LABORATORY KINETIC MEASUREMENTS OF POLYSULFUR REACTIONS IN THE ATMOSPHERE OF VENUS. G. M. Adams[1], J. A. Balcerski[2], F. P. Mills[3,4], [1]Department of Chemistry and Biochemistry, The Ohio State University, Columbus OH, USA, [2]Ohio Aerospace Institute, 22800 Cedar Point Rd, Cleveland OH, USA, , [3]Fenner School of Environment & Society, Australian National University, Canberra, ACT, Australia, [4]Space Science Institute, Boulder CO, USA

Introduction: The atmosphere of Venus is composed of 96.5% CO_2 and 3.5% N_2, along with trace species. Although present in significantly lower quantities than CO_2 or N_2, the minor species, especially those containing sulfur are nonetheless thermochemically and photochemically active. Three important chemical cycles have been identified: the carbon dioxide cycle, the sulfur oxidation cycle, and the polysulfur cycle [1]. In the polysulfur cycle, SO_2 undergoes disproportionation to form SO_3 and S_x (where $2 \leq x \leq 8$). 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 [2].

The identity of the ultraviolet absorber(s) at 320-500 nm in the atmosphere of Venus is a longstanding and as-yet unresolved issue [e.g. 1]. Polysulfur may contribute to the absorption spectra and/or participate in the production of other candidate absorber species [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 for the model sensitivity analysis and prelimary results are detailed in [4]. Model calculations were refined to treat all group 1A reactions separately. The updated results of these sensitivity analyses are reported here.

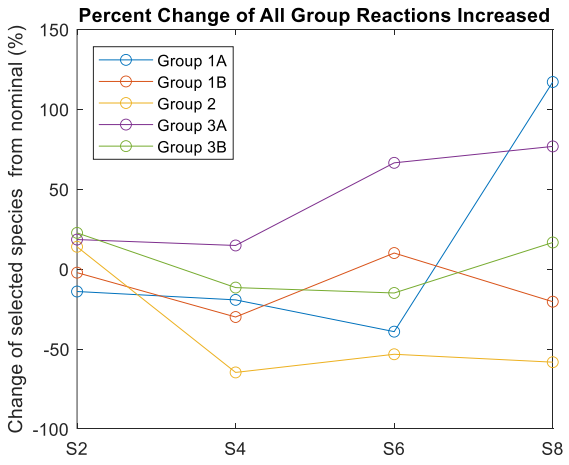

Fig. 1. Increasing all reaction rate coefficients in a group simultaneously.

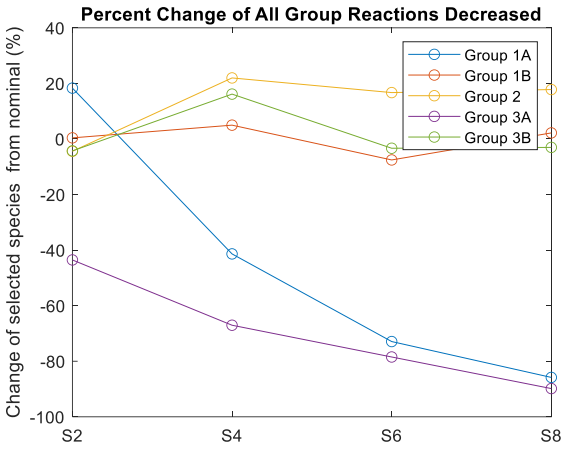

Fig. 2. Decreasing all reaction rate coefficients in a group simultaneously.

The five reactions identified for priority of study were $2S + M = S_2 + M$, $S + S_2 + M = S_3 + M$, $S_3 + S_5 = S_2 + S_6$, $SO + OCS = S_2 + CO_2$, $2S_2O = S_3 + SO_2$.

The reaction rates of polysulfur reactions have not been thoroughly studied constrained. Of the five, only $2S+M=S_2+M$ has a rate found from *ab initio* calculations and laboratory measurements [5,6]. The other four have been modeled with estimated reaction rates from [7].

Five laboratory attempts [6,8,9,10,11] have been made to measure the reaction rate of $2S + M = S_2 + M$, along with two *ab initio* calculation studies [5,12]. The results of these studies have spanned four orders of magnitude [5] and several mechanisms have been suggested [6,8,9]. The most recent laboratory study, Langford and Oldershaw (1973) [6], 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:

$$OCS + h\nu = S(^1D) + CO$$
$$= S(^3P) + CO$$
$$S(^1D) + CO_2 = S(^3P) + CO_2$$
$$2S + CO_2 = S_2 + CO_2$$

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 [6], 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 Teflon tubing coiled around a UV lamp (Fig. 3.). A residual gas analyzer (RGA) was used for chemical detection. This work is ongoing and further study will use an FTIR spectrometer in place of the RGA.

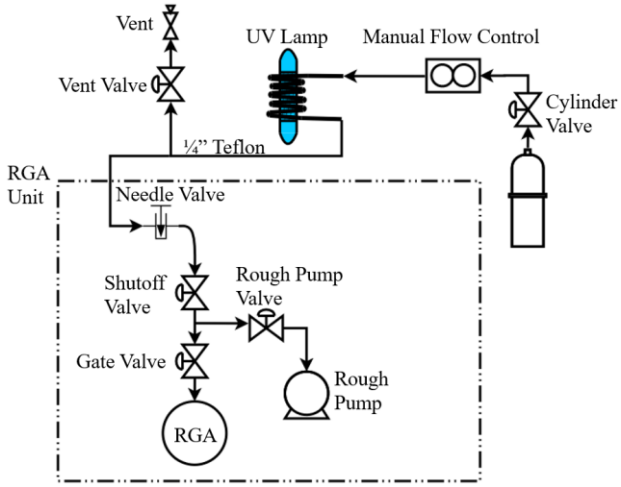

Fig. 3. Macro flow through reactor for the photolysis of OCS.

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