Atmospheric Constraints on Sulfur Reactions Fluxes at the Surface of Venus

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Introduction: It was only a few decades ago when we discovered that the clouds of Venus are made of sulfuric acid (H_2SO_4), and only in recent years did we know that carbonyl sulfide (OCS) is the major carrier of sulfur from the surface to the middle atmosphere. 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. Sulfur chemistry is critical to the composition of the Venus atmosphere [1], and 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.

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: 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]:

$$2(H_2SO_4 \rightarrow SO_3 + H_2O)$$
$$SO_3 + CO \rightarrow CO_2 + SO_2$$
$$SO_3 + OCS \rightarrow CO_2 + (SO)_2$$
$$(SO)_2 + OCS \rightarrow CO + S_2 + SO_2$$
$$CO + SO_2 \rightarrow CO_2 + SO$$
$$\text{Net: } 2H_2SO_4 + CO + 2OCS \rightarrow 2H_2O + 3CO_2 + S_2 + SO_2 + SO$$

and

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

What are the most stable forms of S in the lower atmosphere? The possible forms of S include S_n, whene n = 1 to 8. In thermodynamic equilibrium at the surface of Venus, the relative partitioning of S_n is summarized in Table 1. S_2 is the most abundance sulfur 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_n species in mole fractions. The numbers a(-b) read as ax10^{-b}.

Species	Abundance
S	5.07 (-17)
S_2	1.66 (-7)
S_3	5.59 (-10)
S_4	2.81 (-12)
S_5	1.04 (-12)
S_6	4.76 (-14)
S_7	4.03 (-16)
S_8	1.06 (-17)

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.