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A comparison of observations and model simulations of NO_x/NO_y in the lower stratosphere

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Abstract. Extensive airborne measurements of the reactive nitrogen reservoir (NO_y) and its component nitric oxide (NO) have been made in the lower stratosphere. Box model simulations that are constrained by observations of radical and long-lived species and which include heterogeneous chemistry systematically underpredict the NO_x (= NO + NO_2) to NO_y ratio. The model agreement is substantially improved if newly measured rate coefficients for the OH + NO_2 and OH + HNO_3 reactions are used. When included in 2-D models, the new rate coefficients significantly increase the calculated ozone loss due to NO_x and modestly change the calculated ozone abundances in the lower stratosphere. Ozone changes associated with the emissions of a fleet of supersonic aircraft are also altered.

Introduction

Understanding the mechanisms controlling the abundance of NO_y and its partitioning into component species is an essential requirement for understanding the stratospheric ozone (O_3) layer. Reactions involving NO_x form a catalytic O_3 destruction cycle and also moderate O_3 loss due to other cycles involving reactive hydrogen (HO_x) and halogens (ClO_x-BrO_x) [*cf. Wennberg et al.*, 1994]. The partitioning of the NO_y reservoir between NO_x and other component species involves gas-phase and heterogeneous reactions as well as photolytic processes (see Figure 1) [*cf. Gao et al.*, 1997]. We present here extensive new measurements of NO and NO_y obtained in the high latitude lower stratosphere during summer. This data set provides a unique opportunity to test our understanding of the gas-phase chemistry linking NO_x and nitric acid (HNO_3), which is generally the most abundant NO_y species. Because the continuous daylight present at summer high latitudes limits the heterogeneous production of HNO_3 by N_2O_5 hydrolysis, gas-phase reactions primarily control the balance between NO_x and NO_y. Outside summer polar regions, the N_2O_5 hydrolysis reaction occurring on stratospheric sulfate aerosols is a more important sink of NO_x [*cf. Fahey et al.*, 1993], particularly in the lower stratosphere during winter when heterogeneous pathways account for most of the HNO_3 production [*cf. Gao et al.*, 1997].

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Observations and box model description

The observational data set used here was acquired with instruments on board the NASA ER-2 high altitude aircraft during the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) mission. The mission used deployment sites at latitudes of 37°N, 65°N, and 24°N. In the present study, data from 23 flights are used to examine NO_x/NO_y at high latitudes (> 60°N) in late spring, summer, and early fall periods, and in the tropics in early fall.

Measurements of NO and NO_y are made with a three-channel chemiluminescence detector [*Gao et al.*, 1997]. Because NO_2 measurements are not available for all flights, NO_2 values inferred from the steady state relationship (NO_2*) [*Gao et al.*, 1997] are used throughout for consistency. The agreement between average NO_2* and observed NO_2 values during POLARIS is within 10% (*L. A. Del Negro et al.*, Comparison of modeled and observed values of NO_2 and J_{NO_2} during the POLARIS mission, submitted to *J. Geophys. Res.*, 1998). The uncertainty of the NO_x/NO_y measurements is estimated to be ±20%. Measured aerosol surface area (SA) densities varied between 0.5 and 1.5 $\mu m^2 cm^{-3}$ in the data set used here.

A photochemical steady state box model that includes only the processes shown in Figure 1 is used to calculate NO_x/NO_y in a sampled air parcel. The reaction set used in the model is a subset of the more comprehensive set used by *Salawitch et al.* [1994]. The model is constrained by observed values of NO, OH, ClO, O_3, SA, pressure and temperature, and column O_3 above the aircraft [see references in *Gao et al.*, 1997 for instrument details]. Because NO, OH, and ClO concentrations approach zero at high solar zenith angles (SZAs), data gathered at SZA > 85° are not used in this work. The diurnal dependence of the OH radical was determined empirically and normalized here to values observed along the flight track [*Wennberg et al.*, 1994; *T. F. Hanisco et al.*, unpublished data, 1999]. Modeled $ClONO_2$ values agree with POLARIS in situ observations to within 20% (*R. M. Stimpfle et al.*, The coupling of $ClONO_2$,

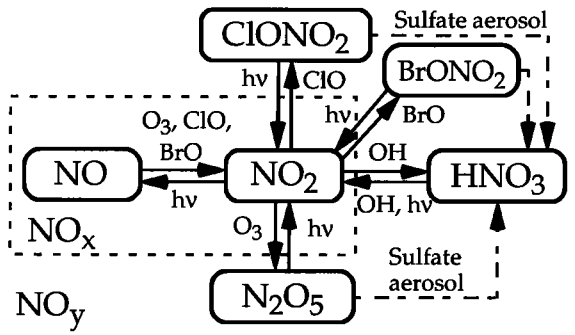

Figure 1. Schematic of the reaction pathways between the principal NO_y component species in the lower stratosphere. Photolysis reactions are indicated by hv. 'Sulfate aerosol' denotes heterogeneous reactions on background aerosol particles.

ClO, and NO_2 in the lower stratosphere from in-situ observations using the NASA ER-2 aircraft, submitted to *J. Geophys. Res.*, 1998). Model BrO values are estimated by calculating the steady state partitioning of the Br_y reservoir as estimated from organic bromine observations [*Wamsley et al.*, 1998]. Unless otherwise noted, gas-phase rate coefficients, absorption cross sections, and reactive uptake coefficients on aerosol are taken from NASA JPL-97 recommendations [*DeMore et al.*, 1997]. Photolysis rates are calculated using a radiation scattering model [*Salawitch et al.*, 1994] which includes effects of overhead O_3, albedo and cloud heights. Reactive uptake coefficients of 0.1 and 0.8 are used for N_2O_5 and $BrONO_2$, respectively. The model does not include $ClONO_2$ hydrolysis since the reactive lifetime in sampled air parcels exceeds 100 days and thus this process has a negligible effect on NO_x/NO_y [*Robinson et al.*, 1997]. With input parameters averaged or interpolated to 100 s intervals, the model is run to a diurnal steady state to yield a value of NO_y consistent with measured NO and rate parameters used in the model. The NO_x/NO_y deduced in this way is then compared with that inferred from NO_2* and the measured values of NO and NO_y.

Results

The comparison of observed and modeled NO_x/NO_y, shown in Figure 2A, includes all stratospheric data from altitudes between 17 and 20 km (50 mb < pressure < 80 mb) with temperatures greater than 204K. The approximately 200,000 s of data are distributed in latitude between 0° and 90°N (< 40°: 5%; 40° - 60°: 17%; > 60°: 78%). In high latitude summer, NO_x reaches 3 parts per billion by volume (ppbv) with NO_x/NO_y in the range of 0.2 to 0.3. Although similar NO_x/NO_y ratios can also be found in the tropical lower stratosphere, the associated NO_x values are typically much less than 3 ppbv.

Most of the steady state model values of NO_x/NO_y fall significantly below observed values. The linear fit (forced through the origin) to the model/data regression has a slope of 0.65. The regression remains virtually unchanged if J_{NO_2} is altered to account for the small difference between NO_2* and observed NO_2 values because J_{NO_2} changes affect NO_2 values on both axes in Figure 2A.

The diurnal steady state assumption is unlikely to be the cause of the observation-model discrepancy in Figure 2A. Back trajectories of the sampled air parcels were calculated using National Center for Environmental Prediction (NCEP) analyzed winds and temperatures. For each parcel, the accumulated latitude change over the previous 10 days was calculated using a weighting function inversely related to the time before aircraft sampling. When those parcels with an effective latitude change of 5° or more (~ 70% of the data) are excluded from the data set, the regression fit to the remaining data is not significantly changed.

The model parameterization of N_2O_5 hydrolysis is also unlikely to be the cause of the NO_x/NO_y discrepancy. Using NCEP back trajectories, sampled air parcels that had recently experienced nearly continuous solar illumination were identified. The acceptance criterion was an SZA of less than 93° for 90% of the preceding 5 day period. As solar illumination becomes continuous, the diurnal conversion of NO_x to HNO_3 through N_2O_5 formation and hydrolysis becomes negligible [*Farman et al.*, 1985; *Brühl et al.*, 1998] and hence the contribution of N_2O_5 hydrolysis to NO_x/NO_y also becomes negligible. The separately averaged data sets in Figure 2A show that, overall, these selected data points are nearly indistinguishable as a group from those that experience interrupted solar illumination. In contrast to the diminished role of N_2O_5 hydrolysis, the contribution of $BrONO_2$ hydrolysis to reducing NO_x/NO_y is greatest for the continuously illuminated parcels [*Randeniya et al.*, 1997]. However, $BrONO_2$ hydrolysis reduces NO_x/NO_y by a maximum of only 5 - 10%. Thus, the hydrolysis reactions of N_2O_5, $ClONO_2$, and $BrONO_2$ are not effective enough in-

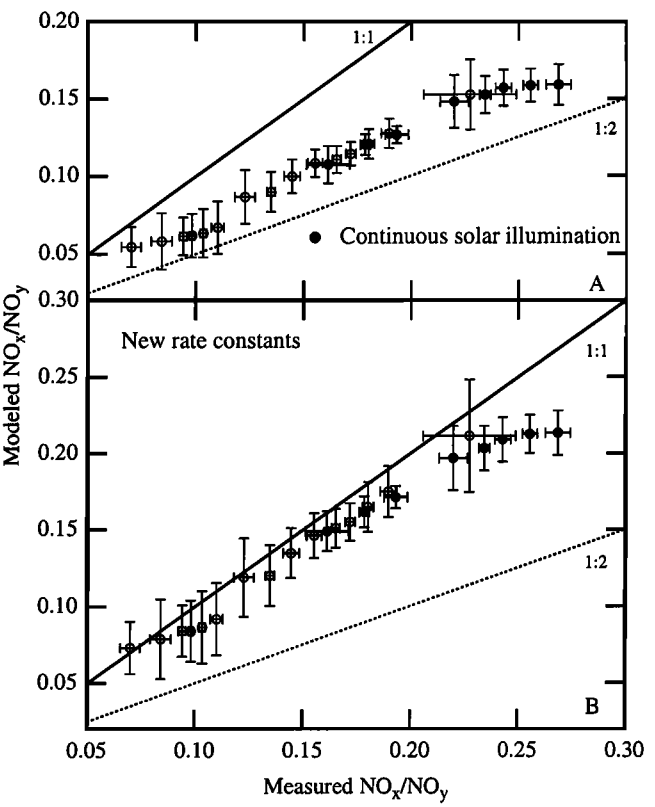

Figure 2. Comparison of modeled and measured values of NO_x/NO_y from POLARIS. The symbols are averages of data as grouped by increasing NO_x/NO_y value. Open symbols are averages of 80 points, each of which represented 100 s of observational data. The solid symbols are separate averages (84 points of 100 s data) for those POLARIS observations for which the sampled air parcel experienced near-continuous solar illumination for the preceding 5 days. The horizontal and vertical bars on each symbol represent the 1-σ sample standard deviation within each group of measured and modeled values, respectively. Results are shown using the model with JPL recommended rate coefficient values (panel A) and with the *Brown et al.* [1999a, b] rate coefficient expressions for (1) and (2) (panel B). The solid and dashed lines represent the 1:1 and 1:2 regression slopes, respectively.

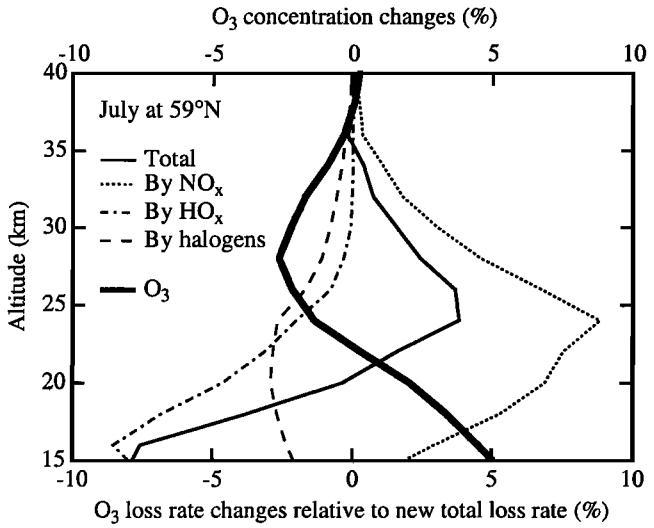

Figure 3. GS model results vs altitude for percentage changes in ozone, its total destruction rate, and the contributions of the NO_x, HO_x, and halogen catalytic cycles for average July 1990 conditions at 59°N with background aerosol conditions. The changes are those that result from using the new *Brown et al.* [1999a, b] values for k_1 and k_2. The percentage changes of the catalytic cycles are shown with respect to the new total ozone loss rate. The percentage changes between the new and old values of the individual loss cycles are larger. For example, at 20 km the NO_x, HO_x, and halogen cycle changes are +23%, -10%, and -22%, respectively. Nearly identical results are obtained with the AER model. The representativeness of the GS model was checked by comparing the average observations at 65°N with the nearest model grid point (64°N). Noon model values of NO_x/NO_y are somewhat lower (< 25%) in the 15 - 20 km region at high latitudes. The longer-lived NO_y, Cl_y, and O_3 species are within 10 - 20% of the average observed values between 15 and 20 km.

dividually or collectively to cause the systematic discrepancy shown in Figure 2A.

In air parcels in which the heterogeneous hydrolysis reactions in Figure 1 do not play a strong role, NO_x/NO_y is primarily controlled by the gas-phase reactions:

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (1)$$

$$OH + HNO_3 \rightarrow NO_3 + H_2O \quad (2)$$

$$HNO_3 + h\nu \rightarrow OH + NO_2 \quad (3)$$

where M is O_2 or N_2. Only a few measurements of the rate coefficient for (1) and (2) (k_1 and k_2) are available at lower stratospheric temperatures (220 ± 20K) and pressures (50 - 150 mb) [*DeMore et al.*, 1997]. *Donahue et al.* [1997] first suggested that recommended values for k_1 may be too high for stratospheric conditions. Recently, *Dransfield et al.* [1999] and *Brown et al.* [1999a] reported laboratory measurements of k_1 for stratospheric conditions that are about 20 - 30% lower than JPL-97 values but consistent with the few previous measurements available below 298K. *Brown et al.* [1999b] also show that k_2 in the lower stratosphere is higher (up to 50%) than JPL-97 values.

Incorporating the new values of k_1 and k_2 of *Brown et al.* [1999a, b] in the model significantly improves the overall agreement with the observations (Figure 2B). The linear fit (forced through the origin) with the new model results has a slope of 0.90. In a similar analysis using balloon observations of NO_x/NO_y at ER-2 altitudes and above, agreement to within

Table 1. Column O_3 change (%) at 59°N in July[a]

EI(SO_2) (g/kg fuel)	JPL 97 rates	*Brown et al.* rates for (1) and (2)
0	-0.5/-0.4	-0.6/-0.6
0.4[b]	-1.3/-0.9	-1.0/-0.5

[a] AER model results for the scenario of 500 HSCT aircraft operating at Mach 2.4 near 18 km cruise altitude with an emission index (EI) of (NO_x) of 5 g/kg fuel. Values are noted for both 2015 and 2050 models years as '2015/2050'. Similar values are calculated for average hemispheric O_3 column changes.

[b] With 50% conversion to small sulfate particles in the plume.

10% is achieved for a 35% reduction of k_1 from JPL-97 values [*Osterman et al.*, 1999]. The *Brown et al.* values of k_1 are not expected to substantially affect the *Gao et al.* [1997] results for winter polar NO_y partitioning since N_2O_5 hydrolysis is generally faster than reaction (1) under the conditions sampled. In contrast, an increase in k_2 will lead to a calculated increase in NO_x/NO_y during winter.

An increase of the HNO_3 photolysis rate in (3) would also improve the observation-model comparisons in Figure 2. In the absence of changes to k_1 and k_2, an increase of approximately 70% is required to yield a regression slope of 0.9. Such a large increase exceeds the reported uncertainties in the underlying measurements of the temperature dependent HNO_3 absorption cross section for lower stratospheric conditions [*Burkholder et al.*, 1993] or in the uncertainties associated with the radiation field calculations [*Gao et al.*, 1997; *Salawitch et al.*, 1994].

Implications

The 2-D dynamical-chemical-radiative model of *Garcia and Solomon* (GS) [1994] and the AER chemistry-transport model [*Weisenstein et al.*, 1996] were used to examine the effects of the *Brown et al.* rates on O_3 and the principal ozone catalytic loss cycles at high latitudes in summer. The results shown in Figure 3 include altitudes between 15 and 40 km in the stratospheric ozone layer in July at 59°N to illustrate the effect of the new k_1 and k_2 values over a range of model temperatures and other conditions. The important features in Figure 3 are (i) that large changes in the rates that control NO_x/NO_y yield much smaller changes in the ozone distribution in the lower stratosphere due to the corresponding changes in HO_x, ClO_x, and BrO_x abundances, and (ii) that the new rates result in a 'cross-over' near 20 km from an increased to a decreased value of the total O_3 destruction rate. Throughout most of the 15 - 40 km region, the magnitude of the NO_x-catalyzed destruction increases (up to 10% near 25 km when expressed as a percentage of the new total O_3 destruction rate) as a direct result of higher NO_x/NO_y values while the contributions from the BrO_x-ClO_x and HO_x catalytic cycles decrease because of moderation by NO_x. Above 25 km, NO_x/NO_y approaches unity and the sensitivity of the O_3 loss cycles to the rate coefficient changes approaches zero. At 25 km, the net increase in O_3 destruction rates reaches a maximum. Because changes in k_2 are largest at low temperatures and affect the abundances of both NO_x and HO_x, the sensitivity of the BrO_x-ClO_x and HO_x cycles to increases in NO_x/NO_x is largest below 25 km and results in a net decrease in the total O_3 loss rate. Changes in the vertical distribution of O_3 due to the new rates are small (< 5%) throughout the 15 - 40 km region, consistent with the calculated changes in the O_3 loss rate.

The increased contribution of the NO_x cycle to O_3 loss rates at mid and high latitudes modifies how emissions from a pro-

posed High Speed Civil Transport (HSCT) stratospheric aircraft fleet are expected to change O_3 in the lower stratosphere [*Stolarski et al.*, 1995]. Whether the *Brown et al.* rates will lead to a larger or smaller depletion for a particular HSCT scenario depends sensitively on the relative emissions of NO_x and sulfur from an HSCT engine. The sulfur emission index (EI) and exhaust plume processes determine the SA changes of the background sulfate aerosol. As an example, Table 1 shows how the *Brown et al.* k_1 and k_2 values affect O_3 column amounts at 59°N in summer for two key HSCT fleet scenarios in a 2015 and 2050 atmosphere. With no sulfur emissions, the changes in the rate coefficients of k_1 and k_2 result in slightly larger O_3 depletion because the role of NO_x in catalytic O_3 loss is greater than its role in moderating the HO_x and halogen cycles. When sulfur is also emitted, the formation of sulfate particles in the plume and their accumulation in the atmosphere causes an increase in background SA densities. Larger SA densities reduce NO_x values through N_2O_5 hydrolysis (for both the NO_x emitted by the aircraft and NO_x in the background atmosphere), resulting in a decrease in the O_3 removal by the NO_x loss cycle compared to the atmosphere without aircraft. The NO_x reduction due to increased SA densities in the atmosphere increases the HO_x and active halogen concentrations, resulting in increases for the corresponding O_3 removal cycles. The effects of increased NO_x concentrations due to aircraft emission must be considered in conjunction with the effects of increased SA densities. The use of the *Brown et al.* rates in this case results in less O_3 depletion because more effective moderation of the HO_x and halogen loss cycles by aircraft-emitted NO_x partially mitigates the effect of aerosol changes.

Concluding remarks

The in situ aircraft observations presented here represent a large new data set with which to examine NO_x/NO_y over a wide range of latitude and season in the lower stratosphere. Representative box model calculations systematically underpredict the observed ratio by about 40%. Because the discrepancy remains in air parcels with continuous solar exposure, the parameterization of the N_2O_5 hydrolysis reaction is unlikely to be the cause. The use of recent laboratory results for the OH + NO_2 and OH + HNO_3 reaction rate coefficients from *Brown et al.* [1999a, b] significantly improves the comparison of measured and modeled NO_x/NO_y for most sampled air parcels. The effect of the rate changes and associated NO_x increases on O_3 concentrations calculated in 2-D models is small (< 5%) throughout most of the lower stratosphere because of the interdependence of the NO_x, BrO_x-ClO_x, and HO_x catalytic loss cycles.

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