Evaluating the Role of Polysulfur in the Atmosphere of Venus

Undergraduate Research Thesis
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By

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Abstract

Polysulfur, S_x where ($2 \leq x \leq 8$), is a speculative species in the atmosphere of Venus. S_x absorbs in the UV region and has been proposed as the identity of the unknown UV absorber in the cloud tops in the middle atmosphere of Venus, where a significant amount of solar flux is absorbed. The middle atmosphere contains the sulfur species SO_2, SO, OCS, and H_2SO_4 and the region is dominated by photochemistry, which should produce $S_{x,}$ from these species, though polysulfur has never be definitively detected in the atmosphere. Large uncertainties in the reaction rates for reactions of polysulfur create large uncertainties in the concentration of S_x in models of the atmosphere. For the first part of this thesis, to determine which reactions should be prioritized for laboratory study, a sensitivity analysis was performed on a model of the atmosphere of Venus. The results identified six reactions that should be prioritized for study, where M is an inert third body: $2S_2+M = S_4+M$, $S_3+S_4 = S_2+S_5$, $Cl+S_4 = S_2+ClS_2$, $SO+OCS = S_2+CO_2$, $2S_2O = S_3+SO_2$, and $O+S_4 = SO+S_3$. The second part of this thesis investigates the beginning of the polysulfur production chain, $2S+M = S_2+M$, using a macro flow through photoreactor. The reaction rate determined from experimental study for the low pressure limit was $k_0 = 9.77 \times 10^{-26}\ e^{206./T}$. In the third part of this thesis, the model of the atmosphere was updated with the new reaction rate, though no change was observed in any species concentration. A previous version of the model was very sensitive to the reaction rate when the low-pressure limit was changed by just one order of magnitude, so the improved reaction rate may have a large impact on the polysulfur concentration as the conditions of the model are refined over time.

A note on terminology: The references used in this thesis come from the work of both planetary scientists and chemists spanning 5 decades and do not always define or agree on compound names. Planetary scientists typically refer to S_x ($2 \leq x \leq 8$) as "polysulfur". S_8 is also sometimes referred to as the "sulfur aerosol" in the context of Venus (see Krasnopolsky (2016) and Zhang et al. (2012)). Chemists historically refer to S_n ($0 < n < \infty$) in either ring or chain configurations as "elemental sulfur" or "allotropes of sulfur". Individual sulfur compounds sometimes are referred to using historic names, like "thiozone" for S_3. The term "polysulfur" has also been used in the name of polysulfides, such as "polysuflur nitride", $(SN)_x$. For clarity, this thesis uses the terminology "polysulfur" to mean S_x ($2 \leq x \leq 8$). Compounds will be specified by their chemical formula when necessary. Elemental sulfur refers to any form of S_n ($0 < n < \infty$).

Introduction

The atmosphere of Venus is composed of 96.5% CO_2 and 3.5% N_2, along with trace species. The atmosphere is rich with chemistry, containing three distinct regions: the lower atmosphere below 60 km, the middle atmosphere from 60-110 km, and the upper atmosphere above 110 km. The main cloud deck begins around 45-50 km and extends to 70 km, though the clouds and hazes can extend as low as 30 km and as high as 90 km (Mills et al., 2007). In the lower atmosphere, just 2.6% of UV radiation reaches the planet (Titov et al., 2007). Together with the high temperatures in the lower atmosphere, the lack of radiation leads to the dominance of thermochemistry at lower altitudes. Half of the solar flux absorbed by the planet is absorbed at the cloud tops, occurring at about 65 km, so the middle atmosphere is dominated by photochemistry. The chemistry of the upper atmosphere is dominated by photodissociation, ion-ion reactions, and ion-neutral reactions (Mills et al., 2007).

At the cloud tops, where the majority of solar flux absorption occurs, dark and bright contrasts have been observed in the ultraviolet range (Mills et al., 2007). Prior to the 1960's, observational data examining the albedo of Venus revealed a decrease in the reflectivity spectrum in the near UV. Hansen (1967), Arking and Potter (1968), and Irvine et al. (1968) all made attempts to fit the observational data to a phase function to investigate the absorber. Results from Hansen (1967) and Arking and Potter (1968) suggested this was due to large cloud particles or droplets. Irvine et al. (1968) suggested this occurred due to scattering by molecular size particles occurring in the atmosphere, consistent with a layer of droplet haze above clouds. The particles responsible for the absorption have come to be known as the "unknown absorber" and remains unidentified.

Of the many candidates suggested for the identity of the absorber, several are sulfur containing compounds. SO_2 and SO both absorb in the near UV, but neither can account for ultraviolet absorption at 320-500 nm (Mills et al., 2007). Elemental sulfur was first suggested as the absorber by Hapke and Nelson (1975) in the form of a cloud made of sulfuric acid and elemental sulfur particles. Candidates for the absorber have fallen in and out of the interest as better observations are taken, better data about the properties and kinetics of molecules are collected, and modeling methods become more sophisticated. The case for elemental sulfur as the absorber has persisted and developed into the case for polysulfur, S_x where ($2 \leq x \leq 8$), where S_8 is a sulfur sink and forms aerosol droplets.

Three dominant chemical cycles have been identified on Venus: the carbon dioxide cycle, the sulfur oxidation cycle, and the polysulfur cycle. In the polysulfur cycle, SO_2 undergoes disproportionation to form SO_3 and S_x (Mills et al., 2007). This cycle also involves the upward transport of OCS and SO_2 and downward transport of S_x which reacts with CO and SO_3 (Zhang et al., 2012). Four sulfur species have been observed in the atmosphere of Venus: SO_2, SO, OCS, H_2SO_4 (Mills et al., 2007). The polysulfur cycle is speculative, as there are no confirmed detections of polysulfur on Venus. The reactions comprising the cycle have not been studied well and many reaction rates for these reactions are estimates. Uncertainty in the potential concentration of polysulfur, which may be or contribute to the production of the absorber, has added to the difficulty of determining the absorber identity.

This thesis takes two approaches to investigate polysulfur concentrations in the atmosphere of Venus. The first, part I, is a model sensitivity analysis of reactions involving polysulfur to identify reactions that should be prioritized for laboratory study. The second, part

II, is a laboratory study of a reaction of polysulfur. The final part, III, updates the model from part I with the reaction rate found in part II.

Part I

Methods

A. Modeling

To identify reactions to be prioritized for laboratory study, a brute force model sensitivity analysis of polysulfur reactions was performed. The model used for this study is a one dimensional diurnally-averaged photochemical model of Venus, based on the 1-D Caltech/JPL KINETICS model (Pinto et al., 2021). The model solves the one dimensional continuation equation for a species of interest, i,

$$P_i - L_i = \frac{\partial n_i}{\partial t} + \frac{\partial \Phi_i}{\partial z}$$

Where n_i is concentration, Φ_i is vertical diffusive flux, and P_i and L_i are chemical production and loss terms. The methods for determining boundary conditions, calculating radiative transfer, solar flux, and photoabsorption cross sections are detailed in Mills (1998). The model extends from altitudes of 58 to 112 km. The layers are 0.2 km from 58-78 km and 2 km from 78-112 km. The model lacked S_8 until Zhang et al. (2012), but S_8 was negligible in their results. Pinto et al. (2021) included S_8 when using the model to investigate $(SO)_2$ and found the potential concentration of S_x was greater than previously calculated by Krasnopolsky (2016), which utilizes a different model. The version of the KINETICS model used by Pinto et al. (2021) including S_8 as a variable species has been updated to include 63 reactions involving polysulfur that have been identified for potential laboratory study, table 1.

B. Reaction Scheme

The reactions scheme is outlined in Mills et al. (2007) and Pinto et al. (2021) and summarized here, where M is an inert third body. SO_2 is the primary sulfur species in the middle atmosphere of Venus. With a sufficient source of additional oxygen atoms, like the photodissociation of CO_2, SO_2 is oxidized to form SO_3. This SO_3 then reacts to form H_2SO_4, condensing to become the cloud layers. Without an additional oxygen source, SO_2 undergoes disproportionation to form SO_3 and S_x.

Polysulfur can also be produced by the photolysis of OCS, which produces an excited state of the sulfur atom. This atom is quenched by CO_2,

$$OCS + hv = CO + S(^{1D})$$

$$S(^{1D}) + CO_2 = CO_2 + S(^{3P})$$

S can react to form S2 and,

$$S + OCS = S_2 + CO$$

$$2S+M = S_2+M$$

which self-propagates through reactions like:

$$S+S_2+M = S_3+M$$

$$2S_3+M = S_6+M$$

$$S_3+S_7 = S_4+S_6$$

Sulfur atoms can also react in sulfur oxidation reactions like:

$$S+S_2O = S_2+SO$$

$$O+S_3 = SO+S_2$$

Cholorosulfane reactions are also included in the model:

$$2ClS = S_2+Cl_2$$

$$S_2+ClS = S_3+Cl$$

The 63 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, 24 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, 8 reactions.

The reference state of the model was calculated with the reaction rates in table 1 and a steady-state was reached. Reaction rate coefficients were increased and decreased by a factor of 10. Each rate coefficient was changed individually and the model was run for each change.

For three body reactions, the three-body low-pressure limit (k_0) and two-body high pressure (k_∞) limiting rate constants are listed. The reaction rate is calculated using the following method from DeMore et al. (1997):

$$k(Z) = \left(\frac{k_0(T)[M]}{1+\left(\frac{k_0(T)[M]}{k_\infty(T)}\right)}\right)0.6^{\{1+[\log_{10}\left(\frac{k_0(T)[M]}{k_\infty(T)}\right)]^2\}^{-1}}$$

When reaction rates of three body reactions were altered, k_0 was increased and decreased by a factor of 10 while k_∞ was held constant.

	Reaction	Group	Rate Constant	Source
R1	$2S+M=S_2+M$	1A	$k_0=2.00\times10^{-33}e^{206./T}$ $k_\infty=2.30\times10^{-14}e^{415./T}$	low P=a high P= a
R2	$S+S_2+M=S_3+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	low P = estimate using a and b high P = estimate using a and b
R3	$S+S_3+M=S_4+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R4	$S+S_4+M=S_5+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R5	$S+S_5+M=S_6+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R6	$S+S_6+M=S_7+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R7	$S+S_7+M=S_8+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R8	$2S_2+M=S_4+M$	1A	$k_0=8.00\times10^{-33}e^{200./T}$ $k_\infty=2.00\times10^{-14}e^{400./T}$	low P = estimate using a and b high P = estimate using a and b
R9	$S_2+S_3+M=S_5+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R10	$S_2+S_4+M=S_6+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R11	$S_2+S_5+M=S_7+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3

	Reaction	Group	Rate Constant	Source
R12	$S_2+S_6+M=S_8+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R13	$2S_3+M=S_6+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R14	$S_3+S_4=S_2+S_5$	1A	$k=4.00\times10^{-11}e^{-200./T}$	Estimate, c
R15	$S_3+S_4+M=S_7+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R16	$S_3+S_5=S_2+S_6$	1A	$k=4.00\times10^{-11}e^{-200./T}$	Estimate, c
R17	$S_3+S_5+M=S_8+M$	1A	$k_0=2.10\times10^{-32}e^{140./T}$ $k_\infty=1.40\times10^{-14}e^{450./T}$	Estimate, set to R3
R18	$S_3+S_6=S_2+S_7$	1A	$k=4.00\times10^{-12}e^{-300./T}$	Estimate, c
R19	$S_3+S_7=S_2+S_8$	1A	$k=3.00\times10^{-11}e^{-200./T}$	Estimate, c
R20	$2S_4+M=S_8+M$	1A	$k_0=8.00\times10^{-33}e^{200./T}$ $k_\infty=2.00\times10^{-14}e^{400./T}$	Estimate, set to R9
R21	$S_4+S_5=S_2+S_7$	1A	$k=2.00\times10^{-12}e^{-200./T}$	Estimate, c
R22	$S_4+S_5=S_3+S_6$	1A	$k=2.00\times10^{-12}e^{-200./T}$	Estimate, c
R23	$S_4+S_6=S_2+S_8$	1A	$k=2.00\times10^{-12}e^{-300./T}$	Estimate, c
R24	$S_4+S_7=S_3+S_8$	1A	$k=5.00\times10^{-12}e^{-200./T}$	Estimate, c
R25	$S+S_3=2S_2$	1B	$k=8.00\times10^{-11}$	Estimate, d
R26	$S+S_4=S_2+S_3$	1B	$k=8.00\times10^{-11}$	Estimate, d
R27	$S+S_5=S_2+S_4$	1B	$k=5.00\times10^{-11}e^{-200./T}$	Estimate, c
R28	$S+S_5=2S_3$	1B	$k=3.00\times10^{-11}e^{-200./T}$	Estimate, c
R29	$S+S_6=S_2+S_5$	1B	$k=5.00\times10^{-11}e^{-300./T}$	Estimate, c
R30	$S+S_6=S_3+S_4$	1B	$k=3.00\times10^{-11}e^{-300./T}$	Estimate, c

	Reaction	Group	Rate Constant	Source
R31	$S+S_7=S_2+S_6$	1B	$k=4.00\times10^{-11}e^{-200./T}$	Estimate, c
R32	$S+S_7=S_3+S_5$	1B	$k=2.00\times10^{-11}e^{-200./T}$	Estimate, c
R33	$S+S_7=2S_4$	1B	$k=2.00\times10^{-11}e^{-200./T}$	Estimate, c
R34	$S+S_8=S_2+S_7$	1B	$k=4.00\times10^{-11}e^{-400./T}$	Estimate, c
R35	$S+S_8=S_3+S_6$	1B	$k=2.00\times10^{-11}e^{-400./T}$	Estimate, c
R36	$S+S_8=S_4+S_5$	1B	$k=2.00\times10^{-11}e^{-400./T}$	Estimate, c
R37	$S_2+S_8=2S_5$	1B	$k=1.00\times10^{-11}e^{-1400./T}$	Estimate, c
R38	$S_3+S_7=S_4+S_6$	1B	$k=1.00\times10^{-11}e^{-200./T}$	Estimate, c
R39	$S_3+S_7=2S_5$	1B	$k=1.00\times10^{-11}e^{-200./T}$	Estimate, c
R40	$S_4+S_6=2S_5$	1B	$k=2.00\times10^{-12}e^{-300./T}$	Estimate, c
R41	$S_4+S_7=S_5+S_6$	1B	$k=5.00\times10^{-12}e^{-200./T}$	Estimate, c
R42	$Cl+S_4=S_2+ClS_2$	2	$k=1.00\times10^{-11}$	Estimate, c
R43	$S+ClS=S_2+Cl$	2	$k=3.00\times10^{-11}$	Estimate, c
R44	$S_2+ClS=S3+Cl$	2	$k=2.00\times10^{-11}$	Estimate, c
R45	$2ClS=S_2+Cl_2$	2	$k=6.00\times10^{-12}$	e
R46	$ClS+ClS_2=Cl_2S+S_2$	2	$k=1.00\times10^{-12}$	Estimate, f
R47	$Cl+ClS_2=S_2+Cl_2$	2	$k=1.00\times10^{-12}$	Estimate, c
R48	O+S3O=S3+O2	3A	$k=1.00\times10^{-13}$	Estimate
R49	$O+S_2O=S_2+O_2$	3A	$k=1.00\times10^{-13}$	Estimate
R50	$S+SO=S_2+O$	3A	$k=1.73\times10^{-11}\times(T/300)^{0.5}\times e^{-11500./T}$	g
R51	$S+S_2O=S_2+SO$	3A	$k=1.00\times10^{-12}e^{-1200./T}$	Estimate, c
R52	$S+OCS=S_2+CO$	3A	$k=6.63\times10^{-20}\times(T/300)^{2.57}\times e^{-1180./T}$	h

	Reaction	Group	Rate Constant	Source
R53	S_2+r-$(SO)_2$=S_3+SO_2	3A	k=1.00 ×10^{-14}	Estimate
R54	SO+OCS=S_2+CO_2	3A	k=1.00 ×10^{-13}	Estimate, i
R55	$2S_2O$=S_3+SO_2	3A	k=1.00 ×10^{-14}	Estimate, f
R56	S+O+M=SO+M	3B	k_0=2.00 ×$10^{-33}e^{206./T}$ k_∞=2.30 ×$10^{-14}e^{415./T}$	Estimate, set to R2
R57	O+S_3=SO+S_2	3B	k=8.00 ×10^{-11}	Estimate, d
R58	O+S_4=SO+S_3	3B	k=8.00 ×10^{-11}	Estimate, d
R59	O+S_5=S_4+SO	3B	k=8.00 ×$10^{-11}e^{-200./T}$	Estimate, d
R60	O+S_6=S_5+SO	3B	k=8.00 ×$10^{-11}e^{-300./T}$	Estimate, d
R61	O+S_7=S_6+SO	3B	k=8.00 ×$10^{-11}e^{-200./T}$	Estimate, c
R62	O+S_8=S_7+SO	3B	k=8.00 ×$10^{-11}e^{-400./T}$	Estimate, c
R63	S_3+SO=S_2O+S_2	3B	k=1.00 ×10^{-12}	Estimate, c

Table 1. Reaction rates of reactions of polysulfur. References: (a) Du et al. (2008), (b) Du et al. (2011), (c) Moses et al. (2002), (d) Moses et al. (1996), (e) Murrells (1988), (f) Mills (1998), (g) Mitchell (1984) accessed from UMIST Astrochemistry database (Woodall et al., 2007), (h) Lu et al. (2006), (i) Baulch et al. (1976).

The total sensitivity measure for each species was calculated as the absolute value of the sum of the change in the mole fraction of the species for the entire column when considering both the results of increasing and decreasing reaction rate. Where σ_x is the sensitivity percentage, z is the column height, x is the number of sulfur atoms per molecule, y is mole fraction of a species, and r = a and r = b represents the full range of reactions, the sensitivity measure for a species is:

$$\sigma_x = \frac{\int \left| y_{x,new} - y_{x,ref} \right| dz \times 100}{\int_a^b \int \left| y_{x,new} - y_{x,ref} \right| dz\, dr}$$

To compare sensitivities between reactions, the average percentage of sensitivity of a reaction for a species was averaged across all polysulfur species to find the average sensitivity of a reaction. The global sensitivity measure calculation is:

$$\sigma_{(2 \le x \le 8)} = \frac{\int_2^8 \int \left| y_{x,new} - y_{x,ref} \right| dz\, dx \times 100}{\int_a^b \int_2^8 \int \left| y_{x,new} - y_{x,ref} \right| dz dx dr}$$

Results

A. Global Sensitivity Measure

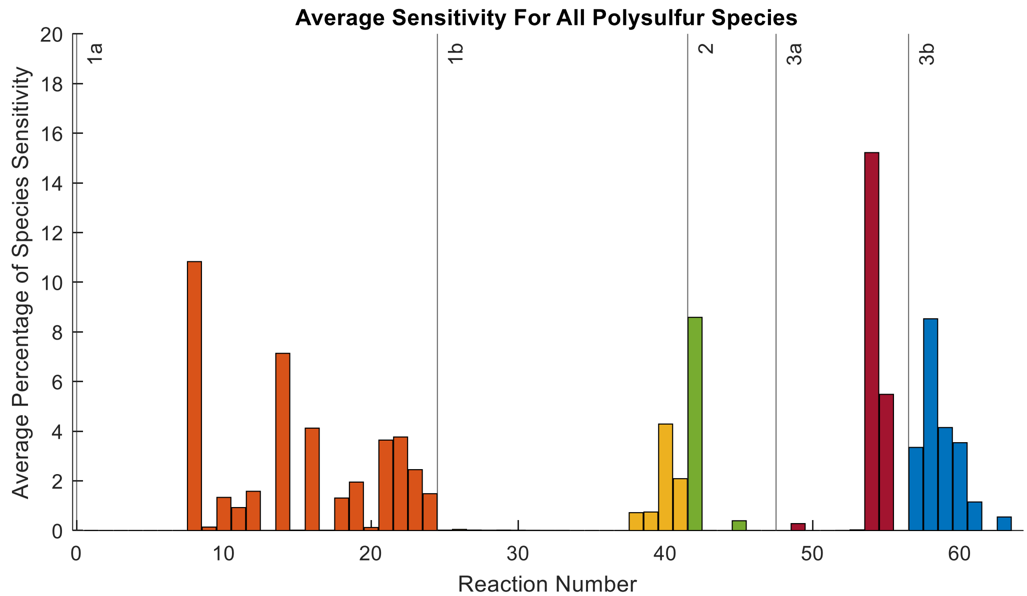

Figure 1.

Figure 1 summarizes the results of the study by comparing the average percent of sensitivity for a species due to a reaction rate when considering both increased and decreased rates. Six reactions had an average percent sensitivity that was greater than 5% for all polysulfur species when considering both increased and decreased rates. The largest average percent sensitivities were the reactions:

(R8) $2S_2+M = S_4+M$ 10.8%

(R14) $S_3+S_4 = S_2+S_5$, 7.1%

(R42) $Cl+S_4 = S_2+ClS_2$, 8.6%

(R54) $SO+OCS = S_2+CO_2$, 15.2%

(R55) $2S_2O = S_3+SO_2$, 5.5%

(R58) $O+S_4 = SO+S_3$, 8.5%

B. Percent change.

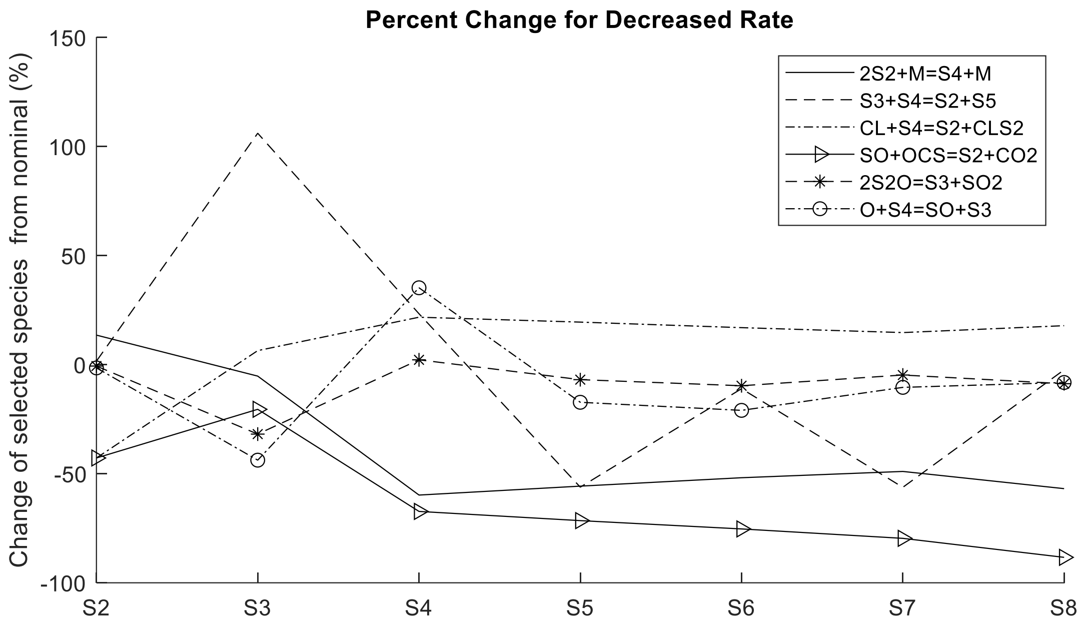

Figure 2.

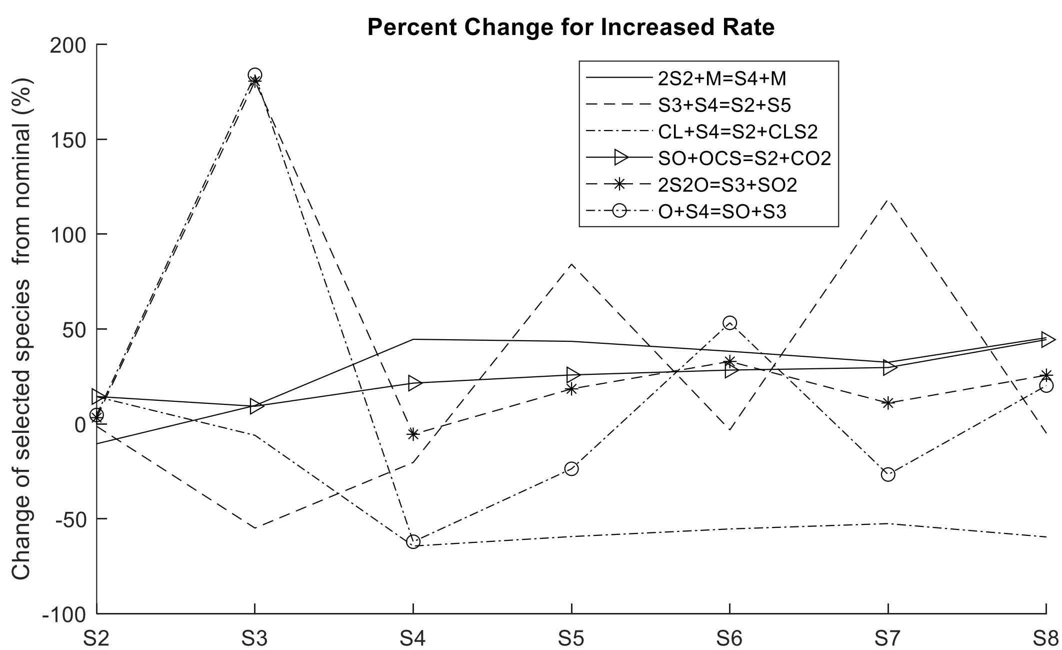

Figure 3.

The impact of the rate change for the six most sensitive reactions was calculated using the percent change of the column concentration of the species from the nominal value, figures 2 and 3. When reaction rate coefficients increase, the greatest impact on the end of the polysulfur chain, S_8, was caused by (R8) $2S_2+M = S_4+M$ 45.4213, (R42) $Cl+S_4 = S_2+ClS_2$ -59.5%, and (R54) $SO+OCS = S_2+CO_2$ 44.4%. When the reaction rate is decreased, the greatest changes in S_8 were caused by the same three reactions: (R54) $SO+OCS=S_2+CO_2$ -88.3%, (R8) $2S_2+M = S_4+M$ -56.8%, and (R42) $Cl+S_4 = S_2+ClS_2$ 17.9%. The other three reactions had high global sensitivity measures because of their influence on other polysulfur molecules. (R14) $S_3+S_4 = S_2+S_5$, resulted in a 118.5% increase on S_7 when rate is increased and a 106.1% increase in S_3 when rate is decreased. (R55) $2S_2O = S_3+SO_2$ resulted in a 180.6% increase in S_3 when rate is increased and a -31.8% decrease in S_3 when rate is decreased. (R58) $O+S_4 = SO+S_3$ resulted in a 183.9% increase in S_3 when rate is increased and a -43.8% decrease in S_3 when rate is decreased.

C. Select Profiles

The profiles for the start and end of the production chain, as well as S_3 due to the large concentration changes, are plotted as number density per cubic centimeter in figures 4, 5, 6, 7, 8, and 9, separated by increased and decreased rate for altitudes 58-63 km, which are located inside of the upper cloud region of the main cloud deck and contain the highest concentration of polysulfur. The profiles for S_8 are reviewed in figures 4 and 5, S_3 in figures 6 and 7, and S_2 in figures 8 and 9.

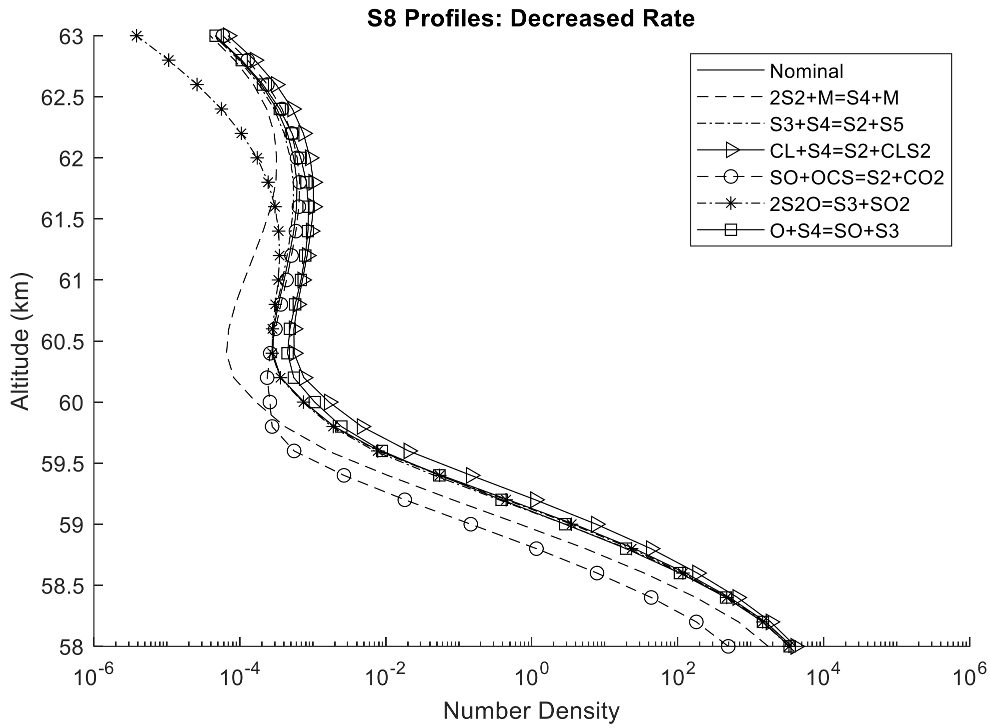

Figure 4.

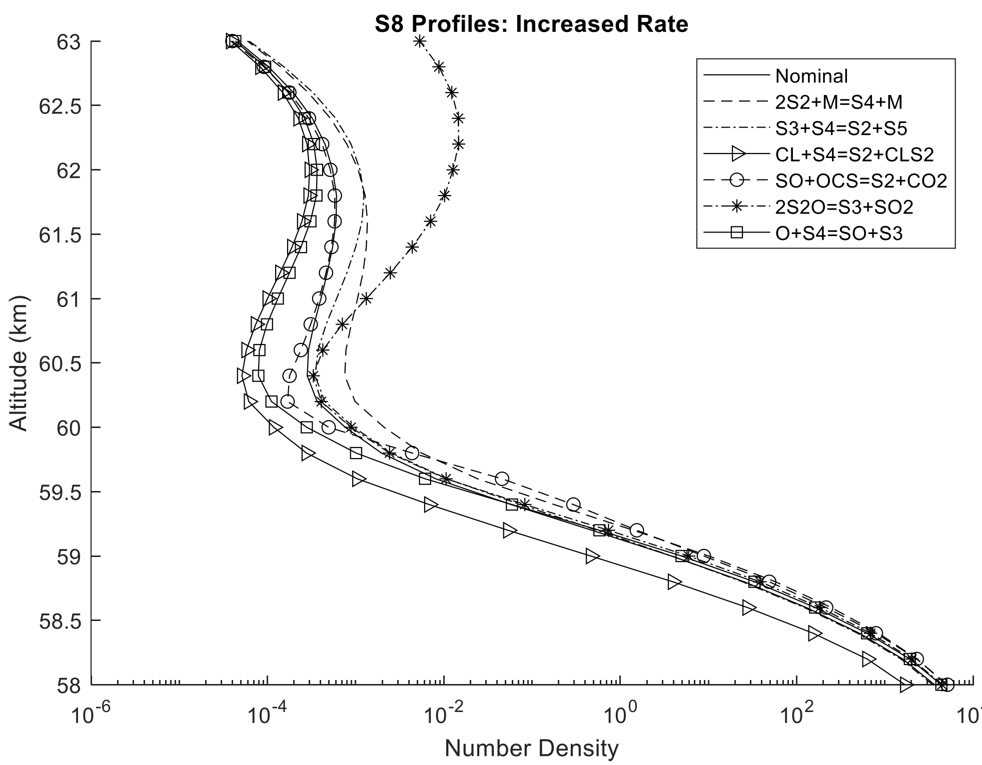

Figure 5.

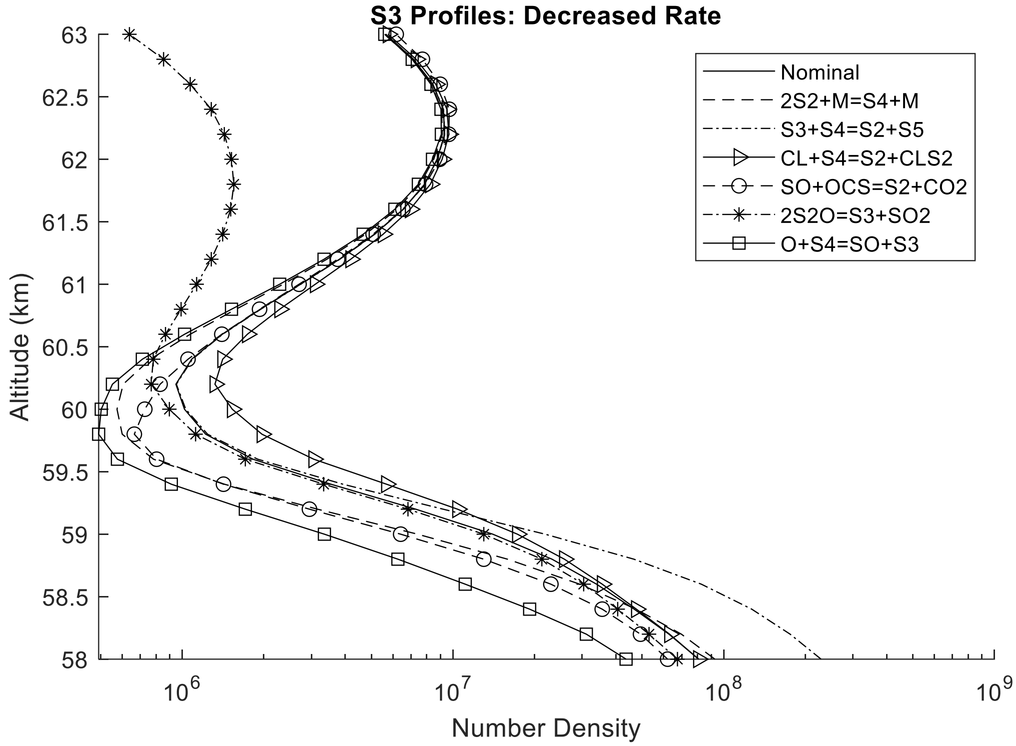

Figure 6.

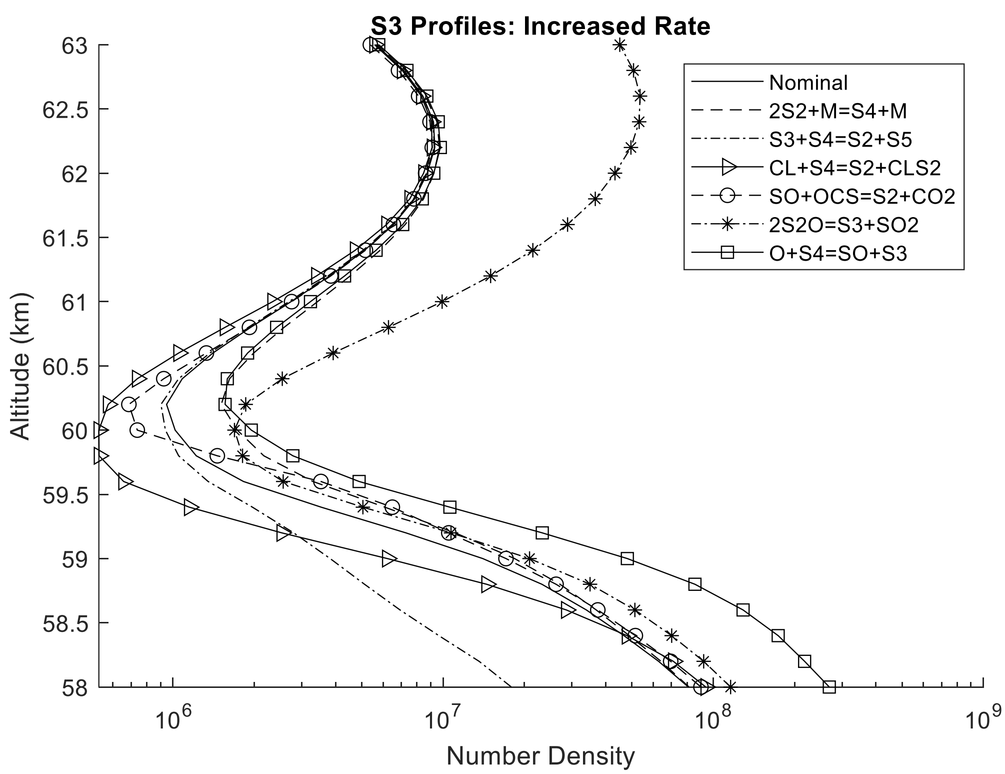

Figure 7.

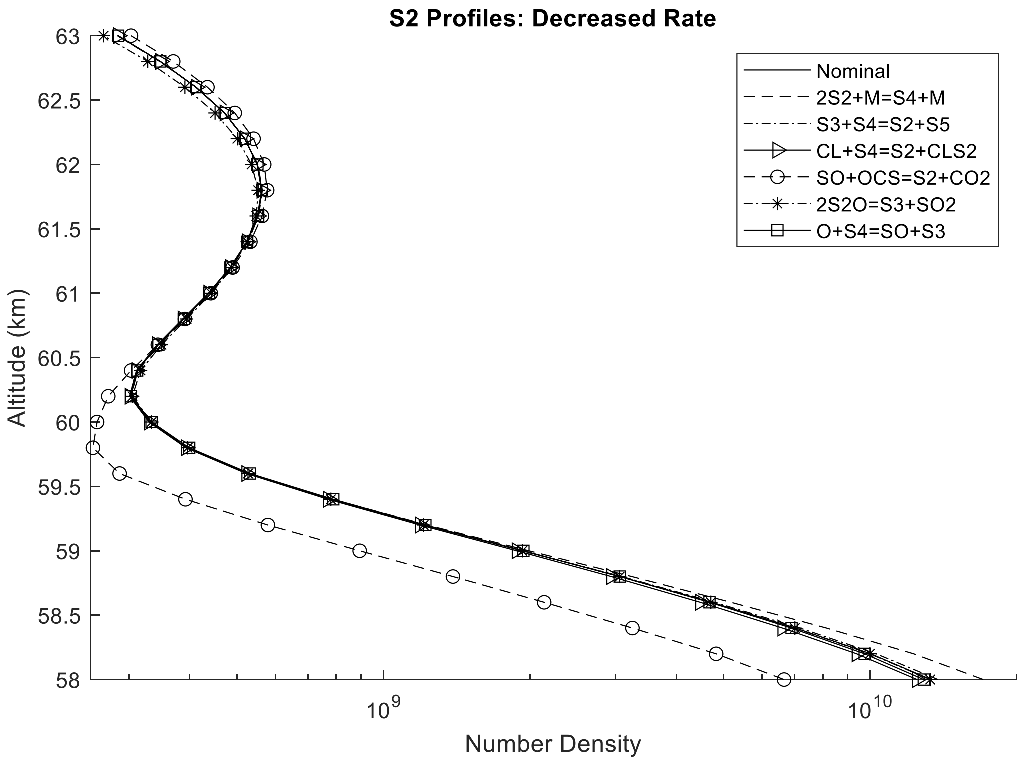

Figure 8.

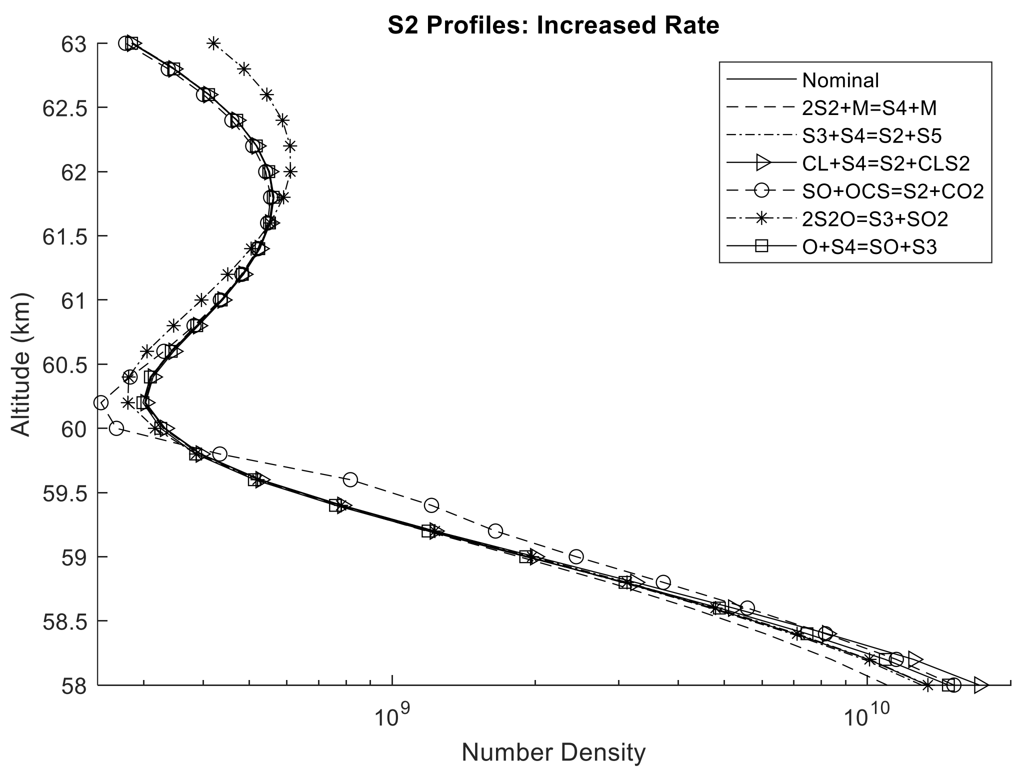

Figure 9.

Discussion

Of the 63 reactions, all but five have estimated reaction rates. Of the five that have experimental and/or calculated rates, there is disagreement between the published values by as much as four orders of magnitude (See: Du S. et al., 2011; Lu C. W. et al., 2006; and Du S. et al., 2008). Because 58 of 63 reactions have estimated reaction rates and the remaining five have large values of uncertainty, the difference in concentrations of polysulfur from the nominal model is potentially much greater than values seen here. All polysulfur species showed considerable sensitivity to at least one reaction rate change. Of the six most sensitive reactions, two are sulfur combination reactions: (R8) $2S_2$+M = S_4+M and (R14) S_3+S_4 = S_2+S_5. One is a chlorosulfane reaction: (R42) Cl+S_4 = S_2+ClS_2. The final three are all sulfur oxidation reactions: (R54) SO+OCS = S_2+CO_2, (R55) $2S_2O$ = S_3+SO_2, (58) O+S_4 = SO+S_3. All six reactions have estimated reaction rates. The largest change was a 183.9% increase in S_3 when the rate of (R58) O+S_4=SO+S_3 was increased. The large concentration sensitivity for S_3 and to a lesser extent, S_4, is of particular interest because together with SO_2, the absorption cross sections provide a close match for the albedo of Venus. The candidacy of the S_3/S_4 combination is proposed in Toon et al. (1982) and reviewed in Mills (2007).

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 (Krasnopolsky, 2016). 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 six identified reactions will help resolve the potential contribution of polysulfur to the unidentified UV absorption.

References

Arking, A., & Potter, J. (1968). The Phase Curve of Venus and the Nature of its Clouds. *Journal of Atmospheric Sciences, 25(4)*, 617-628. doi: https://doi.org/10.1175/1520-0469(1968)025<0617:TPCOVA>2.0.CO;2

Baulch, D. L., Drysdale, D. D., Duxbury, J., & Grant, S. J. (1976). *Evaluated kinetic data for high temperature reactions* (Vol. 3). Butterworth.

DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E., & Molina, M. J. (1997). *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling* (JPL Publication 97-4).

Du, S., Francisco, J. S., Shepler, B. C., & Peterson, K. A. (2008). Determination of the rate constant for sulfur recombination by quasiclassical trajectory calculations. *The Journal of chemical physics*, *128*(20), 204306. https://doi.org/10.1063/1.2919569

Du, S., Germann, T. C., Francisco, J. S., Peterson, K. A., Yu, H. G., & Lyons, J. R. (2011). The kinetics study of the S + S2 → S3 reaction by the chaperone mechanism. *The Journal of chemical physics*, *134*(15), 154508. https://doi.org/10.1063/1.3572226

Hansen, J. E., 1967. [Unpublished doctoral thesis.] University of Iowa.

Hapke, B., & Nelson, R. (1975). Evidence for an Elemental Sulfur Component of the Clouds from Venus Spectrophotometry. *Journal of Atmospheric Sciences, 32(6)*, 1212-1218. doi: https://doi.org/10.1175/1520-0469(1975)032<1212:EFAESC>2.0.CO;2

Irvine, W. M., Simon, T., Menzel, D. H., Pikoos, C., & Young, A. T. (1968, November). Multicolor Photoelectric Photometry of the Brighter Planets. III. Observations from Boyden Observatory. *Astronomical Journal*, *73*, 807-828.

Krasnopolsky, V. A. (2016). Sulfur aerosol in the clouds of Venus. *Icarus, 274*, 33–36. https://doi.org/10.1016/j.icarus.2016.03.010

Lu, C. W., Wu, Y. J., Lee, Y. P., Zhu, R. S., & Lin, M. C. (2006). Experimental and theoretical investigation of rate coefficients of the reaction S(3P)+OCS in the temperature range of 298-985 K. *The Journal of chemical physics*, *125*(16), 164329. https://doi.org/10.1063/1.2357739

Mills, F. P. (1998). *I. Observations and Photochemical Modeling of the Venus Middle Atmosphere II. Thermal Infrared Spectroscopy of Europa and Callisto* [Doctoral thesis, California Institute of Technology].

Mills, F. P., Esposito, L.W., and Yung, Y. L. (2007). Atmospheric Composition, Chemistry, and Clouds. *Exploring Venus as a Terrestrial Planet* (eds L.W. Esposito, E.R. Stofan and T.E. Cravens).

Mitchell, G. F. (1984). Effects of shocks on the sulfur chemistry of a dense interstellar cloud. *The Astrophysical Journal*, 287, 665-670. https://doi.org/10.1086/162723

Moses, J. I. (1996). SL9 Impact Chemistry: Long-term Photochemical Evolution. In K. S. Noll, H. A. Weaver, & P. D. Feldman (Eds.), *The collision of comet shoemaker-levy 9 and Jupiter: IAU colloquium 156* (pp. 243–268). Cambridge University Press.

Moses, J. I., Zolotov, M. Y., & Fegley, B. (2002). Photochemistry of a volcanically driven atmosphere on Io: Sulfur and oxygen species from a pele-type eruption. *Icarus, 156(1),* 76-106. https://doi.org/10.1006/icar.2001.6758

Murrells, T. P. (1988). Elementary reactions of the SCL radical. part1.—rate constants and mechanisms of the reaction CL + C2H4S → SCL + C2H4, SCL + SCL → Products and SCL + Cl2→ SCL2+ cl. *J. Chem. Soc., Faraday Trans. 2*, *84*(1), 67–83. https://doi.org/10.1039/f29888400067

Titov, D.V., Bullock, M.A., Crisp, D., Renno, N.O., Taylor, F.W. and Zasova, L.V. (2007). Radiation in the Atmosphere of Venus. *Exploring Venus as a Terrestrial Planet* (eds L.W. Esposito, E.R. Stofan and T.E. Cravens). https://doi-org.proxy.lib.ohio-state.edu/10.1029/176GM08

Toon, O. B., Turco, R. P., & Pollack, J. B. (1982). The Ultraviolet Absorber on Venus: Amorphous Sulfur. *Icarus, 51(2),* 358-373.

Woodall, J., Agúndez, M., Markwick-Kemper, A. J., & Millar, T. J. (2007). The UMIST database for astrochemistry 2006. *Astronomy and Astrophysics*, *466*(3), 1197-1204. https://doi.org/10.1051/0004-6361:20064981

Young, A. T. (1977, March). An Improved Venus Cloud Model. *Icarus*, *32*, 1-26.

Part II

The dissociation of OCS is expected to be a significant source for sulfur atoms to begin the production of polysulfur. Several mechanisms have been suggested for the reaction $2S+M = S_2+M$ (Langford and Oldershaw, 1973; Fowles et al., 1967; and Basco and Pearson, 1967). The most recent laboratory study of OCS photolysis, Langford and Oldershaw (1973), used the flash photolysis of OCS in CO_2 to study the reaction rate of $2S+CO_2 = S_2+CO_2$. The study confirmed the reaction scheme:

$$OCS + h\nu = S\ (^1D) + CO$$

$$= S\ (^3P) + CO$$

$$S(^1D) + CO_2 = S\ (^3P) + CO_2$$

$$2S + CO_2 = S_2 + CO_2$$

Five laboratory attempts (Basco and Pearson, 1967; Fowles et al. 1967; Fair and Thrush, 1969; Langford and Oldershaw, 1972; and Langford and Oldershaw, 1973) have been made to measure the reaction rate of $2S+M = S_2+M$, along with two *ab initio* calculation studies (Du et al., 2008; and Nicholas at al.,1978). The experimental studies have used OCS, H_2S, and CS_2 as reactants, along with Ar, N_2, and CO_2 as the third body. The *ab initio* studies have used S and H_2S as reactants, with Ar as a third body with S, and no third body with H_2S. The results of these studies have spanned four orders of magnitude. The reaction rates used in part I for the low- and high-pressure limit came from Du et al. (2008). For applications to Venus, CO_2 is the most likely third body because of its high concentration in the atmosphere. The only study of $2S+M = S_2+M$ to begin with OCS and use CO_2 as the third body is Langford and Oldershaw (1973). Despite confirming this mechanism, Langford and Oldershaw were unable to determine a reaction rate due to the arbitrary units of detection used by their equipment. The aim of this study is to obtain this measurement.

Methods

Following the work of Langford and Oldershaw (1973), the photolysis of OCS in CO_2 was used to study the reaction $2S+M = S_2+M$. A macro flow through reactor was constructed using ¼" Teflon tubing coiled around a UV lamp with an output of 0.1405 ± 0.0005 W×cm^{-2}, figure 10. The gas used was 1 mole percent OCS in CO_2 at a rate of 0.005 LPM. A residual gas analyzer (RGA) was used for chemical detection. The experiment was performed at standard temperature and pressure.

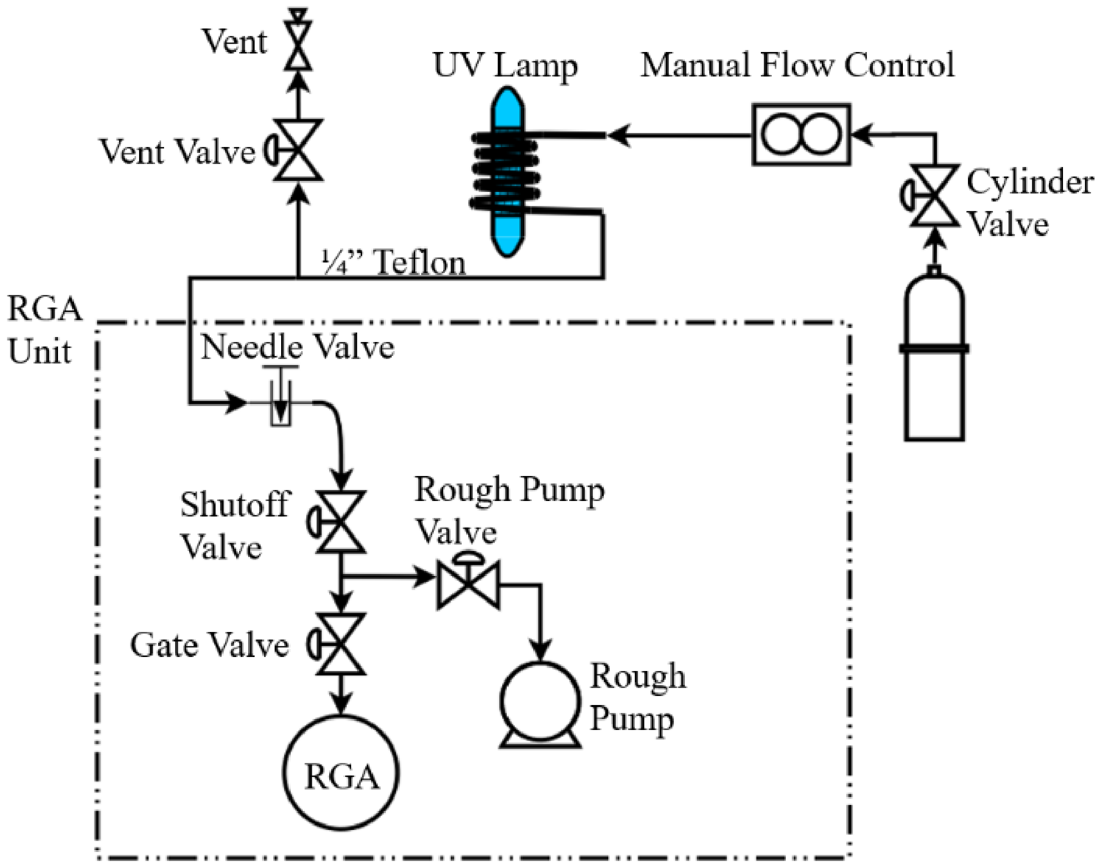

Figure 10. Macro flow through reactor for the photolysis of OCS.

Photolysis of OCS occurs inside of the photoreactor and the sulfur combination reaction occurs along the path from the reactor to the RGA.

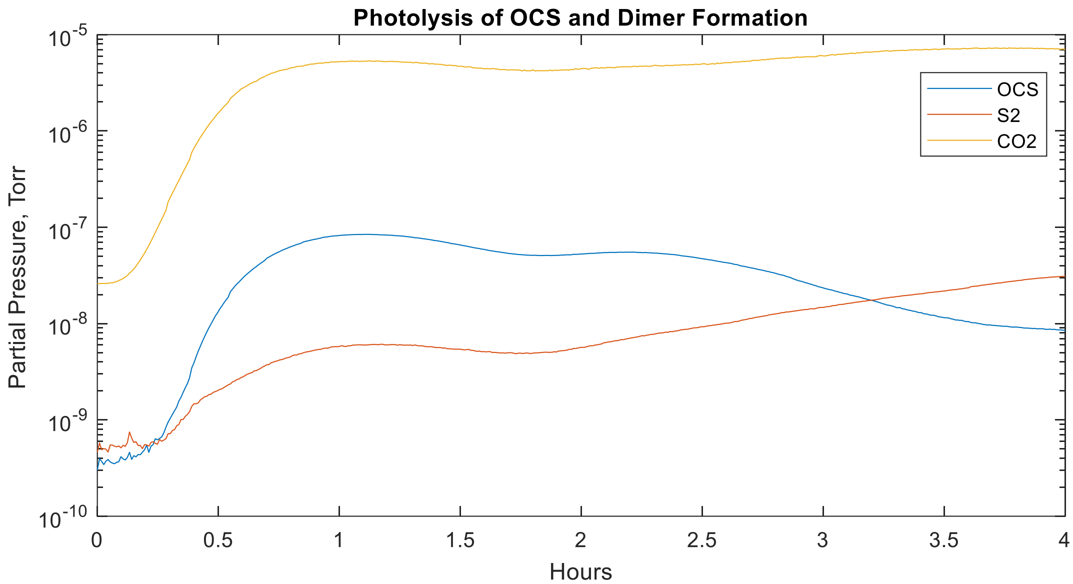

Figure 11. Partial pressure of selected species.

The recombination of S_2 is the rate limiting step of the reaction, leading to the equation,

$$\frac{\mathrm{d}[\mathrm{S_2}]}{\mathrm{dt}} = \frac{1}{2}k[\mathrm{CO_2}][\mathrm{S_2}]^2$$

where the rate of S_2 production is dependent on the amount of S_2 already formed. The linear relationship to determine *k* is

$$[S_2]^{-1}\left(\frac{\frac{\mathrm{d}[\mathrm{S_2}]}{\mathrm{dt}}}{[\mathrm{CO_2}]}\right)^{1/2} = \left(\frac{k}{2}\right)^{1/2}$$

The relationship between $\left(\frac{\frac{\mathrm{d}[\mathrm{S_2}]}{\mathrm{dt}}}{[\mathrm{CO_2}]}\right)^{1/2}$ and $[\mathrm{S_2}]$ is plotted in figure 12, where the slope of the fitted line is $\left(\frac{k}{2}\right)^{1/2}$.

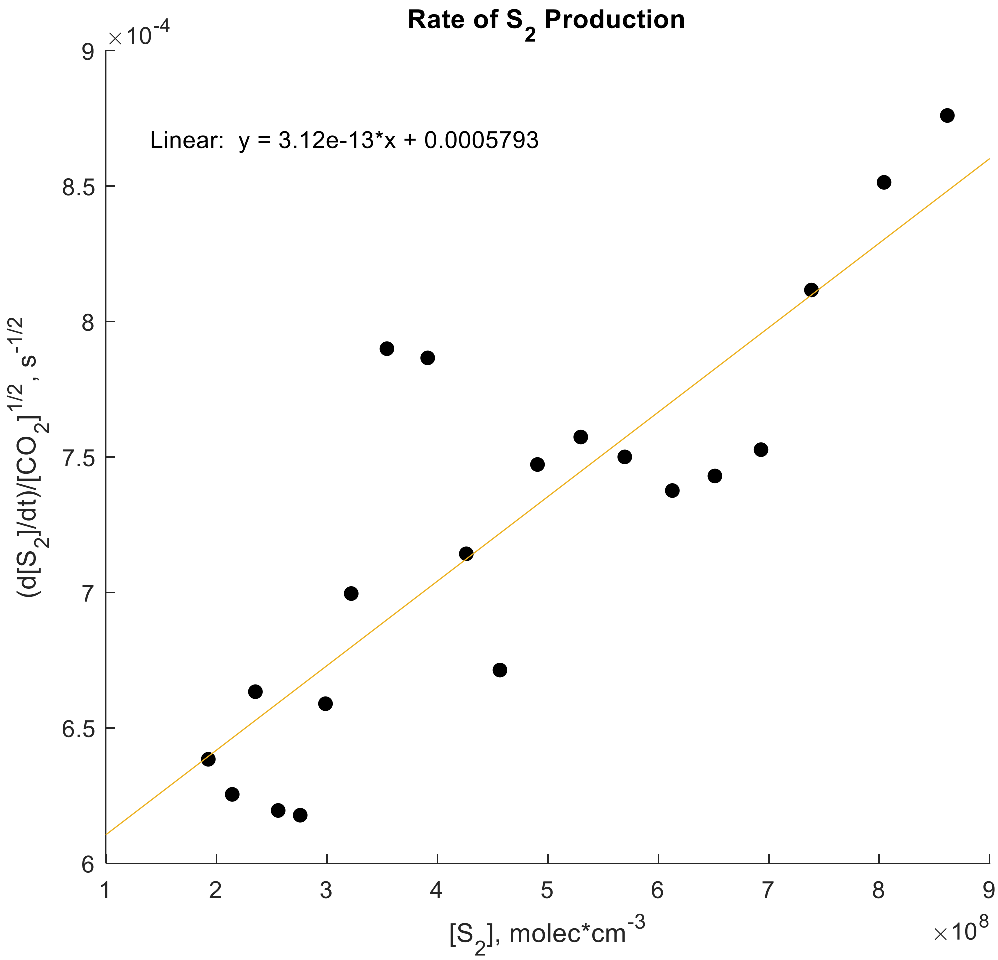

Figure 12. Rate of S_2 production. Each data point represents the average for a 5.33 minute period beginning at the inflection point from figure 11, ~2 hours.

The best fit line has a slope of 3.12×10^{-13} cm^3 $molec^{-1}$ $s^{-1/2}$, so k = 1.95×10^{-25} cm^6 $molec^{-2}$ s^{-1}. Du et al. (2008) found E_a = 1712.684 J/mol (E_a/R = 206 K) at the CCSD(T) level of theory. The temperature dependent form of the rate constant found in this experiment using Ea/R = 206 K is $k_0 = 9.77\times10^{-26}\,e^{206./T}$.

Discussion

The experiment was performed at standard temperature and pressure, so the rate constant can be taken as the low-pressure limit k_0 for use in the KINETICS model for a value of $k_0 = 9.77 \times 10^{-26}\ e^{206./T}$. The value for the activation energy is an estimate itself since it was calculated using Ar as a collision partner. The collider efficiencies of third bodies in pressure dependent reactions is poorly quantified, so the calculation from Du et al. (2008) is retained as an estimate. The estimated reaction rate from Langford and Oldershaw (1973) when comparing results from the flash photolysis of OCS and H_2S was $k = 1 \times 10^{-29}$ cm^6 $molec^{-2}$ s^{-1} while the experimental k here was $k = 1.95 \times 10^{-25}$ cm^6 $molec^{-2}$ s^{-1}. The value found in this study is likely an overestimate because of the assumption that all changes in the 64 peak of the spectrum were due to the production of S_2 and not another species. The increase in the S_2 peak did correspond with a decrease in the OCS peak, so the extent of this overestimation does not make the value of k_0 unreasonable, providing an improved understanding of the rate of $2S+M = S_2+M$ in the atmosphere of Venus.

References

Basco, N., & Pearson, A. E. (1967). Reactions of Sulphur Atoms in Presence of Carbon Disulphide, Carbonyl Sulphide and Nitric Oxide. *Transactions of the Faraday Society, 63,* 2684-2694.

Du, S., Francisco, J. S., Shepler, B. C., & Peterson, K. A. (2008). Determination of the rate constant for sulfur recombination by quasiclassical trajectory calculations. *The Journal of chemical physics*, *128*(20), 204306. https://doi.org/10.1063/1.2919569

Fair, R. W., & Thrush, B. A. (1969). Mechanism of S2 Chemiluminescence in the Reaction of Hydrogen Atoms with Hydrogen Sulphide. *Transactions of the Faraday Society, 65*.

Fowles, P., deSorgo, M., Yarwood, A. J., Strausz, O. P., & Gunning, H. E. (1967). The Reactions of sulfur Atoms. IX. The Flash Photolysis of Carbonyl Sulfide and the Reactions of S(1D) Atoms with Hydrogen and Methane. *Journal of the American Chemical Society, 89(6)*, 1352–1362.

Langford, R.B., & Oldershaw, G.A. (1972). Flash Photolysis of H_2S. *Journal of the Chemical Society, Faraday Transactions, 68*, 1550-1558.

Langford, R.B., & Oldershaw, G.A. (1973). Mechanism of sulphur formation in the flash photolysis of carbonyl sulphide. *Journal of the Chemical Society, Faraday Transactions, 69,* 1389-1397.

Mills, F. P., Esposito, L.W., and Yung, Y. L. (2007). Atmospheric Composition, Chemistry, and Clouds. In Exploring Venus as a Terrestrial Planet (eds L.W. Esposito, E.R. Stofan and T.E. Cravens).

Moses, J. I., Zolotov, M. Y., & Fegley, B. (2002). Photochemistry of a volcanically driven atmosphere on Io: Sulfur and oxygen species from a pele-type eruption. *Icarus, 156(1)*, 76-106. https://doi.org/10.1006/icar.2001.6758

Nicholas, J. E., Amodio, C. A., & Baker, M. J. (1979). Kinetics and Mechanism of the Decomposition of H2S, CH3SH and (CH3)2S in a Radio-Frequency Pulse Discharge. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *1*, 1868-1875.

Pinto, J. P., Li, J., Mills, F. P., Marcq, E., Evdokimova, D., Belyaev, D., & Yung, Y. L. (2021). Sulfur monoxide dimer chemistry as a possible source of polysulfur in the upper atmosphere of Venus. *Nature communications*, *12*(1), 175. https://doi.org/10.1038/s41467-020-20451-2

Zhang, X., Liang, M. C., Mills, F. P., Belyaev, D. A., & Yung, Y. L. (2012). Sulfur Chemistry in the Middle Atmosphere of Venus. *Icarus*, *217*(2), 714-739.

Part III

The updated reaction rate $k_0 = 9.77 \times 10^{-26}\ e^{206./T}$ for $2S + M = S_2 + M$ was entered into the KINETICS model. No concentration of any species in the model changed as a result. The model was not sensitive to the reaction rate at a single order of magnitude change either, part I. In an earlier version of part I, the same sensitivity analysis was performed on the exact version of the model used by Pinto et al. (2021) that first introduced S_8 as a variable species. The most significant change between the two versions is the "Pinto model" had reaction rates set to a "parent" rate. The version of the model used in part I used the same reaction rates, but no longer linked reactions together within the code. Table 2 shows the linked rates from the Pinto model.

Parent Reaction Rate	Additional Reaction Rate(s) Set Equal to the Parent	
$2S_2+M=S_4+M$	$2S_4+M=S_8+M$	
$2S+M=S_2+M$	$S+O+M=SO+M$	
$S+S_2+M=S_3+M$	$S+S_3+M=S4+M$	$S_2+S_4+M=S_6+M$
	$S+S_4+M=S_5+M$	$S_2+S_5+M=S_7+M$
	$S+S_5+M=S_6+M$	$S_2+S_6+M=S_8+M$
	$S+S_6+M=S_7+M$	$2S_3+M=S_6+M$
	$S+S_7+M=S_8+M$	$S_3+S_4+M=S_2+S_5$
	$S_2+S_3+M=S_5+M$	$S_3+S_5+M=S_8+M$

Table 2. Reaction rates used to estimate other polysulfur reactions. All three parent reactions occur in group 1A.

$2S+M = S_2+M$ was linked to $S+O+M = SO+M$. Figures 13 and 14 show the results from the earlier sensitivity analysis. If the sensitivity of 2S+M = S2+M was due to the sensitivity of $S+O+M = SO+M$, then the unlinked, new model should have been sensitive to $S+O+M =$

SO+M. Interestingly, the new model is not sensitive to either. No obvious reason for this difference has been identified in the model code at the time of writing.

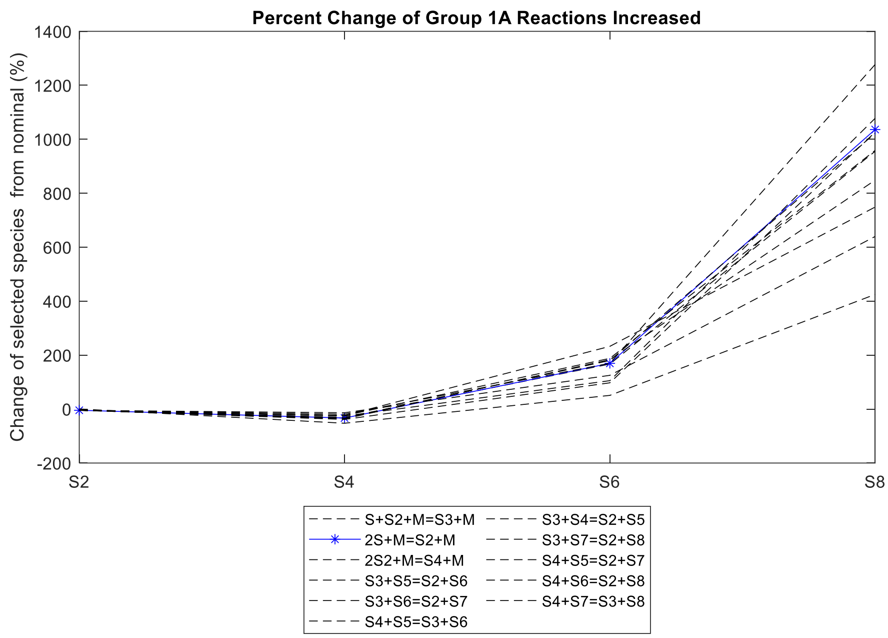

Figure 13.

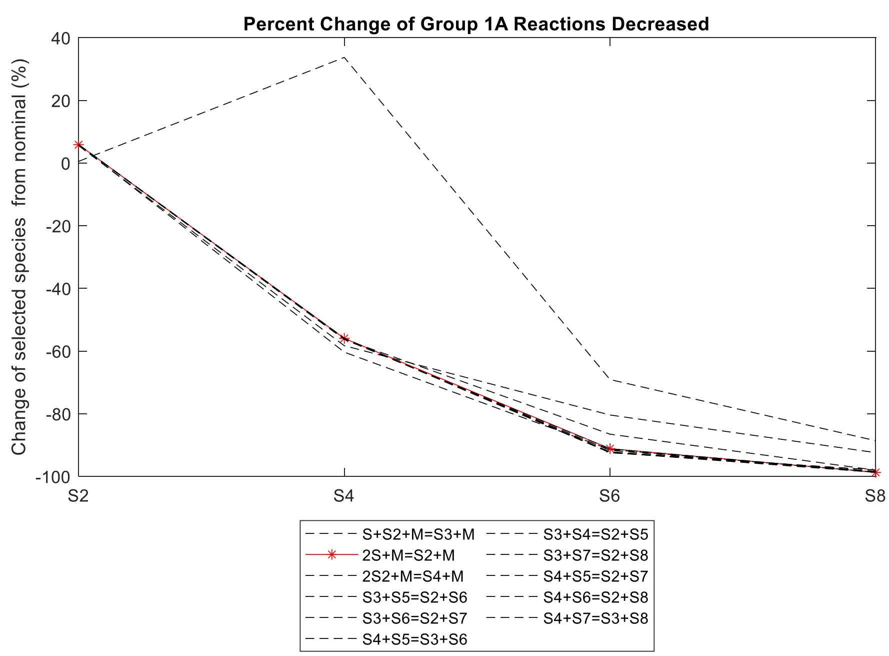

Figure 14.

The Pinto version of the model showed considerable sensitivity to $2S+M = S_2+M$. Though the current version of the model is not sensitive to the reaction, as the model is improved, $2S+M = S_2+M$ may be a high sensitivity species again. Though the impact of the improved rate change cannot be quantified yet, the reaction is expected to have influence over the entire polysulfur production chain because of its role at the beginning of the chain.