Studies of Stratospheric NO_y Chemistry with a Three-Dimensional Chemical Transport Model

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Introduction

NO_y (= N + NO + NO_2 + NO_3 + HNO_3 + $ClONO_2$ + 2×N_2O_5 + HNO_4 + ..) species play an important role in the chemistry of stratospheric O_3 both directly through rapid catalytic cycles involving NO_x and indirectly through their interaction with e.g. halogen species. As stratospheric halogen levels decline the role of NO_x species will again become even more important. However, over the past few years there have been a number of updates to laboratory data related to NO_y chemistry. In addition, studies using 3-D chemical transport models have indicated problems in reproducing the observed abundance of NO_y and its partitioning into its components.

Within the European Union TOPOZ III project we are comparing current CTM models with a range of NO_y observations to test our understanding of NO_y chemistry under different conditions. In this short paper, we will focus on the comparison between the SLIMCAT 3D CTM and a single balloon flight of the JPL Mk IV instrument inside the Arctic vortex.

Measurements

The Mk IV instrument is a high-resolution Fourier Transform Infra-Red (FTIR) spectrometer designed to remotely sense the composition of the earth's atmosphere [*Toon*, 1991]. The instrument provides profiles of the most important components of stratospheric NO_y (e.g., NO, NO_2, HNO_3, HO_2NO_2, N_2O_5 and $ClONO_2$). The data used here was obtained on a flight on December 16, 2002 from Kiruna, Sweden.

SLIMCAT 3D CTM

The SLIMCAT off-line 3-D CTM which is described in detail by *Chipperfield* [1999]. Here horizontal winds and temperatures are specified using ECMWF T42L60 operational analyses. The model has the most important species in the O_x, NO_y, Cl_y, Br_y, HO_x families along with a CH_4 oxidation scheme and long-lived tracers. The model has a detailed gas-phase stratospheric chemistry scheme as well as a treatment of heterogeneous chemistry on liquid and solid aerosols. In the run used here a simple ice-based denitrification scheme is used. For the comparison here the model was sampled at the same local time as the Mk IV observations. the mkiv measurements were made during sunrise, between 7.72-9.63 UT (12-30 km). the time at 22 km tangent point (peak in hno3/noy) was 8.24 UT.

Results

Figure 1 shows the correlation of NO_y versus N_2O on December 16, 2002 from the balloon observations and model. Also shown is estimated NO_y^* from the observations and model. Around this time PSCs were observed by POAM (http://wvms.nrl.navy.mil/POAM/solve2) with the temperatures colder than T_{NAT} and a mini-ozone hole with column O_3 values less than 200DU around the polar vortex. For the Mk IV data the NOy v NO_y^* comparison shows denitrification occurred in the polar vortex in this winter around 30-60 ppbv N_2O (i.e. ∼21-25km). There is ∼4 ppbv NO_y loss around this altitude from the ${NO_y}^*$ and NO_y difference. A signature of renitrification is seen at lower altitudes (N_2O values around 120-150 ppbv). The SLIMCAT model, forced by ECMWF analyses, also captures this denitrification/renitrfication signal remarkably well considering that in this model run the denitrification is based on an ice sedimentation scheme. Further work is need to test more sophisticated scheme [e.g. Davies et al. 2003] on this profile.

The measured and modelled profiles of key NO_y is shown in Figure 2. The SLIMCAT model predicts NO_y through production from N_2O during the ∼10 year spin up of this run. Therefore, Figure 3 shows the comparison of NO_y partitioning. SLIMCAT captures the major features of the NO_y species distributions,

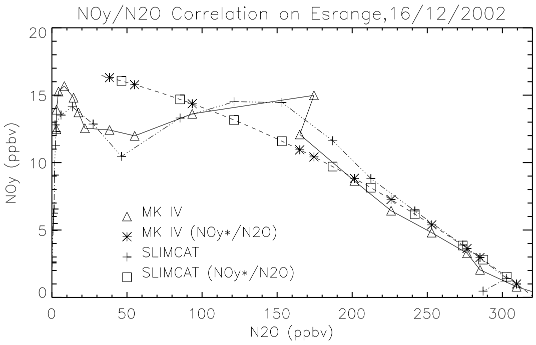

Figure 1. Correlation of NO_y v N_2O on December 16, 2002 for Mk IV data (triangles) and SLIMCAT model (+). Also shown is calculated NO_y^* v N_2O from a third-order polynomial [*Popp, et al.*, 2001] using Mk IV and model N2O.

e.g. for HNO_3 which dominates the NO_y budget in the high latitude winter below 25 km mainly by the heterogeneous reactions on sulfate aerosols via

$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$

The Mk IV N_2O_5 profile shows a significant maximum at 29 km with a mixing ratio of 2.14 ppbv. Below 29km, N_2O_5 decreases rapidly down to 0.01 ppbv at 24km due to the lower stratosphere is highly depleted in NO_x. SLIMCAT reproduces this observed N_2O_5 distribution, but the modelled N_2O_5 is slightly larger than the observations. Moreover, the maximum modelled N_2O_5 has a mixing ratio of 2 ppbv located around 26.6 km.

For ClONO2 the model agrees reasonably well except near 24 km. Here the model underestimates the chlorine activation - Mk IV observed 1.6 ppbv ClO at 24 km while the SLIMCAT model had only 0.18 ppbv (not shown here).

The most significant discrepancy between the model and observations is for NO_2 in the lower stratosphere. Although the observed mixing ratios are small, ~0.06 ppbv at 20 km, these greatly exceed the model values.

Comparisons with HO_2NO_2 are not shown here. Recently, we have included a parameterisation of the near-IR photolysis of this species in the model which led to a much better agreement with balloon data [*Evans et al.*, 2003].

Summary

The NO_y partitioning measured by the JPL MK IV instrument at Kiruna (68^{o}N) on December 16, 2002 has been compared with the SLIMCAT 3-D chemical transport model. The comparison shows that denitrification occurred in the polar vortex (~21-25 km). The model reproduce the observed N_2O-NO_y correlation and the measured NO_y partitioning with the notable exception of NO_2 where the model strongly underestimates the small observations. Further sensitivity experiments will be performed as well as comparisons with other balloon, aircraft and satellite datasets.

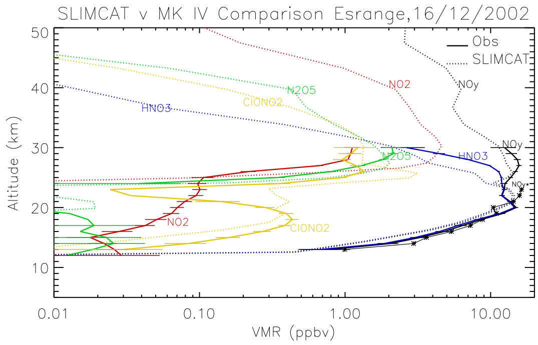

Figure 2. Mk IV-Observed (solid lines) and SLIMCAT-modelled (dashed lines) profiles of NO_y species on December 16, 2002.

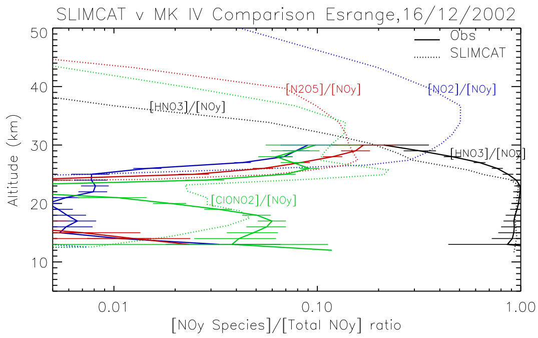

Figure 3. As Figure 2 but for ratios of the individual species with respect to total NO_y.

Acknowledgments This work was supported by the EU through the TOPOZ III project.

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