that the IR observations do not constrain the OCS abundance at lower altitudes. Although there are no observational data for OCS below 26 km altitude, about 5–30 ppmv OCS is predicted from gas phase and gas–solid chemistry near Venus' surface (Fegley and Treiman 1992, Krasnopolsky and Pollack 1994, Zolotov 1996, Fegley *et al.* 1997).

At 36 km altitude, Pollack *et al.* (1993) also found a CO mixing ratio of 23 ± 5 ppmv and a negative gradient of –1.20 ± 0.45 ppmv/km toward Venus' surface. They noted that the apparently coupled variations in OCS (increasing) and CO (decreasing) toward Venus' surface are consistent with the production of OCS by either gas phase thermochemical reactions or gas–solid thermochemical reactions

involving CO as a reactant. The net thermochemical reactions



have indeed been proposed as potential sources of OCS in Venus' lower atmosphere (Von Zahn *et al.* 1983, Prinn 1985, Fegley and Treiman 1992, Krasnopolsky and Pollack 1994). However, the relative importance of these three reactions as OCS sources on Venus is unknown.

Here we use gas chromatography to identify and measure the amounts of carbonyl sulfide (OCS) formed from reactions (1) to (3) in a gas-flow system at temperatures of 470–612°C and ambient atmospheric pressure. We first describe our experimental study and then discuss the implications of our results for OCS thermochemistry near the surface of Venus.

EXPERIMENTAL PROCEDURES

Analysis and Characterization of Solids

X-ray diffraction (XRD) patterns of the starting materials (pyrite from Zacatecas, Mexico) and reaction products were obtained using a Rigaku vertical powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) and Materials Data Incorporated (MDI) software. Calibration was done using silicon powder (NIST 640b). The XRD pattern of the Mexican pyrite is identical to that of a pyrite standard (JCPDS pattern 42-1340). The XRD patterns of the reacted products are discussed later.

Electron microprobe analyses were done with the Washington University JEOL-733 electron microprobe equipped with Advanced Microbeam automation. The operating conditions are the same as those described by Lauretta *et al.* (1996). Electron microprobe analyses gave $46.16 \pm 0.80\%$ Fe and $53.32 \pm 0.68\%$ S (mean of 19 analyses with 2σ errors), in good agreement with the stoichiometric values of 46.55% Fe and 53.45% S. Gravimetric analyses gave a S/Fe atomic ratio of $2.001 \pm 0.001(2\sigma)$. Reflected light microscopy of several pyrite samples did not show any other phases. The measured density is 4.89 g cm^{-3} , in agreement with the tabulated density of 4.89–5.03 g cm^{-3} (Deer *et al.* 1963). The pyrite used in our experiments is pure, stoichiometric FeS_2 .

Gas Mixtures and Gas Analysis

Coleman grade (99.99%) CO_2 and CO_2 mixtures with SO_2 (anhydrous grade, 99.98%), and CO (CP grade 99.5%) were used in this work. The mixtures used contain 99.0–

TABLE I
Observed OCS Concentrations

Temperature (°C)	OCS (ppmv)	Temperature (°C)	OCS (ppmv)
	CO ₂ (run H119)	0.20% CO - 99.80% CO ₂ (run H153)	
538	9.24	471	19.0
567	27.6	498	60.4
583	61.7	524	211
597	109	551	574
612	194	580	899
	0.50% CO - 0.50% SO ₂ - 99.00% CO ₂ (run H144)	0.50% CO - 99.50% CO ₂ (run H152)	
473	55.9	471	49.3
500	209	498	157
527	631	524	504
554	1,420	552	1,290
		578	2,260

100% CO_2 , 0–0.50% CO, and 0–0.50% SO_2 (Table I). The gas mixtures are either certified standards accurate to $\pm 5\%$ of the labeled concentration of the minor component, or mixtures prepared with calibrated electronic mass flow controllers in our laboratory. All gases were further purified by passing them through hot copper turnings and magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) to remove any O_2 and H_2O impurities. No O_2 or H_2O were found by gas chromatography in the purified gas mixtures at our detection limits of ~ 1 ppmv. The concentrations of any residual O_2 and H_2O in the purified gases are expected to be significantly below 1 ppmv.

A Hewlett Packard 5890 Series II Gas Chromatograph with an electronic integrator was used to identify and measure OCS and for quality control of gas mixing. The analyses were done using a Porapak Q column at 60°C, a carrier gas flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$, and a thermal conductivity detector at 120°C. The carrier gas was UHP grade (99.999%) helium, which was further purified using an Alltech Associates gas purifier. Gas lines connected the gas mixing boards and furnace exhausts to an automated gas sampling valve on the gas chromatograph.

Carbonyl Sulfide Formation Experiments

The OCS formation reactions were studied at ambient atmospheric pressure in a gas mixing vertical tube furnace

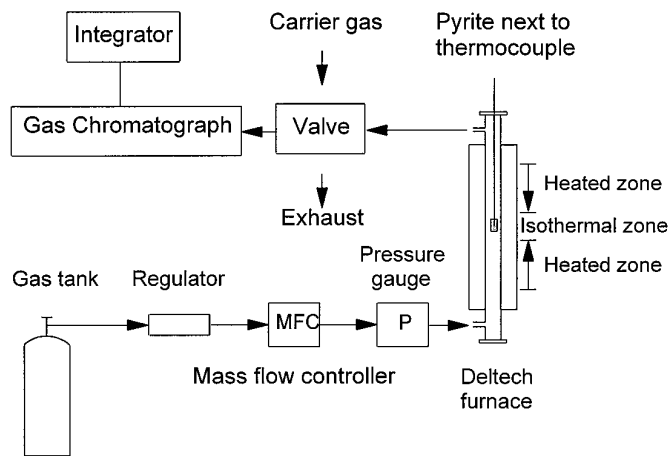


FIG. 1. Schematic diagram of the experimental setup used to study OCS formation.

(Deltech, Denver, CO). The experimental setup is shown schematically in Fig. 1. Reaction (1) was studied by passing the gas mixture through the hot zone of the furnace without any pyrite inside. Reactions (2) and (3) were studied by hanging pyrite pieces (~ 2 grams) by fine platinum wires in the furnace. Initially the pyrite pieces were suspended inside the water-cooled gas outlet fitting at the top of the furnace. After gas chromatography verified that all air had been flushed out, the pyrite samples were then lowered into the 5-cm long isothermal hot zone. Calibrated Pt–PtRh thermocouples measured the temperature right next to the samples. The gaseous products were identified and quantified by gas chromatography. After completing experiments at one temperature, the furnace temperature was raised to the next reaction temperature, and the process was repeated.

The reaction temperatures are 470–612°C. For reference, surface temperatures on Venus range from $\sim 385^\circ\text{C}$ on Maxwell (~ 10 km) to $\sim 478^\circ\text{C}$ in Diana Chasma (~ -2 km). It was impractical to do experiments at lower temperatures because the OCS abundance decreases rapidly with decreasing temperature and analytical errors increase.

During the experiments, gas-flow rates in the furnace were fixed at $150\text{ cm}^3\text{ min}^{-1}$ (STP) using electronic mass flow controllers. Prior experimental work in our vertical tube furnaces shows that this flow rate is fast enough to prevent gas unmixing by thermal diffusion but is slow enough for pyrite vaporization to saturate the gas with sulfur vapor (Lauretta *et al.* 1996, Hong and Fegley 1997a). The inside diameter of the furnace muffle tube is ~ 5 cm (2 inches), so the linear flow rate is 7.4 cm min^{-1} . Thus, the mean residence time in the 5-cm long isothermal hot zone is 40 s. To a good first approximation, gas reactions are quenched after leaving the hot zone (see Haber 1908).

We show below that 40 s is long enough for some reactions to proceed but not others, so we also obtain qualitative kinetic data from the experiments.

Chemical Equilibrium Calculations

The chemical equilibrium calculations in this paper were done using a code and thermodynamic data base described by Fegley *et al.* (1997). The code simultaneously considers mass balance and chemical equilibrium to iteratively solve for the equilibrium abundances of all gases considered in the calculation. Thermodynamic data used throughout this paper are taken from Gurvich *et al.* (1989–1994).

RESULTS

Identification and Measurement of OCS

Carbonyl sulfide was identified and measured by gas chromatography using a commercial standard (98.3 ± 2 ppmv OCS in He, GasPro). Replicate analyses of the OCS standard were reproducible within $\pm 10\%$ (2σ error). The OCS in our experiments was identified by comparison of retention times with the OCS standard. For example, gas chromatograms of the standard OCS sample (Fig. 2d) and of the OCS peak from heating pyrite at 471°C in 0.50% CO–CO₂ (Fig. 2c) have identical retention times. Under the same conditions, the retention times of other sulfur gases (SO₂, SO₃, H₂S, and CS₂) are different than that of the OCS standard and the OCS peaks from the experiments. The amount of OCS produced in the experiments was determined from the observed peak areas calibrated to the peak area of the OCS standard. The uncertainties (2σ) of the reported OCS concentrations are about $\pm 10\%$, and the detection limit for OCS is ~ 1 ppmv.

Reaction (1)

The chromatogram in Fig. 2a shows no detectable OCS in a 0.50% SO₂–0.50% CO–CO₂ mixture heated at 471°C , although the predicted equilibrium OCS concentration is ~ 740 ppmv under the experimental conditions. The absence of OCS is probably due to kinetic effects, as we discuss below.

Reaction (2)

Before studying OCS production from pyrite heated in CO–CO₂ gas mixtures, we first heated pyrite in purified CO₂. The chromatogram in Fig. 2b shows that OCS was not detected when pyrite was heated in purified CO₂ at 471°C . We did detect measurable amounts of OCS when pyrite was heated at higher temperatures (538 to 612°C). Table I and Fig. 3 show the OCS concentration data.

X-ray diffraction patterns of partially reacted pyrite heated in purified CO₂ or CO–CO₂ mixtures show only

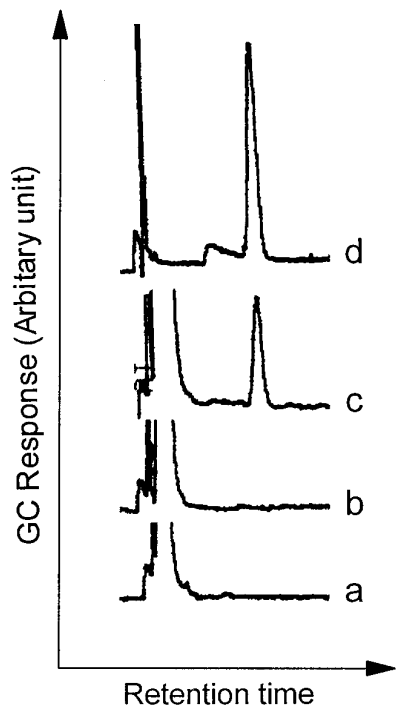
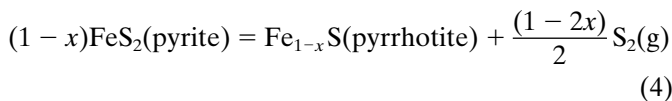


FIG. 2. Typical gas chromatograms of the OCS standard and reaction products. (a) A chromatogram of a 0.50% CO–0.50% SO₂–CO₂ gas mixture heated at 470°C without pyrite. No OCS is detected. (b) A chromatogram for pyrite heated in purified CO₂ at 471°C. No OCS is detected. (c) A chromatogram showing 49.3 ppm OCS formed by heating pyrite at 471°C in 0.50% CO–CO₂. (d) A chromatogram of the OCS standard (98.3 ppm OCS in He). The small peak before OCS is H₂S, an impurity present in the gas cylinder.

pyrite and pyrrhotite (Fe_{1-x}S), and the pyrrhotite compositions are in agreement with those predicted by the Fe–S phase diagram (Stølen and Grønvold 1987) at our experimental temperatures. The presence of pyrrhotite and the absence of Fe₃O₄ indicates that pyrite thermally decomposed to pyrrhotite and sulfur vapor and did not react with the gas. There is no evidence that the observed OCS formed via reaction (2). Instead, the OCS formed via another reaction, probably involving sulfur vapor evolved from the pyrite.

Our earlier studies (Hong and Fegley 1997a) using the transpiration method (Merten and Bell 1967) to measure the sulfur vapor pressure over pyrite (441–591°C) in a flow system show that pyrite decomposes via the net thermochemical reaction:



in He, N₂, CO₂, and CO₂–CO–SO₂ gas mixtures. The S₂ vapor pressure is the same in all these gases and is given by

$$\log_{10} P_{\text{S}_2}(\text{bars}) = 16.20 - 15,700/T, \quad (5)$$

where T is the temperature of the pyrite sample in Kelvins (Hong and Fegley 1997a). We also note that Thompson and Tilling (1924) and Schwab and Philinis (1947) reported that pyrite does not react with CO₂. Thus we conclude that pyrite is only a source of sulfur vapor and is not directly involved in OCS formation in our experiments.

Reaction (3)

We studied reaction (3) by heating pyrite in CO–CO₂ gas mixtures because under our experimental conditions, S₂ is the dominant allotrope in the sulfur vapor evolved from pyrite (Toulmin and Barton 1964, Hong and Fegley 1997a).

Heating pyrite in CO–CO₂ mixtures, instead of in purified CO₂, greatly increased the amount of OCS formed. For example, the chromatogram in Fig. 2c shows that 49 ppmv OCS formed by heating pyrite at 471°C in a 0.50% CO–CO₂ mixture. In comparison, the chromatogram in Fig. 2b does not show a OCS peak, indicating that <1 ppmv OCS formed by heating pyrite in purified CO₂ at the same temperature. In addition, the data in Fig. 3 and Table I show that at the same temperature, much higher OCS concentrations are observed in a 0.20% CO–CO₂ mixture than in purified CO₂.

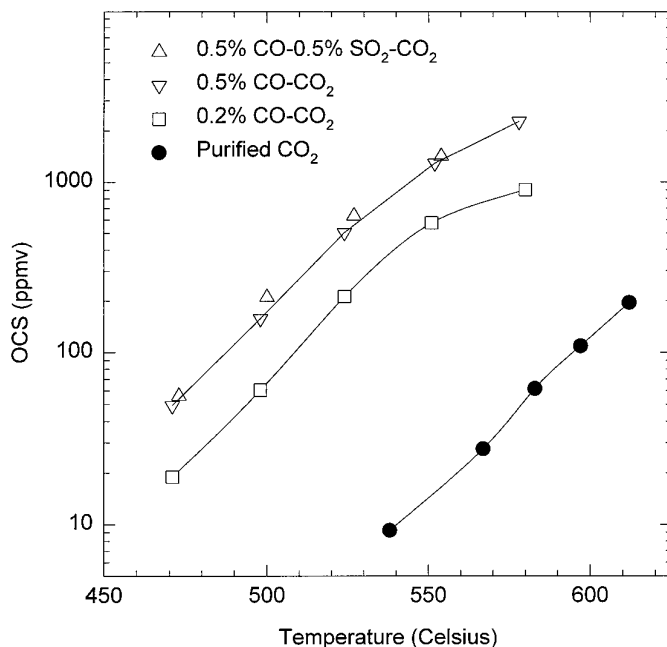


FIG. 3. A comparison of the amounts of OCS observed from heating pyrite in CO₂ and in three gas mixtures: 0.20% CO–99.80% CO₂, 0.50% CO–99.50% CO₂, and in 0.50% CO–0.50% SO₂–CO₂. The lines connect the points and are not fits to the data, which are listed in Table I.

TABLE II
Comparison of OCS Concentrations in Two CO–CO₂
Gas Mixtures

Temperature (°C)	OCS (ppmv)		Ratio
	0.2% CO	0.5% CO	
471	19.0	49.3	2.59
498	60.4	157	2.60
524	211	504	2.39
551	574	1,290	2.25
580	899	2,260	2.51
			2.47±0.15 obs.
			2.50 predicted

We also found that the amount of OCS formed in the CO–CO₂ mixtures is directly proportional to the amount of CO in the gas. Figure 3 and Table II compare OCS concentrations observed in CO–CO₂ mixtures containing 0.20% CO or 0.50% CO. The 0.50% CO mixture contains 2.47 ± 0.15 times as much OCS as the 0.20% mixture, identical to the CO concentration ratio (2.50). The OCS concentration is directly proportional to the CO concentration indicating that reaction (3) is the dominant OCS formation reaction under the experimental conditions.

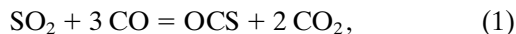
Reaction (1) Again

Finally, we also studied reaction (1) by heating pyrite in a CO–SO₂–CO₂ gas mixture. Figure 3 also compares OCS concentrations observed in 0.50% CO–CO₂ and 0.50% CO–0.50% SO₂–CO₂. Within the OCS measurement uncertainties ($\pm 10\%$ 2σ error), the two sets of data plot exactly on the same line, showing again that SO₂ is not involved in OCS formation under laboratory conditions.

DISCUSSION AND APPLICATIONS TO VENUS

Reaction (1)

We first consider the net thermochemical reaction



which is predicted to convert SO₂, the major sulfur-bearing gas, to OCS in Venus' lower atmosphere. No OCS was detected when a 0.50% CO–0.50% SO₂–CO₂ mixture was heated at 471°C and ambient atmospheric pressure. Based on our OCS detection limit of 1 ppmv, the observed upper limit for the OCS/SO₂ ratio in this experiment is $\leq 2.0 \times$

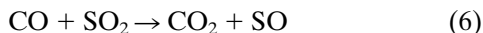
10^{-4} ($1 \times 10^{-6}/5000 \times 10^{-6}$). However, thermodynamic calculations using the code and data base described by Fegley *et al.* (1997) predict an equilibrium OCS/SO₂ ratio of 0.26 for reaction (1) under our experimental conditions. The observed upper limit ($\leq 2.0 \times 10^{-4}$) for the OCS/SO₂ ratio is at least 1300 times smaller than the equilibrium OCS/SO₂ ratio (0.26). This disagreement shows that reaction (1) is far from equilibrium under our experimental conditions. The large departure from equilibrium indicates that reduction of SO₂ to OCS by reaction with CO is a slow process.

Although the 40 s residence time in the isothermal hot zone contributes to the departure from equilibrium, other observations also indicate that reaction (1) is a slow reaction. Ferguson (1918) studied equilibria in CO–SO₂–N₂ mixtures using different types of gas-flow systems. He noted that the mixtures did not react appreciably below 900°C. Ferguson also reported OCS/SO₂ ratios for a gas mixture (initially 73.4% CO and 26.6% SO₂) that was heated at 1000°C with and without platinized porcelain as a catalyst in the isothermal hot zone of the furnace. The observed percentages and ratios are 10.4% OCS, 5.0% SO₂ (an OCS/SO₂ ratio of 2.1) after heating for 24 min without the catalyst, and 2.4% OCS, 1.7% SO₂ (an OCS/SO₂ ratio of 1.4) after heating for 24 min with the catalyst. By comparison, the calculated equilibrium OCS/SO₂ ratio is 12.1 at the same temperature. The observed OCS/SO₂ ratios are smaller than the equilibrium value because the gas mixture did not equilibrate. Ferguson's qualitative observations and the reported gas chemistry indicate that reaction (1) did not equilibrate at $\sim 1000^\circ\text{C}$ under his experimental conditions, which are over 500°C higher than Venus surface temperatures.

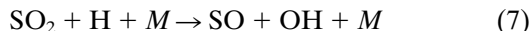
It also appears that reaction (1) does not equilibrate in Venus' lower atmosphere. Krasnopolsky and Pollack (1994) found that if equilibrium is assumed, reaction (1) predicts absurd OCS mixing ratios much greater than unity and OCS/SO₂ ratios much greater than the observed values (Pollack *et al.* 1993). For example, at 500 K (29 km altitude), the observed OCS mixing ratio on Venus is a few ppmv while the equilibrium OCS mixing ratio from reaction (1) is 20,000. At 734 K (~ 0 -km altitude) the equilibrium OCS mixing ratio is about 13 ppmv and the equilibrium OCS/SO₂ ratio is about 0.07, while modeling of the observed OCS gradient implies about 28 ppmv OCS and an OCS/SO₂ ratio of about 0.28. Krasnopolsky and Pollack (1994) concluded that reaction (1) does not equilibrate above a few km altitude on Venus and that the disagreement reflects the kinetic control of the OCS profile at higher altitudes.

More recently, Fegley *et al.* (1997) modeled the kinetics of several reactions in the C–O–S system by comparing chemical lifetimes (t_{chem}) to convective mixing times (t_{mix}). They considered two elementary reactions, either of which

may be the slow step for the conversion of SO₂ to OCS in two different mechanisms. The first reaction



is quenched at 748 ± 13 K, equivalent to an elevation of -1.0 ± 1.7 km below Venus' modal radius. The second reaction



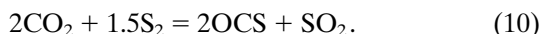
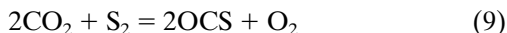
is quenched at 693 ± 9 K (6.1 ± 1.1 -km altitude). In both cases conversion of SO to OCS is assumed to be more rapid. Their kinetic modeling, thermodynamic calculations, and reanalyses of several Venera spacecraft experiments led Fegley *et al.* (1997) to conclude that gas phase thermochemical reactions between oxidized and reduced species in the C–O–S system, such as the conversion of SO₂ to OCS, probably equilibrated only at altitudes below 0.7 km (730 K), and are quenched at higher altitudes where temperatures are below 730 K.

Thus, our experimental results, the earlier work of Ferguson (1918), and theoretical modeling of atmospheric chemistry (Krasnopolsky and Pollack 1994, Fegley *et al.* 1997) all suggest that reaction (1), the conversion of SO₂ to OCS, is probably slow in Venus' lower atmosphere and of minor importance as a source of OCS.

Reaction (2)

We now consider the proposed formation of OCS by chemical weathering of pyrite. As mentioned earlier, reaction (2) does not occur under our experimental conditions. Instead pyrite is only a source of sulfur vapor that then reacts to form OCS. At the temperatures we studied, S₂ is the dominant allotrope in sulfur vapor (Toulmin and Barton 1964, Hong and Fegley 1997a). Formation of OCS from S₂ vapor and CO₂ could proceed via two different pathways. Carbon dioxide could react directly with S₂ to form OCS. Alternatively, CO could form by some other reaction and then react with S₂ to form OCS.

Formation of OCS by reaction of CO₂ and S₂ may occur by net reactions such as



Reactions (8) to (10) also predict the formation of significant amounts of SO₂ or O₂. However, our gas chromatographic analyses show only OCS without any O₂ or SO₂ above the ~ 1 ppmv detection limit. Also, OCS formation by reaction (9) produces O₂ and should cause pyrite oxida-

tion to iron oxides from the O₂ formed. Again, this is not observed.

We prefer the second alternative, OCS formation by reaction of S₂ with small amounts of CO. The CO is either a trace impurity remaining in the purified CO₂ or was made by some reaction involving CO₂. It is unlikely that CO present as an impurity in the gas can account for the observed OCS because the amount of OCS formed increases with increasing temperature and reaches 194 ppmv at 612°C. Instead, it is more plausible that CO is formed from CO₂ by a reaction that produces more CO with increasing temperature.

In any case, only small amounts of OCS are formed by heating pyrite in purified CO₂. A linear fit to the amount of OCS produced is

$$\log_{10} \text{OCS (ppmv)} = 16.93(\pm 0.07) - 12940(\pm 870)/T, \quad (11)$$

where temperature is in Kelvins. No detectable OCS was found in experiments done at 471°C. However Eq. (11) gives ~ 0.3 ppmv OCS at 471°C. For comparison, 19, 49, and 55 ppmv OCS were formed by heating pyrite at about the same temperature in CO₂ gas mixtures containing 0.20% CO, 0.50% CO, and (0.50% CO + 0.50% SO₂), respectively. The amount of OCS formed in purified CO₂ at 471°C is only 0.6–1.6% of the amount formed in the CO-bearing gas mixtures. At the highest temperatures studied, the data in Table I show that the amount of OCS formed in purified CO₂ is still only a few percent of the amount formed in the CO gas mixtures.

Reaction (3)

The reaction of CO and sulfur vapor to form OCS is well known and, as noted by Ferm (1957), was first reported about 130 years ago. Reaction (3) occurs at temperatures at least as low as 250°C (Lewis and Lacey 1915). We calculated the extent of reaction ξ ,

$$\xi = \frac{(\text{OCS})_{\text{obs}}}{(\text{OCS})_{\text{eq}}} \quad (12)$$

to see how closely equilibrium was attained in our experiments. The extent of reaction varies from 0 (for no reaction) to 1 (for complete equilibrium). The observed OCS concentrations were taken from Table I. The predicted equilibrium OCS concentrations were calculated from

$$\begin{aligned} K_3 &= \frac{P_{\text{OCS}}^2}{P_{\text{CO}}^2 P_{\text{S}_2}} = \frac{P_{\text{OCS}}^2}{(P_{\text{CO, in}} - P_{\text{OCS}})^2 P_{\text{S}_2}} \\ &= \frac{X_{\text{OCS}}^2}{(X_{\text{CO, in}} - X_{\text{OCS}})^2 X_{\text{S}_2}} \times \frac{1}{P_T}, \end{aligned} \quad (13)$$

where P_i and X_i are gas partial pressures and mole fractions, and P_T is the total pressure (~ 1 bar). The terms $P_{\text{CO,in}}$ and $X_{\text{CO,in}}$ are the initial CO pressure and mole fraction in the gas mixture, which are reduced by the formation of OCS. The S_2 pressure in Eq. (13) is the S_2 equilibrium vapor pressure over pyrite from Eq. (5). The S_2 pressure is not reduced by OCS formation because S_2 is continually vaporized from the pyrite in the isothermal hot zone of the furnace.

Finally, to solve Eq. (13) for X_{OCS} we make use of the fact that the equilibrium constant for reaction (3) is also equal to

$$K_3 = \exp(-\Delta G^\circ/RT), \quad (14)$$

where R is the ideal gas constant and ΔG° for reaction (3) is taken from the tabulation of Gurvich *et al.* (1989–1994). We then solved Eq. (13) for the OCS concentration (X_{OCS}) for the three different CO-bearing gas mixtures (0.20% CO–CO₂, 0.50% CO–CO₂, and 0.50% CO–0.50% SO₂–CO₂) by substituting for the S_2 partial pressure and K_3 using Eqs. (5) and (14) and taking $P_T = 1$ bar. The observed OCS concentrations, the predicted equilibrium concentrations, and the extent of reaction ξ are listed in Table III.

Equilibrium OCS concentrations for the 0.20% CO–CO₂ mixture range from 1074 (471°C) to 1566 ppmv (580°C), while the observed values go from 19 to 899 ppmv over the same temperature range. The extent of reaction varies smoothly from ~ 0.018 to 0.57, with a closer approach to equilibrium at 580°C, the highest temperature studied.

A similar situation applies to the 0.50% CO–CO₂ mixture where the extent of reaction varies from ~ 0.018 at 471°C to ~ 0.58 at 578°C. Finally, the extent of reaction for the 0.50% CO–0.50% SO₂–CO₂ mixture varies from 0.021 at 473°C to 0.38 at 554°C. Figure 4 shows that the extent of reaction is the same (at the same temperature) in all three CO-bearing gas mixtures.

Inside the furnace, ξ values of ~ 0.02 are observed at $\sim 470^\circ\text{C}$ when CO and sulfur vapor have ~ 40 s to react in the hot zone. However, gases have a much longer time to react near the surface of Venus. The convective mixing time (t_{mix}) near the surface of Venus is given by H^2/K_{eddy} , where H is the pressure scale height (~ 16 km at the surface) and K_{eddy} is the vertical eddy diffusion coefficient. Calculated t_{mix} values range from about 30 days to 8 years, for K_{eddy} values of 1×10^6 to 1×10^4 cm² s⁻¹, respectively. A nominal K_{eddy} value of 1×10^4 cm² s⁻¹ and a convective mixing time of 8 years seem preferable (Fegley *et al.* 1997). Our preliminary kinetic results (Hong and Fegley 1997b) indicate that only 3 h are needed for reaction (3) to reach a ξ value of ~ 0.99 (i.e., almost complete equilibrium) in the 0.20% CO–CO₂ gas mixture at 471°C under our experimental conditions. We also calculate that several months

TABLE III
Observed and Calculated Equilibrium OCS Concentrations

Temperature (°C)	OCS Concentration (ppmv)		ξ (obs./equil.)
	Observed	Equilibrium	
0.20 % CO - 99.80 % CO ₂			
471	19.0	1,074	0.018
498	60.4	1,226	0.049
524	211	1,353	0.156
551	574	1,466	0.392
580	899	1,566	0.574
0.50 % CO - 99.50 % CO ₂			
471	49.3	2,686	0.018
498	157	3,065	0.051
524	504	3,384	0.149
552	1,290	3,675	0.351
578	2,260	3,899	0.580
0.50 % CO - 0.50 % SO ₂ - 99.00 % CO ₂			
473	55.9	2,715	0.021
500	209	3,091	0.068
527	631	3,417	0.185
554	1,420	3,694	0.384

is sufficient for reaction (3) to achieve equilibrium ($\xi = 0.99$) near the surface of Venus (740 K).

Thus, we used reaction (3) to calculate the OCS equilibrium abundance at Venus' modal radius (6051.4 km), where the temperature and pressure are 740 K (467°C) and 95.6 bars, respectively (Ford and Pettengill 1992, Seiff *et al.* 1986). Rearranging Eq. (13) to solve for the equilibrium OCS mixing ratio gives

$$X_{\text{OCS}} = [K_3 \cdot X_{\text{CO}}^2 \cdot X_{S_2} \cdot P_T]^{1/2}, \quad (15)$$

where K_3 is calculated from Eq. (14). Fegley *et al.* (1997) concluded that the CO mixing ratio at Venus' surface is 3–20 ppmv, with a nominal value of ~ 9 ppmv. This conclusion is based on thermochemical equilibrium and kinetic calculations of gas chemistry, reanalysis of the results of the CONTRAST experiment on Venera 13 and 14, a review of spacecraft and Earth-based observations of CO, and a reassessment of the magnetite–hematite phase boundary based on the Venera 9 and 10 lander spectral reflectance

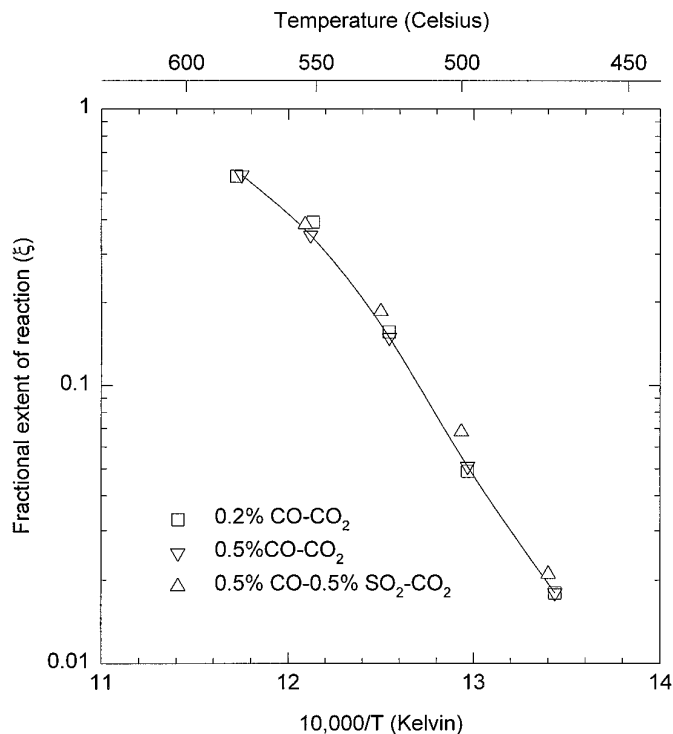


FIG. 4. The fractional extent of reaction (ξ) in three CO-bearing gas mixtures. The same extent of reaction is observed in all three CO gas mixtures studied.

data and new thermodynamic data. Fegley (1997) derived S_2 mixing ratios of 14–42 parts per billion by volume (ppbv) based on Venera 11–14 spacecraft observations of sulfur vapor near the surface of Venus (<12-km altitude) and thermodynamic data for sulfur vapor allotropes. As discussed by Fegley (1997), thermodynamic modeling (San'ko 1980, Zolotov 1985) reproduces the sulfur vapor vertical profile observed by the Venera spacecraft below 12–14 km on Venus. Thus, below 12–14 km the sulfur vapor profile is apparently controlled by thermodynamic equilibrium and may not be perturbed by photochemistry. This is generally consistent with Prinn's (1979) suggestion that photochemistry of sulfur vapor allotropes may be important at altitudes above about 10 km. Here we use a nominal value of 28 ppbv for the S_2 mixing ratio at the surface of Venus.

Substituting the nominal CO and S_2 mixing ratios into Eq. (15) yields an equilibrium OCS mixing ratio of 5 ppmv. The equilibrium OCS abundance ranges from 1 to 14 ppmv when the low and high values, respectively, for CO and S_2 are substituted into Eq. (15). The calculated OCS mixing ratios from reaction (3) are lower than the 28 ppmv OCS predicted by kinetic modeling of the higher altitude OCS and CO observations (Krasnopolsky and Pollack 1994) and also are lower than the 16–29 ppmv OCS calculated from thermochemical models assuming complete gas phase

equilibrium (Fegley *et al.* 1997). We take 5 ppmv and a range of 1–14 ppmv as the OCS abundance from reaction (3) near Venus' surface.

Although our estimate of 1–14 ppmv OCS is lower than other recent calculations of the OCS mixing ratio it is important to remember that the OCS abundance is observationally unconstrained below 26 km altitude on Venus (Pollack *et al.* 1993). Also, because of a lack of kinetic data, Krasnopolsky and Pollack (1994) stated that their kinetic modeling did not include some reactions which may be important for CO and OCS in the lowest 20 km of Venus' atmosphere. Finally, Fegley *et al.* (1997) concluded that gas phase thermochemical equilibrium is only reached, if at all, in the lowest levels of Venus' atmosphere at temperatures above about 730 K. The 16–29 ppmv OCS that they predict from complete gas phase equilibrium includes a contribution from reaction (1), the conversion of SO_2 to OCS. However we find reaction (1) to be slow relative to reaction (3). As discussed earlier, Ferguson (1918) also finds reaction (1) to be slow even at temperatures as high as 1000°C.

On the other hand, the OCS abundance near Venus' surface may be larger than calculated here because our result applies only to reaction (3) and other OCS sources need to be studied. For example, the oxidation of pyrrhotite has also been proposed as a source of OCS (Lewis 1970, Fegley and Treiman 1992). We have made preliminary experiments which show that OCS is produced when natural pyrrhotites are heated in CO–CO₂ gas mixtures. Although pyrrhotite is thermodynamically unstable on Venus' surface, its decomposition rate is a function of grain size. Thus, large pyrrhotite masses may be present for long times and be a source of OCS (Fegley *et al.* 1995) and of the sulfur vapor near the surface. Small pyrrhotite grains, like those found in terrestrial basalts, will decompose more rapidly than large magmatic masses. In any case, it is unlikely that pyrite is the source of the observed sulfur vapor on Venus because the sulfur vapor partial pressure in Venus' atmosphere is less than the equilibrium sulfur vapor pressure over pyrite, which is unstable and rapidly decomposes on Venus (Fegley *et al.* 1995, Fegley 1997).

Volcanic outgassing on Venus may also be a source of OCS, as it is on Earth (Symonds *et al.* 1994). The volcanism rate estimated from steady-state models for replenishing SO_2 lost by reaction with Venus' surface ranges from 0.1 to 10 km³ year⁻¹, with a nominal value of 1 km³ year⁻¹ (Fegley and Prinn 1989). For comparison, the average rate of subaerial volcanism on Earth is ~1 km³ year⁻¹ and the total volcanism rate is about 20 km³ year⁻¹ (Fegley and Treiman 1992). It is important to search for volcanic activity on Venus, probably by looking for volcanic signatures such as (1) localized variations in SO_2 , H_2O , OCS, and other volcanically outgassed species, (2) changes in the "average" atmospheric thermal structure in the vicinity of

volcanic gas plumes, (3) increased atmospheric dust levels in the vicinity of volcanic gas plumes, and (4) spatial and temporal variations in the surface thermal flux around volcanic vents. Such searches are probably best made from an orbiting spacecraft with spectroscopic instrumentation.

SUMMARY

The major results of this work are as follows:

(1) No detectable OCS was observed by heating a 0.50% CO–0.50% SO₂–CO₂ mixture at 471°C, although the predicted equilibrium OCS concentration is ~740 ppmv. No additional OCS was observed when pyrite was heated in a 0.50% CO–0.50% SO₂–CO₂ mixture at 473–554°C relative to the amount formed by heating pyrite in a 0.50% CO–CO₂ mixture over the same temperature range. Thus, there is no evidence for reaction (1) under our experimental conditions.

(2) Small amounts of OCS are formed by heating pyrite in purified CO₂ at 538 to 612°C, but the amount of OCS formed is undetectable (<1 ppmv) at 471°C. There is no evidence that pyrite is reacting with the gas. Reaction (2) did not occur under our experimental conditions. Instead the pyrite is only a source of sulfur vapor which then reacts to form OCS. The mechanism of OCS formation in CO₂ is still not clear, but is plausibly from reaction of S₂ with CO produced from the CO₂ by some other reaction.

(3) Carbonyl sulfide is formed by heating pyrite in CO-bearing gases at temperatures of 470 to 580°C in the laboratory. The amount of OCS formed is significantly greater than that formed by heating pyrite in purified CO₂ at the same temperatures, and is directly proportional to the CO content of the gas.

(4) The experimental data suggest that both sulfur vapor and CO are needed to form OCS in the laboratory and that OCS formation proceeds via reaction (3).

(5) Reaction (3) is much more rapid than reaction (1) under our experimental conditions. The measured extent of reaction (ξ) for reaction (3) varies from ~0.02 to ~0.58 from ~470 to ~580°C, while the upper limit to ξ for reaction (1) at 470°C is $\leq 1.3 \times 10^{-3}$ (1 ppmv/743 ppmv).

(6) The experimental data, kinetic calculations, and equilibrium calculations indicate that CO and S₂ in Venus' lower atmosphere react to form OCS via reaction (3) as originally hypothesized in the Venus sulfur cycle (Von Zahn *et al.* 1983, Prinn *et al.* 1985). The experimental data also support the concept that the coupled increase in OCS and decrease in CO with decreasing altitude is due to OCS formation at the expense of CO. The calculated OCS equilibrium abundance from reaction (3) at the surface of Venus (740 K) is 1–14 ppmv with a nominal value of 5 ppmv. Other OCS sources, such as pyrrhotite oxidation, and volcanic outgassing may also produce OCS and lead to a higher OCS abundance at Venus' surface.

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