Chapter 6: Overall summary, general conclusions and directions for future Research

6.1 Introduction

Considerable uncertainties concerning the relative importance of various OCS sources limits the usefulness of a mass balance analysis to confirm that there are sufficient fluxes of OCS into the stratosphere to maintain the SSA loading in the absence of volcanic eruptions. There are strong indications that tropospheric SO_2 and sulfate fluxes into the stratosphere by convective events are equally important sources of sulfur in the SSA. However, the transport and exchange mechanisms are not well understood. Because of the many uncertainties in input parameters, model results remain speculative.

In this thesis, isotopic composition data was used in an attempt to constrain the mass balance analysis of the SSA.

6.2 Chapter 2 summary and future perspectives

In Chapter 2, we estimated the apparent sulfur isotopic enrichment factor for the stratospheric processing of OCS, $\varepsilon_{\text{apparent}} \sim 73$ ‰, using high-resolution FT-IR data recorded by the NASA/JPL MkIV instrument between 1991 and 2000.

However, the Rayleigh distillation plot provides only a rough estimate for ε because the analysis is only strictly correct where ε = constant. On the other hand, ε is in fact a function of wavelength, i.e., $\varepsilon(\lambda)$, and altitude, and there are the additional isotopic effects during OCS oxidation by O and by OH.

An obvious use of our current results would be to corroborate model results of the relative contributions of the different loss pathways. In order to do this, it is necessary to estimate independently the isotopic enrichment factors for the two chemical loss pathways for stratospheric OCS as well as that for OCS photolysis.

In Chapter 3, we determined the wavelength-dependent isotopic fractionation ratio, $\varepsilon(\lambda)$, for the UV photolysis of OCS. The methods used in Chapter 4 to estimate the isotopic fractionation ratio for the chemical oxidation of SO_2 by OH can be used to estimate the isotopic enrichment associated with the chemical loss pathways for stratospheric OCS, provided that they proceed via equilibrium with a transition state. Work is in progress to determine the isotopic fractionation rate of the OCS + OH reaction which proceeds via a stable intermediate, based on reported transition states [*Wilson and Hirst*, 1995].

6.3 Chapter 3 summary and future perspectives

In Chapter 3, we measured the UV absorption spectra of $OC^{32}S$ and $OC^{34}S$ in order to estimate the wavelength-dependent isotopic enrichment factor, $\varepsilon(\lambda)$, of the photolysis of OCS at room temperature. Because of the difficulty in measuring the absorption spectra of OCS with the accuracy necessary to quantify the effects of isotopic substitution, we invoked area normalization to examine the qualitative effects of isotopic substitution. The limitations of this approach were discussed in Chapter 3.

Contrary to expectations, we found that the absorption spectrum of $OC^{34}S$ was broader than that of $OC^{32}S$. Our analysis suggests that diabatic crossing at the excited state is important in determining the overall photolysis rate. The spectra might therefore be expected to be highly temperature dependent. At wavelengths within the stratospheric solar window (~200-220 nm), the wavelength-dependent isotopic enrichment factor $\varepsilon(\lambda)$ is expected to be positive and large, consistent with our estimate derived from the MkIV data.

It has been suggested that the discrepancy between the simple ZPE model (described in Chapter 3) and experimental isotopic enrichment factors in the photolysis of N_2O may arise from the contribution from bending "hot bands" [*Zhang et al.*, 2000], which is an effect not considered in the ZPE model that considers that all molecules are promoted from their corresponding ground state. Laboratory measurements of the absorption spectra of OCS show a pronounced temperature dependence on the red side of the absorption maximum [*Wu et al.*, 1999], whereas the solar window falls completely to the blue side of the absorption maximum. In any case, experiments carried out at low temperatures should resolve some of the uncertainties associated with this work.

6.4 Chapter 4 summary and future perspectives

In Chapter 4, we used RRKM (unimolecular dissociation) theory to compute the isotopic enrichment factor during the rate-limiting formation of the $HOSO_2$ adduct from SO_2 and OH as a function of pressure and temperature. The isotopic enrichment factor is positive and large throughout the troposphere and stratosphere. The average isotopic fractionation ratio throughout the troposphere and into the stratosphere is ~1.14, corresponding to an isotopic enrichment factor of ε = 140‰. This predicted result is consistent with the observed sulfur isotopic effects in the SSA following the 1963 eruption at Mt. Agung in Bali, Indonesia.

The calculation was anchored against an experimentally measured pre-exponential factor. Nevertheless, there are some uncertainties and inconsistencies between the parameters used in the RRKM calculation. However, sensitivity analyses showed that the estimated isotopic fractionation ratio was rather insensitive to these parameters. An *ab initio* study of the $HOSO_2$ adduct formation should help to reduce some of the uncertainty regarding the location of the transition state, but with the transition state used in our RRKM calculations were unable to locate a saddle point on the PES in a preliminary *ab initio* calculation.

6.5 Chapter 5 summary and future perspectives

In Chapter 5, we used the comprehensive results from Chapters 2-4 in a 1-D model of the isotopic composition of gaseous sulfur species in the atmosphere and of stratospheric sulfate aerosols. 1-D model results showed that both OCS and SO_2 are important sources of SSA sulfur. The model results show that SO_2 contributes a large fraction of stratospheric sulfate sulfur, especially at low altitudes. SO_2 that reaches the tropopause is highly depleted in ^{34}S due to the high, positive values of ε associated with the homogeneous oxidation of SO_2 by OH. The SSA sulfate produced from SO_2 oxidation is therefore depleted in ^{34}S. This scenario is consistent with the measured values of $\delta^{34}S$ for SSA particles. In this case, the combination of highly enriched-OCS derived-sulfate and highly depleted-SO_2 derived-sulfate yields a relatively low average value for $\delta^{34}S$.

Steady-state results predicted by the 1-D model yield a high $\delta^{34}S_{\text{SSA sulfate}}$ value in the range of 29 to 33 ‰. This range is significantly higher than the value reported in

Chapter 5 (~ 6.8 ‰) or that reported by Castleman et al.(1974) of 2.3 ‰. Comparison of these results with those reported elsewhere clearly indicate that the relative contribution of SO_2 is underestimated. This underestimation of the flux of SO_2 into the Junge layer leads to an overestimated $\delta^{34}S_{SSA}$. Future work requires the incorporation of detailed heterogeneous chemistry in both the troposphere and stratosphere and the explicit treatment of aerosol microphysics.

References

Castleman, J.A.W., H.R. Munkelwitz, and B. Manowitz, Isotopic studies of the sulfur component of the stratospheric aerosol layer, *Tellus*, *26*, 222-234, 1974.

Wilson, C., and D.M. Hirst, High-level ab initio study of the reaction of OCS with OH radicals, *J. Chem. Soc., Faraday Trans.*, *91*, 793-798, 1995.

Wu, C.Y.R., F.Z. Chen, and D.L. Judge, Temperature dependent photoabsorption cross sections of OCS in the 2000-2600 A region, *J. Quant. Spectrosc. Radiat. Transfer*, *61*, 265-71, 1999.

Zhang, H., P.O. Wennberg, V.H. Wu, and G.A. Blake, Fractionation of $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ during photolysis at 213 nm, *Geophys. Res. Lett.*, *27*, 2481-2484, 2000.