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

Yong Hong and Bruce Fegley, Jr.

Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Campus Box 1169, Washington University, One Brookings Drive, St. Louis, Missouri 63130-4899
E-mail: bfegley@levee.wustl.edu

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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 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).

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

\[
\begin{align*}
\text{SO}_2 + 3\text{ CO} &= \text{OCS} + 2\text{ CO}_2 \quad (1) \\
3\text{ FeS}_2 \text{ (pyrite)} + 4\text{ CO}_2 + 2\text{ CO} &= \text{Fe}_3\text{O}_4 \text{ (magnetite)} \\
&+ 6\text{ OCS} \quad (2) \\
2\text{ CO} + \text{ S}_2 &= 2\text{ OCS} \quad (3)
\end{align*}
\]

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 CuKα radiation (λ = 1.540598 Å) 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 ± 0.80% Fe and 53.32 ± 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 ± 0.001(2σ). 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 FeS₂.

**Gas Mixtures and Gas Analysis**

Coleman grade (99.99%) CO₂ and CO₂ mixtures with SO₂ (anhydrous grade, 99.98%), and CO (CP grade 99.5%) were used in this work. The mixtures used contain 99.0–100% CO₂, 0–0.50% CO, and 0–0.50% SO₂ (Table I). The gas mixtures are either certified standards accurate to ±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 (Mg(ClO₄)₂) to remove any O₂ and H₂O impurities. No O₂ or H₂O were found by gas chromatography in the purified gas mixtures at our detection limits of ~1 ppmv. The concentrations of any residual O₂ and H₂O 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 cm³ 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...
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 ±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 ±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 show only
\[ \log_{10} P_S^2(\text{bars}) = 16.20 - \frac{15700}{T}, \tag{5} \]

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 an 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. 2. Typical gas chromatograms of the OCS standard and reaction products.](image)

(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 ppmv OCS formed by heating pyrite at 471°C in 0.50% CO–CO2. (d) A chromatogram of the OCS standard (98.3 ppmv OCS in He). The small peak before OCS is H2S, an impurity present in the gas cylinder.

Pyrite and pyrrhotite (Fe1–xS), 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:

\[
(1 - x)\text{FeS}_2(\text{pyrite}) = \text{Fe}_{1-x}\text{S}(\text{pyrrhotite}) + \frac{(1 - 2x)}{2} \text{S}_2(\text{g}) \tag{4}
\]

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

![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.](image)
TABLE II
Comparison of OCS Concentrations in Two CO–CO₂ Gas Mixtures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OCS (ppmv) 0.2% CO</th>
<th>OCS (ppmv) 0.5% CO</th>
<th>Ratio</th>
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</thead>
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<tr>
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<tr>
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<td>899</td>
<td>2,260</td>
<td>2.51</td>
</tr>
</tbody>
</table>

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 (±10% or 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

\[ \text{SO}_2 + 3 \text{CO} = \text{OCS} + 2 \text{CO}_2, \]  

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 ≤2.0 × 10⁻⁴ (1 × 10⁻⁶/5000 × 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 (≤2.0 × 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 upper limit (≤2.0 × 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.

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/SO₂ 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 SO$_2$ to OCS in two different mechanisms. The first reaction

$$\text{CO} + \text{SO}_2 \rightarrow \text{CO}_2 + \text{SO} \quad (6)$$

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

$$\text{SO}_2 + \text{H} + \text{M} \rightarrow \text{SO} + \text{OH} + \text{M} \quad (7)$$

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 SO$_2$ 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 SO$_2$ 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, S$_2$ is the dominant allotrope in sulfur vapor (Toulmin and Barton 1964; Hong and Fegley 1997a). Formation of OCS from S$_2$ vapor and CO$_2$ could proceed via two different pathways. Carbon dioxide could react directly with S$_2$ to form OCS. Alternatively, CO could form by some other reaction and then react with S$_2$ to form OCS.

Formation of OCS by reaction of CO$_2$ and S$_2$ may occur by net reactions such as

$$2\text{CO}_2 + \text{S}_2 = \text{OCS} + \text{CO} + \text{SO}_2 \quad (8)$$
$$2\text{CO}_2 + \text{S}_2 = 2\text{OCS} + \text{O}_2 \quad (9)$$
$$2\text{CO}_2 + 1.5\text{S}_2 = 2\text{OCS} + \text{SO}_2. \quad (10)$$

Reactions (8) to (10) also predict the formation of significant amounts of SO$_2$ or O$_2$. However, our gas chromatographic analyses show only OCS without any O$_2$ or SO$_2$ above the ~1 ppmv detection limit. Also, OCS formation by reaction (9) produces O$_2$ and should cause pyrite oxidation to iron oxides from the O$_2$ formed. Again, this is not observed.

We prefer the second alternative, OCS formation by reaction of S$_2$ with small amounts of CO. The CO is either a trace impurity remaining in the purified CO$_2$ or was made by some reaction involving CO$_2$. It is unlikely that CO is quenched at 748 K, equivalent to an elevation of −1.0 ± 1.7 km below Venus’ modal radius. The second reaction

$$\text{SO}_2 + \text{H} + \text{M} \rightarrow \text{SO} + \text{OH} + \text{M} \quad (7)$$

is quenched at 693 ± 9 K (6.1 ± 1.1-km altitude). In both cases conversion of SO$_2$ 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 SO$_2$ 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 SO$_2$ to OCS, is probably slow in Venus’ lower atmosphere and of minor importance as a source of OCS.

**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 as low as 250°C (Lewis and Lacey 1915). We calculated the extent of reaction $\xi$,

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

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

$$K_3 = \frac{P_{\text{OCS}}^2}{P_{\text{CO}}P_{\text{S}_2}} = \frac{P_{\text{OCS}}^2}{(P_{\text{CO,in}} - P_{\text{OCS}})P_{\text{S}_2}} \quad (13)$$

$$= \frac{X_{\text{OCS}}}{(X_{\text{CO,in}} - X_{\text{OCS}})X_{\text{S}_2}} \times \frac{1}{P_r}.$$
FORMATION OF OCS ON VENUS

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 \( \text{S}_2 \) pressure in Eq. (13) is the \( \text{S}_2 \) equilibrium vapor pressure over pyrite from Eq. (5). The \( \text{S}_2 \) pressure is not reduced by OCS formation because \( \text{S}_2 \) is continually vaporized from the pyrite in the isothermal hot zone of the furnace.

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

\[
K_3 = \exp(-\Delta G^o/RT),
\]

where \( R \) is the ideal gas constant and \( \Delta G^o \) for reaction (3) is taken from the tabulation of Gurvich et al. (1989–1994).

Equilibrium OCS concentrations for the 0.20% CO±CO_2 mixture range from 1074 (471 \( ^\circ \text{C} \)) to 1566 ppmv (580 \( ^\circ \text{C} \)), 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 \( ^\circ \text{C} \), the highest temperature studied.

A similar situation applies to the 0.50% CO±CO_2 mixture where the extent of reaction varies from ~0.018 at 471 \( ^\circ \text{C} \) to ~0.58 at 578 \( ^\circ \text{C} \). Finally, the extent of reaction for the 0.50% CO±0.50% SO_2±CO_2 mixture varies from 0.021 at 473 \( ^\circ \text{C} \) to 0.38 at 554 \( ^\circ \text{C} \). 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, \( \xi \) values of ~0.02 are observed at ~470°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 \( (t_{\text{mix}}) \) near the surface of Venus is given by \( H^2/K_{\text{eddy}} \), where \( H \) is the pressure scale height (~16 km at the surface) and \( K_{\text{eddy}} \) is the vertical eddy diffusion coefficient. Calculated \( t_{\text{mix}} \) values range from about 30 days to 8 years, for \( K_{\text{eddy}} \) values of \( 1 \times 10^6 \) to \( 1 \times 10^4 \) cm² s⁻¹, respectively. A nominal \( K_{\text{eddy}} \) value of \( 1 \times 10^4 \) 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 \( \xi \) value of ~0.99 (i.e., almost complete equilibrium) in the 0.20% CO±CO_2 gas mixture at 471°C under our experimental conditions. We also calculate that several months 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

\[
X_{\text{OCS}} = [K_3 \cdot X_{\text{CO}} \cdot X_{\text{S}_2} \cdot P_T]^{1/2},
\]

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.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OCS Concentration (ppmv)</th>
<th>( \xi ) (obs./equil.)</th>
</tr>
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<tbody>
<tr>
<td>471</td>
<td>19.0</td>
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<tr>
<td>498</td>
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</tr>
<tr>
<td>580</td>
<td>899</td>
<td>1,566</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OCS Concentration (ppmv)</th>
<th>( \xi ) (obs./equil.)</th>
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<tbody>
<tr>
<td>473</td>
<td>55.9</td>
<td>2,715</td>
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<tr>
<td>500</td>
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<td>3,091</td>
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<td>631</td>
<td>3,417</td>
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<tr>
<td>554</td>
<td>1,420</td>
<td>3,694</td>
</tr>
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</table>

TABLE III

Observed and Calculated Equilibrium OCS Concentrations

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OCS Concentration (ppmv)</th>
<th>( \xi ) (obs./equil.)</th>
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<td>580</td>
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<td>0.50% CO - 99.50% CO_2</td>
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<tr>
<td>0.50% CO - 0.50% SO_2 - 99.00% CO_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>55.9</td>
<td>2,715</td>
</tr>
<tr>
<td>500</td>
<td>209</td>
<td>3,091</td>
</tr>
<tr>
<td>527</td>
<td>631</td>
<td>3,417</td>
</tr>
<tr>
<td>554</td>
<td>1,420</td>
<td>3,694</td>
</tr>
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</table>
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 SO2 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 (<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 S2 mixing ratio at the surface of Venus.

Substituting the nominal CO and S2 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 S2 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.

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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 SO2 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.

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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 ~1.3 x 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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REFERENCES


