

# Is Carbonyl Sulfide a Precursor for Carbon Disulfide in Vegetation and Soil? Interconversion of Carbonyl Sulfide and Carbon Disulfide in Fresh Grain Tissues in Vitro

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The interconversion of carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>) was studied in the roots and shoots of barley and chickpeas. Ratios of conversion gases, *K*, 40 h after the addition of COS or CS<sub>2</sub> are recorded. The proportion of COS converted to each of CS<sub>2</sub>, CO, and H<sub>2</sub>S and the proportion of CS<sub>2</sub> converted to COS were greater in roots than in shoots. More COS was converted to CS<sub>2</sub> than CS<sub>2</sub> to COS in roots and shoots of barley and chickpeas. The amount of COS converted to H<sub>2</sub>S and CO was 8 times the amount converted to CS<sub>2</sub> in barley and 3–4 times the amount in chickpeas. Carbonyl sulfide may be a precursor for CS<sub>2</sub> in vegetation and soil, just as the reverse is true in the atmosphere. These two different results might form a cycle of COS and CS<sub>2</sub>.

**Keywords:** *Fumigants; COS; CS<sub>2</sub>; interconversion; sulfur cycle*

## INTRODUCTION

Carbon disulfide (CS<sub>2</sub>) is the oldest fumigant used for large commercial scale insect control in grain and soil (Bond, 1984). It is currently used in certain parts of the world. Carbonyl sulfide (COS) is a potential stored product fumigant (Desmarchelier, 1994). Both COS and CS<sub>2</sub> are present in the atmosphere, soil, and some food (Sze and Ko, 1979a; Munnecke, 1967; Von Schildknecht and Rauch, 1962). They play important roles in the chemistry of the global atmosphere and in the biogeochemical sulfur cycle (Sze and Ko, 1979a, 1980; Turco et al., 1980; Gregory et al., 1993). Recent investigations have shown that the fluxes of COS are much greater from areas of high biological productivity (Adams et al., 1981; Khalil et al., 1984) and that vegetation and soil provide a major global sink for COS (Bremner and Banwart, 1976; Crutzen, 1983; Brown and Bell, 1986; Brown et al., 1986; Kluczewski et al., 1985). It is noteworthy that sorption of COS by moist soils was accompanied by the release of a small amount of CS<sub>2</sub> (Bremner and Banwart, 1976). Understanding the interconversion of COS and CS<sub>2</sub> is important for the fate of these chemicals as grain fumigants, to understanding the global sulfur cycle, and to understanding utilization of the gases by plants. Here we report the interconversion of COS and CS<sub>2</sub> in fresh seed tissues (roots and shoots).

## MATERIALS AND METHODS

**Preparation of Sprouted Grain.** Australian barley (var. Schooner) and chickpea (Desi-type var. Amethyst) were used for preparing sprouted grain. Fifty seeds were saturated with ~40 mL of distilled water and wrapped in two rolled crepe filter papers (500 × 330 mm each). The seeds were arranged 3 cm apart on the top half of the sheet (i.e., 250 × 330 mm), using a seed counting board, and the lot was covered by folding the lower half over them. Each doubled sheet was saturated

with water and loosely rolled from one side to together, perpendicular to the base. It was then held together with a rubber band and put in an upright position in the germination cabinet for 7 days, at 25 °C.

**Treatment of Sprouted Grain with COS and CS<sub>2</sub>.** The samples (1.0 g) of barley roots, barley shoots, chickpea roots, and chickpea shoots were placed at 25 °C in 120 mL glass vials fitted with Mininert Teflon valves. Either 0.7 mmol of COS (Matheson Gas Products, Cucamonga, CA) or CS<sub>2</sub> (Ajax, Sydney, Australia) was added by gastight syringe. A control was used for each sample and treatment. Each experiment was replicated three times.

**In Vitro COS, CS<sub>2</sub>, H<sub>2</sub>S, CO, CO<sub>2</sub>, and O<sub>2</sub> Assay.** COS, CS<sub>2</sub>, and H<sub>2</sub>S were determined on a Shimadzu GC6AM GC (Shimadzu Seisakusho, Kyoto, Japan), equipped with a flame photometric detector (FPD). Separation was achieved on a 1 m × 3 m i.d. glass column packed with HayeSep Q (Alltech Associates, Baulkham Hills, Australia, catalog no. 2801) at 140 °C and carrier flow (N<sub>2</sub>) of 40 mL/min at 0.8 psi. Analysis of CO, CO<sub>2</sub>, and O<sub>2</sub> was carried out using a Fisher model 1200 gas partitioner with 80–100 mesh Columpak PQ (6.5 ft × 1/8 in.) and 60–80 mesh molecular sieve 13X (11 ft × 3/16 in.) columns in series. The conditions used were as follows: carrier gas, helium, at a flow rate of 30 mL/min; oven temperature, 50 °C.

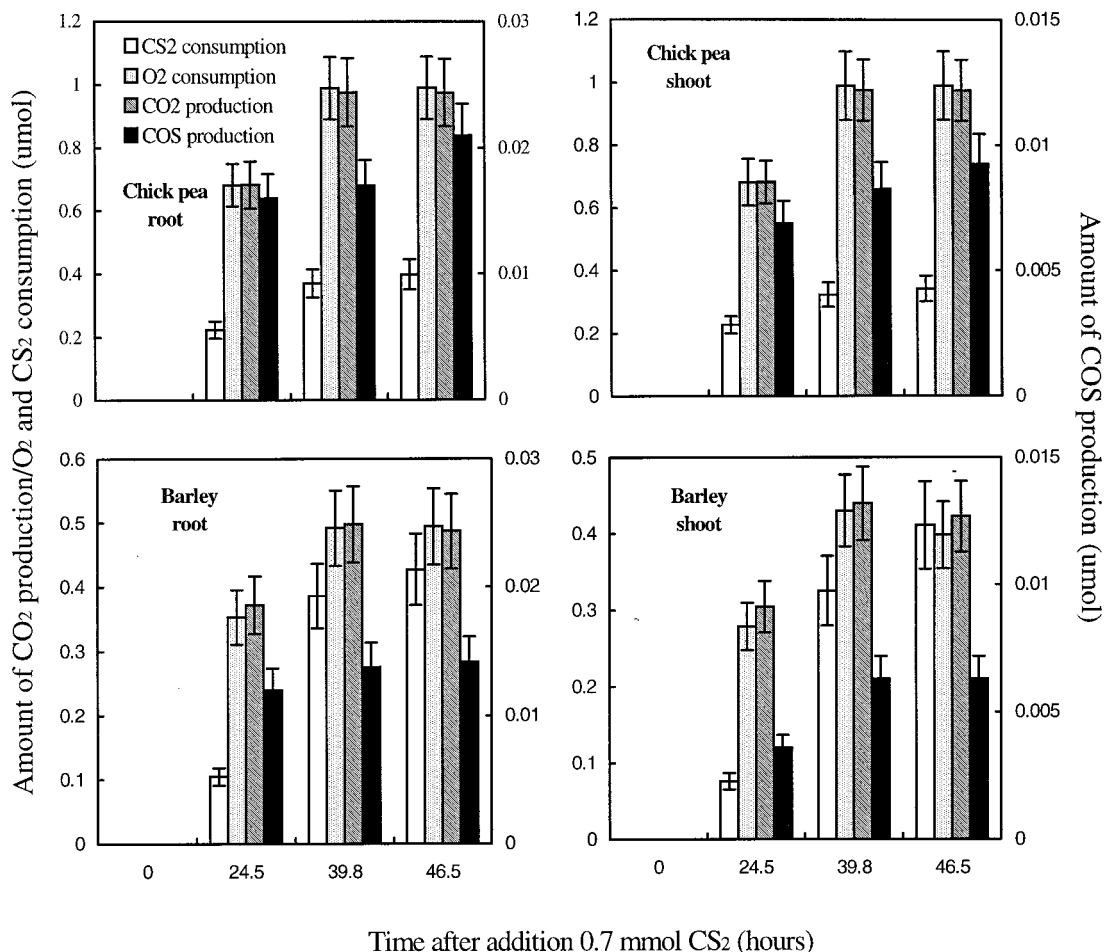
The headspace gas of 40 μL for sulfur-containing gas and 0.3 mL for CO, CO<sub>2</sub>, and O<sub>2</sub> was taken using a gastight syringe and injected into the GC at timed intervals. Each GC determination was the mean of duplicate injections. Concentrations were calculated on the basis of peak areas. Peak areas were calibrated periodically using a standard gas. Sulfur-containing standard gas was prepared by injecting a measured volume of known concentration of H<sub>2</sub>S (Aldrich, Castle Hill, Australia), COS, and CS<sub>2</sub> into an Erlenmeyer flask (1.1 L measured volume) containing five glass beads (2–3 mm o.d.). The standard for non-sulfur gases was a cylinder (BOC, Sydney, Australia) of known composition of CO, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>.

## RESULTS AND DISCUSSION

Known reactions relevant to vegetation and soil fluxes (emission and sink) of COS and CS<sub>2</sub> include the following:

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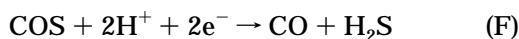
**Figure 2.** Production of CO<sub>2</sub> and (right-hand scale) COS and consumption of O<sub>2</sub> and CS<sub>2</sub> after addition of 0.7 mmol of CS<sub>2</sub> to roots or shoots of barley or chickpeas. (Error bars indicate the SE of the replicated treatments.)

**Table 1. Ratio of Gas Concentrations (*K*) at 40 h after the Addition COS or CS<sub>2</sub> to Roots or Shoots of Barley and Chickpeas at 25 °C**

process	ratio ( <i>K</i> )	barley			chickpea		
		<i>K<sub>r</sub></i> <sup>a</sup> (SE) <sup>c</sup>	<i>K<sub>s</sub></i> <sup>b</sup> (SE)	<i>K<sub>r</sub>/K<sub>s</sub></i> (SE)	<i>K<sub>r</sub></i> (SE)	<i>K<sub>s</sub></i> (SE)	<i>K<sub>r</sub>/K<sub>s</sub></i> (SE)
COS → CS <sub>2</sub>	[CS <sub>2</sub> ]/[COS]	0.10 (0.02)	0.01 (0.002)	10 (2.1)	0.17 (0.03)	0.006 (0.003)	29 (2.8)
COS → CO	[CO]/[COS]	0.80 (0.18)	0.08 (0.02)	10 (2.3)	0.62 (0.13)	0.02 (0.005)	29 (2.5)
COS → H <sub>2</sub> S	[H <sub>2</sub> S]/[COS]	0.80 (0.21)	0.08 (0.02)	10 (1.8)	0.60 (0.11)	0.02 (0.004)	30 (3.2)
CS <sub>2</sub> → COS	[COS]/[CS <sub>2</sub> ]	0.04 (0.10)	0.014 (0.01)	2.8 (0.4)	0.06 (0.01)	0.03 (0.008)	2 (0.5)
CS <sub>2</sub> → CO	[CO]/[CS <sub>2</sub> ]	0 <sup>d</sup>	0		0	0	
CS <sub>2</sub> → H <sub>2</sub> S	[H <sub>2</sub> S]/[CS <sub>2</sub> ]	0	0		0	0	

<sup>a</sup> *K<sub>r</sub>* is the ratio (*K*) of concentrations over roots. <sup>b</sup> *K<sub>s</sub>* is the constant (*K*) of concentrations over shoots. <sup>c</sup> SE is standard error of three replicates. <sup>d</sup> A value of zero indicates CO or H<sub>2</sub>S was undetectable.

Because the proportional conversions of COS to COS and to H<sub>2</sub>S were identical in each system, it is concluded that reaction F occurs.



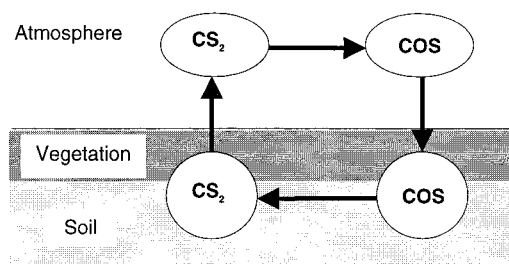
CO is produced in the headspace of wheat in sealed storage (Reuss et al., 1994) at levels that may cause a problem for worker safety. We have also found in the laboratory that COS is produced during storage of wheat and barley in sealed containers at levels of 25–600 ppb (w/w). CO levels in the headspace over grain may result via decomposition of COS. If so, sprouting of grain in sealed storage would be expected to increase production of both COS and CO.

Sze and Ko (1979b) suggested that CS<sub>2</sub> is a precursor for atmospheric COS, and they also pointed out that the

ocean might be a source for atmospheric CS<sub>2</sub>. However, we argue here that COS is also a precursor for CS<sub>2</sub> in vegetation and soil and that vegetation and soil might be a major source for atmospheric CS<sub>2</sub>. These two different results might form a cycle of COS and CS<sub>2</sub> (Figure 3).

## CONCLUSION

The interconversion of COS and CS<sub>2</sub> is a pleasing result from the point of view of effect of COS and CS<sub>2</sub> as fumigants on the environment and also indicates that residues of these two chemicals in food appear to be more natural than those from other fumigants. Carbonyl sulfide may be a precursor for CS<sub>2</sub> in vegetation and soil. This result and the reverse in the atmosphere might form a cycle of COS and CS<sub>2</sub>.



**Figure 3.** Schematic diagram of the global cycle of COS and CS<sub>2</sub>.

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