

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

W. Feng, M.P. Chipperfield and S. Davies

Institute for Atmospheric Science, School of the Environment, University of Leeds, Leeds, U.K.

B. Sen, G. Toon, J. F. Blavier and J. Margitan

JPL, NASA, U.S.A.

Introduction

NO_y (= $\text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + \text{ClONO}_2 + 2 \times \text{N}_2\text{O}_5 + \text{HNO}_4 + \dots$) 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/NO_y) 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 NO_y 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/renitrification signal remarkably well considering that in this model run the denitrification is based on an ice sedimentation scheme. Further work is needed to test more sophisticated schemes [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,

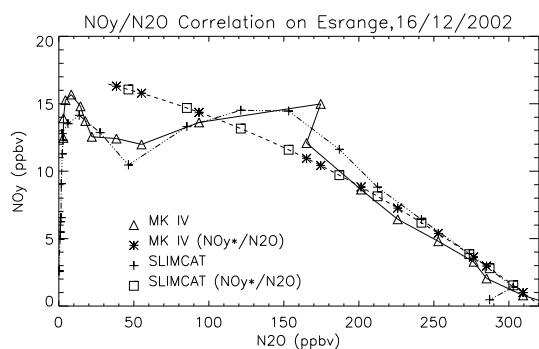


Figure 1. Correlation of NO_y v N₂O on December 16, 2002 for Mk IV data (triangles) and SLIMCAT model (+). Also shown is calculated NO_y* v N₂O from a third-order polynomial [Popp, et al., 2001] using Mk IV and model N₂O.

e.g. for HNO₃ which dominates the NO_y budget in the high latitude winter below 25 km mainly by the heterogeneous reactions on sulfate aerosols via



The Mk IV N₂O₅ profile shows a significant maximum at 29 km with a mixing ratio of 2.14 ppbv. Below 29 km, N₂O₅ decreases rapidly down to 0.01 ppbv at 24 km due to the lower stratosphere is highly depleted in NO_x. SLIMCAT reproduces this observed N₂O₅ distribution, but the modelled N₂O₅ is slightly larger than the observations. Moreover, the maximum modelled N₂O₅ 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 NO₂ 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 HO₂NO₂ 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°N) on December 16, 2002 has been compared with the SLIMCAT 3-D

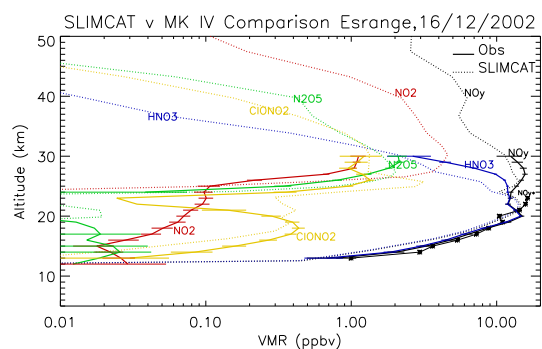


Figure 2. Mk IV-Observed (solid lines) and SLIMCAT-modelled (dashed lines) profiles of NO_y species on December 16, 2002.

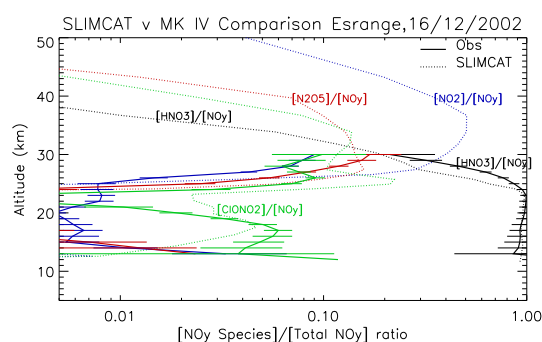


Figure 3. As Figure 2 but for ratios of the individual species with respect to total NO_y.

chemical transport model. The comparison shows that denitrification occurred in the polar vortex (~21-25 km). The model reproduce the observed N₂O-NO_y correlation and the measured NO_y partitioning with the notable exception of NO₂ 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.

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