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 ~10^5 times those in the terrestrial atmosphere. Four sulfur species have been firmly identified: SO_2, SO, OCS, and H_2SO_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 (S_x), or SO_2. The presence of thiozone (S_3) and polysulfur in the clouds has been inferred. New observations from Venus Express quantify the abundances of key sulfur species and relate OCS and 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, SO_2 is oxidized to SO_3, leading to the formation of H_2SO_4. In the lower atmosphere SO_3 eventually reacts with CO to restore SO_2 and CO_2. (2) OCS is the major carrier of sulfur from the surface to the middle troposphere, where it is converted to CO and S_x. At or near the surface, the reverse reaction occurs, resulting in the recombination of CO and S_x to 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 OCS and 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 OCS by conversion to CO in the lower atmosphere. The total loss rate of 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 OCS at this rate to maintain the concentration of 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]:

$$2(H_2SO_4 \rightarrow SO_3 + H_2O)$$
$$SO_3 + CO \rightarrow CO_2 + SO_2$$
$$SO_3 + OCS \rightarrow CO_2 + (SO)_2$$
$$(SO)_2 + OCS \rightarrow CO + S_2 + SO_2$$
$$CO + SO_2 \rightarrow CO_2 + SO$$

Net: $$2H_2SO_4 + CO + 2OCS \rightarrow 2H_2O + 3CO_2 + S_2 + SO_2 + SO$$

and

$$CO + (1/n)S_n \rightarrow OCS$$

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. S_2 is the most abundance S_x species.

The following reaction has also been suggested [4]:

$$S_2 + CO \rightarrow OCS + S$$

It is known that

$$S + CO + M \rightarrow OCS + M$$

Together, these two reactions may restore the OCS that is lost in the middle atmosphere.

Table 1. Relative concentrations of S species in mole fractions. The numbers a(-b) read as ax10^{-b}.

Species	Abundance
OCS	2.6(-5)
H_2S	2.8(-7)
SO_2	1.0(-4)
S_2O	1.7(-8)
S	5.1 (-17)
S_2	1.7 (-7)
S_3	5.6 (-10)
S_4	2.8 (-12)
S_5	1.0 (-12)
S_6	4.7 (-14)
S_7	4.0 (-16)
S_8	1.0 (-17)

Secular Changes in SO_2 and H_2O above Cloudtops

Both SO_2 and H_2O are removed by the formation of H_2SO_4. As H_2SO_4 aerosols are removed, they represent a net sink of SO_2 and H_2O, thereby explaining their rapid decrease with altitude. The abundances of SO_2 and H_2O are of the same order of magnitude. An excess of H_2O would result in the rapid removal of SO_2 and vice versa. We argue that this mutual control of SO_2 and H_2O serves to amplify any temporal variability of the Hadley circulation into secular changes for SO_2 and H_2O above the cloudtops. We will study ~100 (earth) years of GCM runs to examine this plausible mechanism for the observed secular changes in SO_2 and H_2O 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.