

Preliminary modelling of NO_x photochemistry on Venus

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Abstract

The observational discovery of NO [3] in the Venus cloud layers revived interest in odd nitrogen chemistry on Venus. Based on column-integrated results from numerical modelling, the discovery paper proposed that odd nitrogen chemistry needed to be considered more closely because it might have important effects on the dominant chemical cycles on Venus [3]. A more detailed preliminary assessment of the potential impacts of odd nitrogen chemistry is being made using a 1-d global-average photochemical model. Two scenarios are being examined. One introduced heterogeneous oxidation of CO [10] and the other adjusted the thermal stability of ClCO to enhance the rate of oxidation of CO. Preliminary model simulations suggest odd nitrogen chemistry may have significant effects on specific aspects of the modelled chemistry, such as SO and SO_2 abundances at 80–90 km altitude [10]. However, the global-scale impact of odd nitrogen chemistry appears to be small.

1. Introduction

A puzzling unresolved question is what process(es) is (are) responsible for the chemical stability of CO_2 on Venus. Heterogeneous oxidation of CO [6] and enhancement of the thermal stability of ClCO [7] can both reduce the modelled O_2 abundance so that it is closer to its observational upper limit [4], but both probably distort the CO profile outside the observational bounds [5]. Nitrogen oxide chemistry is known to modify catalytic chemistry cycles on Venus, [11] and the impact of nitrogen oxide chemistry on the catalytic chemistry in Venus' atmosphere has not been examined in detail [3]. This modelling study examines the effects of introducing nitrogen oxide chemistry into two Venus atmospheric chemistry models—one in which heterogeneous oxidation of CO is an important

pathway for production of CO_2 and one in which oxidation of CO via ClCO is markedly enhanced.

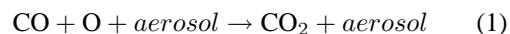
2. Photochemical Model

Details on the model have been published [5], so only a summary description [5] is provided here. The version used, customised from the Caltech/JPL code [1], is one-dimensional, steady-state, and “global average,” with vertical transport over 58 to 112 km in 2-km thick layers. Photoabsorption and chemical kinetic data were drawn from critically reviewed compilations (e.g., [2]) when possible.

Vertical transport via eddy diffusion was set based on observations. The H_2O profile was fixed to match the equilibrium vapor pressure over 75 wt% sulfuric acid, which is still commonly assumed as the composition of the upper cloud layer and overlying haze although Venera measurements indicate the composition is 85 wt% [4]. At the lower boundary, the mixing ratio for CO_2 was set to 0.965, HCl to 0.4 ppm, OCS to 1 ppb, and SO_2 to 1 ppm.

Thermal decomposition of ClCO was decreased by a factor of 1.5 times the assessed uncertainty in the equilibrium constant for ClCO formation and decomposition. This significantly increases the efficiency of CO oxidation via chlorine catalytic chemistry, particularly at about 80 – 90 km altitude.

Heterogeneous oxidation of CO on aerosols was included with a reactive uptake coefficient, $\gamma_{rxn} = 10^{-5}$. This means Reaction 1, when activated, is a primary pathway for oxidation of CO when integrated over all modelled altitudes [6].



The nitrogen oxide chemistry introduced in this preliminary assessment [11], includes 26 reactions and 7 species. Most rate coefficients and cross sections were

taken from the latest stratospheric chemistry assessment [8]. Coupling between nitrogen oxide and chlorine oxide chemistry via chlorine nitrate was not included. Neither was oxidation of SO_2 to SO_3 by NO_x .

Production of odd nitrogen was simulated by specifying the NO mixing ratio at the lower boundary. It was varied from the nominal observed value of 5.5 ppb [3] to 30 ppb to assess the impact of observational sampling uncertainty.

3. Preliminary Results

The largest changes in SO and SO_2 occur near 85 km. At these altitudes the modelled odd nitrogen chemistry intensifies the rate of interchange between SO and SO_2 by oxidising SO to SO_2 , which also increases the modelled abundances of SO because photodissociation of SO_2 to form SO is very rapid at these altitudes. The net effect is to reduce the rate of loss of SO_x ($= \text{SO} + \text{SO}_2$) via production of S_8 and SO_3 at these altitudes.

Preliminary results are broadly consistent with those published previously [3]. The effect of odd nitrogen chemistry on SO and SO_2 abundances at 80–90 km suggests odd nitrogen chemistry may need to be considered when interpreting altitude-resolved observations of SO and SO_2 [9]. However, even in this case, the impact of odd nitrogen chemistry is relatively small for the observed 5.5 ppb abundance of NO below 60 km. Further, odd nitrogen chemistry does not appear to have a substantial impact on global-scale measures, such as the column abundance of O_2 , S_8 production, or H_2SO_4 production.

Odd nitrogen chemistry partially counteracts problems previously identified with calculated CO. The shift, however, is quite small. Simulations using more nominal chemical input data will be examined.

4. Summary and Conclusions

Some of the effects of odd nitrogen chemistry in a Venusian mesospheric photochemical model have been examined for a model scenario in which heterogeneous oxidation of CO is important. There are potentially significant impacts on specific aspects of the modelled chemistry, e.g., SO and SO_2 abundances at 80–90 km, but the overall effects from the observed NO abundance are small. Further work is underway to examine other scenarios that could be affected more substantially by odd nitrogen chemistry. Continued observational measurements of NO on Venus are required to establish the typical abundance of NO on Venus and its geographic and vertical distribution.

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References

- [1] Allen, M., et al: *J. Geophys. Res.* vol. 86, pp. 3617–3627, 1981.
- [2] DeMore, W. B., et al: *Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation Number 12*, JPL Publication 97-4, 1997.
- [3] Krasnopolsky, V. A.: *Icarus*, vol. 182, pp. 80–91, 2006.
- [4] Krasnopolsky, V. A.: *Plan. Sp. Sci.*, vol. 54, pp. 1352–1359, 2006.
- [5] Mills, F. P. and Allen, M.: *Plan. Sp. Sci.*, vol. 55, pp. 1729–1740, 2007.
- [6] Mills, F. P., et al: in *Advances in Geosciences Volume 3: Planetary Science (PS)*, ed. W-H Ip and A. Bhardwaj, World Scientific Publishing Co., pp. 109–117, 2006.
- [7] Pernice, H., et al: *PNAS*, vol. 101, pp. 14007–14010, 2004.
- [8] Sander, S. P., et al: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 15*, JPL Publication 06-2, 2006.
- [9] Sandor, B. J., et al: *Icarus*, vol. 208, pp. 49–60, 2010.
- [10] Shunmuga Sundaram, M., et al: *Proc. 10th Australian Space Science Conference*, 27–30 September 2010, Brisbane, Australia, 2010.
- [11] Yung, Y. and DeMore, W.: *Icarus*, vol. 51, pp. 199–247, 1982.