

### The Sulfur Cycle of Venus: New Insights from Venus Express

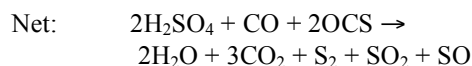
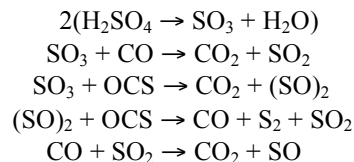
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**Introduction:** Sulfur chemistry is critical to the composition of the Venus atmosphere [1]. Due to the lack of an ocean, most of sulfur species on Venus reside in the atmosphere, attaining concentrations  $\sim 10^5$  times those in the terrestrial atmosphere. Four sulfur species have been firmly identified:  $\text{SO}_2$ ,  $\text{SO}$ ,  $\text{OCS}$ , and  $\text{H}_2\text{SO}_4$  (vapor and in aerosols). Strong absorption in spectrophotometer data from VENERA 11 and 12 at 450-600 nm between 10 and 30 km has been attributed variously to gaseous elemental sulfur, polysulfur ( $\text{S}_x$ ), or  $\text{SO}_2$ . The presence of thiozone ( $\text{S}_3$ ) and polysulfur in the clouds has been inferred. New observations from Venus Express quantify the abundances of key sulfur species and relate  $\text{OCS}$  and  $\text{CO}$  in the middle atmosphere [3].

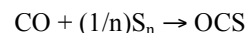
We now understand that the sulfur cycle on Venus consists of at least two cycles. (1) Above the cloud-tops,  $\text{SO}_2$  is oxidized to  $\text{SO}_3$ , leading to the formation of  $\text{H}_2\text{SO}_4$ . In the lower atmosphere  $\text{SO}_3$  eventually reacts with  $\text{CO}$  to restore  $\text{SO}_2$  and  $\text{CO}_2$ . (2)  $\text{OCS}$  is the major carrier of sulfur from the surface to the middle troposphere, where it is converted to  $\text{CO}$  and  $\text{S}_x$ . At or near the surface, the reverse reaction occurs, resulting in the recombination of  $\text{CO}$  and  $\text{S}_x$  to  $\text{OCS}$ .

**Two Types of Chemistry:** The chemical regimes in the atmosphere of Venus vary from photochemistry in the middle atmosphere to thermal equilibrium chemistry in the lower atmosphere and the surface [2]. Recent data of  $\text{OCS}$  and  $\text{CO}$  from ground-based and Venus Express observations provide a unique opportunity for advancing our understanding of chemistry and transport in the lower atmosphere of Venus. The combination of data and modeling provides strong evidence for the loss of  $\text{OCS}$  by conversion to  $\text{CO}$  in the lower atmosphere. The total loss rate of  $\text{OCS}$  in the lower atmosphere is about 23,000 Tg-S/yr [3]. This is a robust result that does not depend on the details of the model. The surface of Venus must supply  $\text{OCS}$  at this rate to maintain the concentration of  $\text{OCS}$  in steady state in the atmosphere. The implications for surface chemistry are discussed.

**Equilibrium Chemistry at or near the Surface:** While the chemistry of sulfur in the atmosphere above the clouds is fairly well understood, this is not true in the lower atmosphere and at the surface, where reactions such as the following have been proposed but are poorly understood [4]:

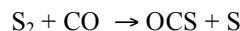


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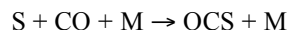


What are the most stable forms of sulfur species in the lower atmosphere? In thermodynamic equilibrium at the surface of Venus, the relative partitioning of sulfur species is summarized in Table 1.  $\text{S}_2$  is the most abundance  $\text{S}_x$  species.

The following reaction has also been suggested [4]:



It is known that



Together, these two reactions may restore the  $\text{OCS}$  that is lost in the middle atmosphere.

Table 1. Relative concentrations of S species in mole fractions. The numbers a(-b) read as $a \times 10^{-b}$ .	
Species	Abundance
$\text{OCS}$	2.6(-5)
$\text{H}_2\text{S}$	2.8(-7)
$\text{SO}_2$	1.0(-4)
$\text{S}_2\text{O}$	1.7(-8)
$\text{S}$	5.1 (-17)
$\text{S}_2$	1.7 (-7)
$\text{S}_3$	5.6 (-10)
$\text{S}_4$	2.8 (-12)
$\text{S}_5$	1.0 (-12)
$\text{S}_6$	4.7 (-14)
$\text{S}_7$	4.0 (-16)
$\text{S}_8$	1.0 (-17)

**Secular Changes in SO<sub>2</sub> and H<sub>2</sub>O above Cloudtops**

Both SO<sub>2</sub> and H<sub>2</sub>O are removed by the formation of H<sub>2</sub>SO<sub>4</sub>. As H<sub>2</sub>SO<sub>4</sub> aerosols are removed, they represent a net sink of SO<sub>2</sub> and H<sub>2</sub>O, thereby explaining their rapid decrease with altitude. The abundances of SO<sub>2</sub> and H<sub>2</sub>O are of the same order of magnitude. An excess of H<sub>2</sub>O would result in the rapid removal of SO<sub>2</sub> and vice versa. We argue that this mutual control of SO<sub>2</sub> and H<sub>2</sub>O serves to amplify any temporal variability of the Hadley circulation into secular changes for SO<sub>2</sub> and H<sub>2</sub>O above the cloudtops. We will study

~100 (earth) years of GCM runs to examine this plausible mechanism for the observed secular changes in SO<sub>2</sub> and H<sub>2</sub>O observed by Venus Express and previous missions.

**References:** [1] Mills F.P. et al. (2007). *Exploring Venus as a Terrestrial Planet*, eds. Esposito, L.W., E. Stofan, T. Cravens, American Geophysical Union, Washington, DC 73-100. [2] Prinn R.G. (1975). *J. Atmos. Sci.*, Vol. 32 1237-1247 [3] Yung Y.L. et al. (2008) in press. *J. Geophys. Res.* [4] Krasnopolsky V.A. (2007). *Icarus* doi:10.1016/j.icarus.2007.04.028.