

MODEL SENSITIVITY ANALYSIS OF POLYSULFUR REACTIONS IN THE ATMOSPHERE OF VENUS.

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Introduction: The atmosphere of Venus is composed of 96.5% CO₂ and 3.5% N₂, along with trace species. Three dominant chemical cycles have been identified: the carbon dioxide cycle, the sulfur oxidation cycle, and the polysulfur cycle [1]. In the polysulfur cycle, SO₂ undergoes disproportionation to form SO₃ and S_x (2 ≤ x ≤ 8). This cycle also involves the upward transport of OCS and SO₂ and downward transport of S_x which reacts with CO and SO₃ [2].

The identity of the ultraviolet absorber at 320-500 nm in the atmosphere of Venus is an unresolved issue [1]. Polysulfur may be the absorber or may contribute to the production of the absorber [3]. Uncertainty in the potential concentration of polysulfur has added to the difficulty of determining the absorber identity. To resolve the concentration uncertainties, better laboratory data for reactions in the polysulfur cycle are needed. A model sensitivity analysis of polysulfur reactions was performed to identify reactions to prioritize for laboratory study.

Methods: The model used for the sensitivity analysis was a one-dimensional (1-D) diurnally-averaged photochemical model of Venus, based on the 1-D Caltech/JPL KINETICS model [4]. The model extended from altitudes of 58 to 112 km. The layers are 0.2 km from 58-78 km and 2 km from 78-112 km [3]. Of the ~500 reactions in the model, 49 reactions involving polysulfur were identified for potential laboratory study. Sulfur chemistry reaction schemes of the photochemical model are detailed in [2,3].

The 49 reactions were split into five groups based on reaction type and effect on x in S_x: group 1A: sulfur reactions that increase the larger x of the reactants, 11 reactions; group 1B: sulfur reactions that decrease the larger x, 17 reactions; group 2: chlorosulfane reactions, 6 reactions; group 3A: sulfur oxide reactions that increase the larger x, 8 reactions; and group 3B: sulfur oxide reactions that decrease the larger x, 7 reactions.

Reaction rate coefficients were increased and decreased by a factor of 10. Initially, all reaction rate coefficients in a group were changed simultaneously in the same direction, and then each rate coefficient was changed individually.

Preliminary Results: Figures 1 and 2 compare the results of the five groups. The percent changes in the concentrations of S₂, S₄, S₆, and S₈ compared to the nominal model run are plotted.

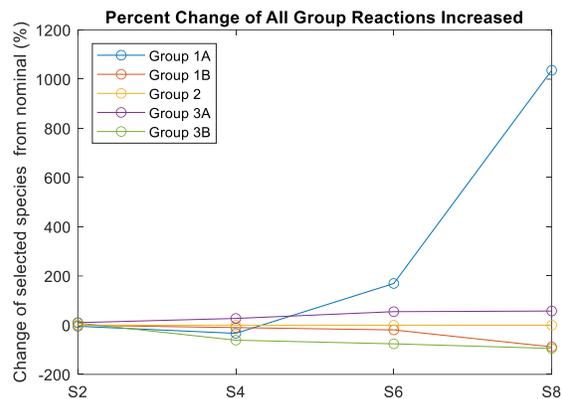


Fig. 1. Increasing all reaction rate coefficients in a group simultaneously.

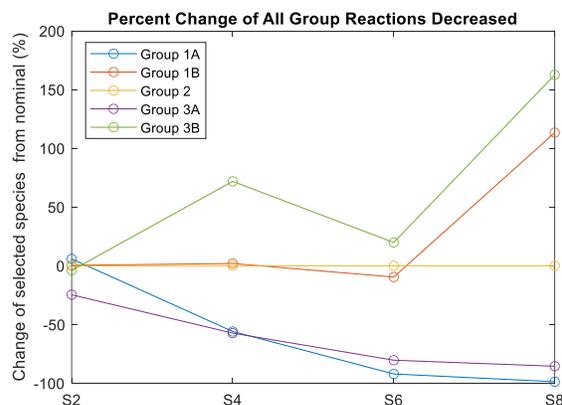


Fig. 2. Decreasing all reaction rate coefficients in a group simultaneously.

When reaction rate coefficients increase, Figure 1, the largest change was caused by the sulfur reactions that increase x (group 1A). The concentration of the final molecule in the polysulfur production chain, S₈, increased by 1,036.1%. The largest decrease in S₈ occurred in the sulfur oxide reactions that decrease x (group 3B) by 95.5%. When the reaction rates decrease, Figure 2, the largest change in S₈ was caused by group 3B by 163.6%. The largest decrease occurred in group 1A by 98.7%, nearly eliminating S₈.

Group 1A has the largest increase in Figure 1 and the largest decrease in Figure 2. The results of altering one reaction rate coefficient at a time in group 1A are shown in Figures 3 and 4. When increasing reaction rates, 5 of the 11 reactions in group 1A increase S₈ by more than 1,000%, Figure 3. The greatest increase is S₃+S₄=S₂+S₅ by 1,277.2%. The other reactions

increasing S_8 by over 1,000% were $2S+M=S_2+M$, $S_3+S_5=S_2+S_6$, $S_3+S_6=S_2+S_7$, and $S_4+S_5=S_3+S_6$. When rates were decreased, Figure 4, the five reactions identified decreased S_8 by or greater than 98%.

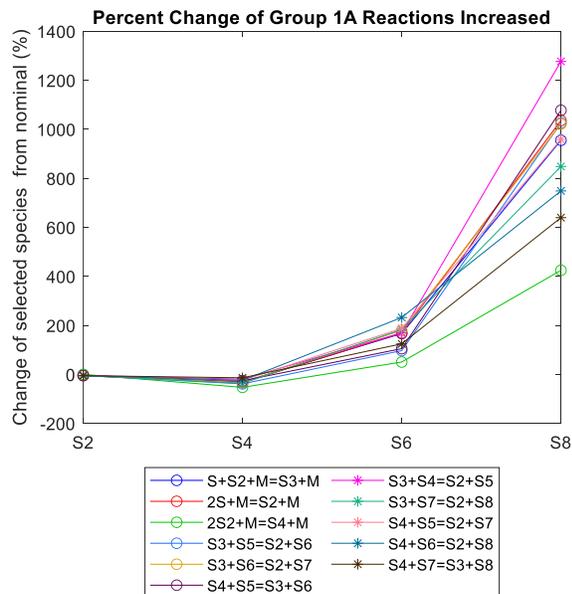


Fig. 3. Increasing the rate coefficients of group 1A reactions individually.

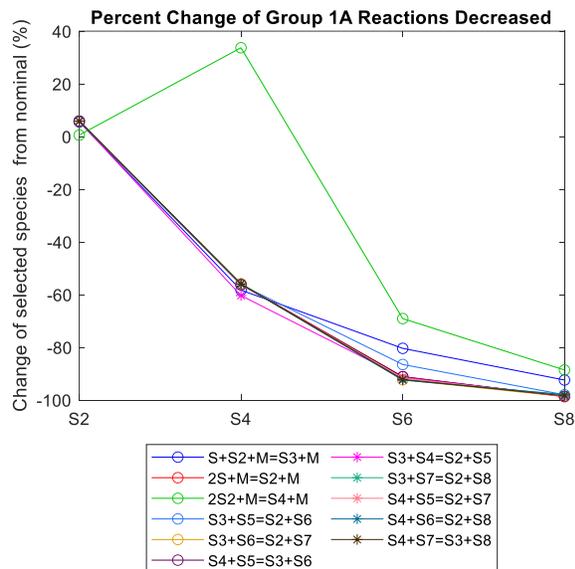


Fig. 4. Decreasing the rate coefficients of group 1A reactions individually.

Note that other reaction rate coefficients were set to match the rate coefficients for these two reactions as indicated in Table 1. These calculations are being refined to treat each of these reactions separately.

Parent Reaction Rate	Additional Reaction Rate(s) Set Equal to the Parent
$2S_2+M=S_4+M$	$2S_4+M=S_8+M$
$2S+M=S_2+M$	$S+O+M=SO+M$
	$S+S_3+M=S_4+M$ $S_2+S_4+M=S_6+M$
	$S+S_4+M=S_5+M$ $S_2+S_5+M=S_7+M$
$S+S_2+M=S_3+M$	$S+S_5+M=S_6+M$ $S_2+S_6+M=S_8+M$
	$S+S_6+M=S_7+M$ $2S_3+M=S_6+M$
	$S+S_7+M=S_8+M$ $S_3+S_4+M=S_2+S_5$
	$S_2+S_3+M=S_5+M$ $S_3+S_5+M=S_8+M$

Table 1. Reaction rates used to estimate other polysulfur reactions. All three parent reactions occur in group 1A.

Preliminary Conclusions: The reaction rates of polysulfur reactions have not been studied well. The rates of the most sensitive group (1A) have all been estimated except for the three parent reactions noted in Table 1, and *ab initio* and laboratory results for the three parent reactions have spanned four orders of magnitude [5-7]. Of the five identified reactions for study, only $2S+M=S_2+M$ has a rate found from *ab initio* calculations [7]. The other four have estimated reaction rates from [8].

Gas-phase polysulfur has previously been assessed as a poor candidate for the unidentified UV absorber because models did not predict high enough concentrations to account for the UV absorptions [9]. However, the impacts of uncertainties in rate coefficients are sufficiently large that the concentrations of gas-phase polysulfur in the atmosphere of Venus may be larger than previous models have predicted and may be large enough to contribute to the unidentified UV absorption. Laboratory study of the five identified reactions will help resolve the potential contribution of polysulfur to the unidentified UV absorption.

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References: [1] Mills F. P. et al. (2007) *Exploring Venus as a Terrestrial Planet*, 73–100. [2] Zhang X. et al. (2011) *Icarus* 217, 714-739. [3] Pinto J. P. et al. (2021) *Nat. Commun.* 12, 175. [4] Allen M. et al. (1981) *JGR* 86, 3617-3627. [5] Du S. et al. (2011) *J Chem Phys* 134, 154508. [6] Lu C.-W. et al. (2006) *J Chem Phys* 125, 164329. [7] Du S. et al. (2008) *JCP* 128, 204306. [8] Moses J. I. et al. (2002) *Icarus* 156, 76-106 [9] Krasnopolsky V. (2016) *Icarus* 274, 12.