

Partitioning of NO_y species in the summer Arctic stratosphere

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Abstract. Volume mixing ratio profiles of the quantitatively significant NO_y species NO, NO₂, HNO₃, HNO₄, ClNO₃ and N₂O₅ were measured remotely from 8 to 38 km by the JPL MkIV FTIR solar absorption spectrometer during balloon flights from Fairbanks, Alaska (64.8°N, 147.6°W) on May 8 and July 8, 1997. The observed ratio of NO_x (NO+NO₂) to NO_y (total reactive nitrogen) is 10 to 30% greater than calculated by a steady state model using standard photochemistry constrained by MkIV measurements of long lived precursors (e.g., H₂O, CH₄, CO and N₂O) and SAGE II aerosol surface area. The persistence of this discrepancy to 38 km altitude suggests that processes involving aerosols, such as the reduction of HNO₃ on the surface of soot particles, cannot be the sole explanation. The most likely resolution to this discrepancy is that the rate of NO₂+OH +M→HNO₃+M (the dominant sink of NO_x in the Arctic stratosphere during times of near continuous solar illumination) is significantly slower than the currently recommended rate.

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Introduction

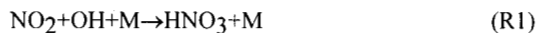
Reactions involving NO_x (NO+NO₂) directly catalyze the removal of stratospheric O₃ and also affect the efficiency of the halogen and hydrogen O₃-destroying catalytic cycles [e.g., Salawitch *et al.*, 1994]. An accurate assessment of the effects on O₃ of anthropogenic activities such as emissions of NO_x from a proposed fleet of supersonic aircraft is contingent upon gaining a good understanding of the ratio of NO_x to total NO_y (NO_x + NO₃ + HNO₃ + 2×N₂O₅ + HNO₂ + HNO₄ + ClNO₃ + BrNO₃). The high latitude summer stratosphere provides an opportunity to examine the partitioning of NO_y gases for conditions where heterogeneous processes, normally the dominant sink of NO_x in the lower stratosphere, are inefficient due to the long periods of daylight that limit the conversion of NO_x to N₂O₅.

The JPL MkIV spectrometer obtains remote observations in solar absorption. It made simultaneous measurements of the volume mixing ratio (vmr) profiles of the dominant NO_y gases (NO, NO₂, HNO₃, ClNO₃, N₂O₅, HNO₄) as well as O₃, CH₄, H₂O, N₂O, HCl, HOCl, CO and others, during balloon flights on May 8 (970508) and July 8, 1997 (970708) from Fairbanks, Alaska (64.8°N, 147.6°W) as part of the ADEOS validation and POLARIS missions. Sen *et al.* [1998] describe the observational technique and data retrieval procedure and provide an extensive discussion of the measurement uncertainty. Observations on 970508 were obtained during local sunrise while the instrument was at float (~38 km), whereas observations on 970708 were obtained during ascent close to the time of sunset. Measurements of NO and NO₂ for both flights have been obtained by accounting for variations in the abundance of these gases along the line of sight during sunrise or ascent. These "diurnal corrections" are not a significant source of uncertainty for NO₂ and NO_x at all altitudes, nor for NO above 25 km [Sen *et al.*,

1998]. The accuracy of the spectroscopic parameters used for gas retrievals are estimated to be 5% for N₂O, 8% for NO, 10% for NO₂ and 15% for ClNO₃, HNO₃ and N₂O₅. The error bars used here for the MkIV measurements represent the 1σ precision, based on considerations such as residuals in spectral fitting, combined in quadrature with these spectroscopic uncertainties.

The photochemical steady state model used in our analysis is constrained by MkIV measurements of O₃, NO_y (obtained from NO_x+HNO₃+ClNO₃+2×N₂O₅+HNO₄, since the other gases make an insignificant contribution to the total), Cl_y (inferred from HOCl+ClNO₃+HCl and model ClO), H₂O, CH₄, CO, temperature, and pressure as well as SAGE II zonal, monthly mean aerosol surface area [L. W. Thomason, private communication, 1998] and Br_y [Wamsley *et al.*, 1998] inferred from MkIV N₂O vmr profiles. The model assumes that production and loss rates for each species balance over a 24 hour period, for the latitude and temperature profile of the observations, allowing for full diurnal variation of each gas [e.g., Sen *et al.*, 1998]. The standard calculation discussed below (referred to as JPL97) uses reaction rates and absorption cross sections from DeMore *et al.* [1997]. We also show model calculations using kinetic parameters from DeMore *et al.* [1994] (JPL94) to document the change in calculated NO_x/NO_y for the summer polar stratosphere due to the updated recommendations for gas phase processes. All calculations use the branching ratio for ClO+OH→HCl+O₂ from Lipson *et al.* [1997] and reaction probabilities for heterogeneous reactions on sulfate aerosols from DeMore *et al.* [1997].

As discussed below, the JPL97 model calculations underestimate measured profiles of NO_x/NO_y and NO₂/HNO₃ for both MkIV flights. The JPL94 model results in better agreement with the observations, due mainly to a slower rate for



relative to the JPL97 recommendation. However, observed NO_x/NO_y and NO₂/HNO₃ are still systematically underestimated by the JPL94 model. To explore the sensitivity of the calculated ratios to changes in the key kinetic parameters that regulate NO_x, a third set of calculations is also shown (Model B), identical to the JPL97 calculation except for a 35% reduction in the rate for (R1). A decrease to the rate of (R1) cannot easily be distinguished from a comparable increase in the photolysis rate of HNO₃ for the conditions of these flights, since these processes are the major sink and source of NO_x, respectively. Model B should be viewed as a surrogate for the combined change in these kinetic parameters necessary to bring the model into better agreement with observation for NO_x/NO_y. The 35% reduction in (R1) was chosen because it provides the best agreement with measured NO_x/NO_y and NO₂/HNO₃ at all altitudes, for both flights. Our intent in carrying out these comparisons is to highlight areas for which future research might improve our understanding of atmospheric chemistry, rather than “deriving rate constants” from atmospheric observations. We have chosen to vary the rate of (R1) since it has recently undergone revision by the JPL panel and is the subject of recent laboratory studies, discussed below, that support a slower rate than the JPL97 rate.

NO_x/NO_y ratio and nitrogen partitioning

MkIV observations of the NO_x/NO_y ratio are larger than calculated values using the JPL97 model at all altitudes above 15 km for both flights (Figure 1). This discrepancy is also apparent for comparisons with observations of the NO₂/HNO₃ ratio (Figure 2). Since NO_x becomes the dominant NO_y species for

altitudes above ~28 km, the NO_2/HNO_3 ratio provides a more sensitive test of our understanding of nitrogen partitioning at higher altitudes. The percentage difference between measured and calculated NO_x/NO_y versus altitude for the 970508 flight is shown in Figure 3a. The largest difference between observation and the JPL97 calculation occurs near 18 km, with the measured ratio exceeding the model by 30% for May and 34% for July.

Loss of NO_x is dominated by $\text{NO}_2+\text{OH}+\text{M}$ (R1) at all altitudes for both flights (Figure 3b). Production of NO_x occurs primarily by photolysis of HNO_3 . The reaction HNO_3+OH makes its largest contribution to production of NO_x (~30% of the total) below 22 km with diminishing importance at higher altitudes. Heterogeneous reactions, normally the dominant NO_x sink for the lower stratosphere, make a small contribution to loss of NO_x (~15% of the total at 20 km for 970508) because short periods of darkness limit the efficiency of the $\text{N}_2\text{O}_5+\text{H}_2\text{O}(\text{sulfate})$ sink (significant amounts of N_2O_5 are produced only at night). Heterogeneous sinks of NO_x are less important for the 970708 flight, which encountered air with nearly continuous solar illumination. The $\text{BrNO}_3+\text{H}_2\text{O}(\text{sulfate})$ reaction is the dominant heterogeneous sink of NO_x below 22 km for 970508, and at all altitudes for 970708. The effect of long periods of solar illumination on NO_x was evaluated by setting solar declination to 0° (i.e., equinox) and keeping all other JPL97 model parameters fixed: in this case, calculated NO_x/NO_y at 20 km is reduced from 0.15 to 0.02 for 970508 and from 0.24 to 0.07 for 970708.

The JPL97 calculation provides a reasonably good simulation of the altitude profiles of the various NO_y gases observed by MkIV on 970508 (Figure 4a). However, the observed profile for NO_2 is systematically underestimated by the model for altitudes above 16 km, while HNO_3 is consistently overestimated above 25 km. The observed NO/NO_2 ratio on 970508 (not shown) tends to be lower than calculated below 27 km. *Sen et al.* [1998] offered several possible explanations of a previously noted discrepancy for NO/NO_2 at midlatitudes that should apply equally well to these high latitude observations. However, this issue is unlikely to have a major impact on our understanding of NO_x/NO_y since different processes regulate these two ratios.

One of the most dramatic differences between the high-latitude and midlatitude MkIV observations is the sunrise mixing ratio profile of N_2O_5 (Figure 4b). Above ~25 km, the vmr of N_2O_5 is lower in the high latitude region because of shorter nights that limit its formation. For altitudes below ~20 km, N_2O_5 is enhanced at high-latitudes because the relatively high values of NO_x and O_3 (the value of $[\text{NO}_x][\text{O}_3]$, which regulates nighttime formation of N_2O_5 , is a factor of ~30 larger for the high-latitude air at 16 km than for mid-latitude air at 16 km) allow for rapid formation of N_2O_5 even during the short periods of darkness. The larger amounts of NO_x and O_3 observed at high-latitudes are caused mainly by differences in tropopause height (~9 km for 65°N ; ~16 km for 35°N). The ability of the model to capture the dramatic differences in N_2O_5 between the two geographic regions indicates that the processes linking NO_x and N_2O_5 are well represented by current photochemical theory.

The JPL94 model exhibits better agreement with the MkIV observations than the JPL97 model, but still underestimates the observed NO_x/NO_y and NO_2/HNO_3 ratios at all altitudes (Figures 1, 2 and 3a). The JPL94 model uses a slower rate constant for (R1) and smaller values for the quantum yield of $\text{O}(^1\text{D})$ from photolysis of O_3 that lead to a reduction in calculated OH. Both of these differences lead to larger values for calculated NO_x relative to the JPL97 model due primarily to a reduction in the loss rate of NO_x by (R1).

Excellent agreement between model and measured NO_x/NO_y and NO_2/HNO_3 is obtained at all altitudes, for both flights, allowing for a 35% reduction in the JPL97 rate of $\text{NO}_2+\text{OH}+\text{M}$ (Model B calculation in Figures 1 through 4). This simulation also results in the best agreement with observed N_2O_5 . Similarly good agreement with all MkIV observations is obtained if we were to allow for a comparable increase in the photolysis rate of HNO_3 , since these two reactions dominate the partitioning of reactive to reservoir NO_y at all altitudes.

Examination of the MkIV observations and model results in the context of other measurements suggests the discrepancy between theory and observation of NO_x/NO_y and NO_2/HNO_3 is real. Comparison of NO_y vs. N_2O measured by MkIV to ER-2 observations demonstrates that the MkIV observations of NO_y are accurate and complete, and that the uncertainty estimates for NO_y are realistic [Sen *et al.*, 1998]. Uncertainties in calculated OH are unlikely to be the cause of the discrepancy because concentrations of OH measured in the Arctic stratosphere between 30 and 50 km on 970430 by the FIRS-2 instrument [Jucks *et al.*, 1998] and near 20 km by an ER-2 instrument during POLARIS [P. O. Wennberg, private communication] typically exceed our model calculations by 15 to 20%. Adjusting our model to give better agreement with measured OH would, keeping all else fixed, lead to a larger discrepancy for the two ratios due to the dominant role of (R1). Variations in latitude of the sampled air masses several days prior to observation may affect the NO_x/NO_y ratio due to its dependence on length of night. However, calculated NO_x/NO_y vs. latitude (keeping all else fixed in the model) approaches a constant value with increasing latitude near the location of the observations and the photochemical lifetime of NO_x is fairly short (~5 days at 20 km for 970708, and shorter at higher altitudes). Neglecting past variations in latitude of the sampled air masses in the model simulations is therefore unlikely to be the primary cause of the discrepancy. Finally, an analysis of extensive ER-2 observations has revealed a similar discrepancy for NO_x/NO_y near 20 km during Arctic summer [Gao *et al.*, 1999].

The discrepancy between observed and calculated NO_x/NO_y and NO_2/HNO_3 likely means either the rate of one or more of the processes identified in Figure 3b is represented incorrectly in the model or a key process that cycles reservoir NO_y species to NO_x is omitted. It has been proposed that $\text{HNO}_3 \rightarrow \text{NO}_2$ on the surface of soot particles may provide an important source of NO_x not represented in most models [e.g., Lary *et al.*, 1997]. Stratospheric soot is believed to originate from combustion in aircraft engines and should have little influence above ~20 km. The persistence of the discrepancy to ~35 km argues against reactions on soot, or any process involving aerosols, being the sole explanation. Additionally, the recent laboratory study by Choi and Leu [1998] has shown $\text{HNO}_3 \rightarrow \text{NO}_2$ does not occur on soot for stratospheric conditions. At this time, there are no proposed "missing" processes capable of resolving the discrepancy at all altitudes.

It is unlikely that uncertainties in the rate of HNO_3+OH could entirely resolve the discrepancy since this reaction is a relatively minor source of NO_x (Figure 3b). Brown *et al.* [1999b] describe laboratory measurements that show the rate of HNO_3+OH may be ~33% faster than the JPL97 rate for conditions near 20 km. For altitudes below ~25 km, where HNO_3+OH is a non-negligible source of NO_x , calculated NO_x would agree more closely with observation allowing for this faster rate. However, a significant reduction (e.g., 30%) in the JPL97 rate of (R1) or a comparable increase in the photolysis rate of HNO_3 would still

be required to obtain good agreement with measured NO_x/NO_y and NO_2/HNO_3 above 20 km.

Discussion and Implications

A substantial reduction in the JPL97 rate of $\text{NO}_2+\text{OH}+\text{M}$ (R1) is a viable resolution for most of the discrepancy between calculations and the MkIV observations of NO_x/NO_y and NO_2/HNO_3 . Donahue *et al.* [1997] reported a value for k_1 [the rate constant of (R1)] at room temperature that was ~20% slower than the DeMore *et al.* [1994] (JPL94) rate. The JPL97 fit for k_1 included the Donahue *et al.* [1997] data, but was done using a different weighting method than that used for previous recommendations. Consequently, for temperatures and pressures of the lower stratosphere, the JPL97 value for k_1 is considerably faster than the JPL94 value as well as the "historical" laboratory measurements of k_1 [Anderson *et al.*, 1974; Anastasi and Smith, 1976; Wine *et al.*, 1979].

Recently Dransfield *et al.* [1999] and Brown *et al.* [1999a] have reported laboratory measurements of k_1 that are ~20 to 30% slower than the JPL97 value for temperatures and pressures of the lower stratosphere. These new laboratory measurements for k_1 agree well with the "historical" data and are being incorporated into a reevaluation of the JPL rate for $\text{NO}_2+\text{OH}+\text{M}$ [D. M. Golden, private communication, 1998]. It is likely that the reevaluated rate for (R1) will be less than the full 35% reduction of the JPL97 rate necessary to give "best" agreement with the observations. The remaining discrepancy lies within the measurement uncertainty, but may suggest the need for minor revisions in our treatment of HNO_3 photolysis, $\text{OH}+\text{HNO}_3$, or the $\text{BrNO}_3+\text{H}_2\text{O}$ heterogeneous sink of NO_x .

Numerous previous studies (based on JPL94 kinetics) have documented good agreement between theory and observations of NO_x/NO_y acquired in the lower stratosphere at midlatitudes [e.g., Salawitch *et al.*, 1994; Gao *et al.*, 1997; Sen *et al.*, 1998]. For each of these studies, heterogeneous chemistry was the dominant sink of lower stratospheric NO_x and a reduction in k_1 therefore would have been inconsequential. Lary *et al.* [1997], Morris *et al.* [1997], and Sen *et al.* [1998] have shown that observed NO_x/NO_y at midlatitudes exceeds calculated values at altitudes where (R1) is a significant sink of NO_x . These discrepancies are consistent with the present study, whose most notable aspect is the dominant role of (R1) for loss of NO_x at all altitudes.

A reduction in the rate of $\text{NO}_2+\text{OH}+\text{M}$ will increase the calculated contribution of NO_x to catalytic removal of stratospheric O_3 at all altitudes for polar regions during periods of near continuous solar illumination. Allowing in the model for a 35% reduction in k_1 (Model B) leads to small (< 10%) increases in the total O_3 loss rate at altitudes below ~18 km for conditions of the two MkIV flights because decreases in the efficiency of O_3 loss due to the HO_x and ClO_x cycles offset the increase in O_3 loss due to NO_x . The change in the total O_3 loss rate for the Model B calculation increases with altitude from 18 to 24 km, reaching a maximum increase of ~25% (compared to JPL97) between 24 and 28 km. Multi-dimensional models are required to assess the implications of a reduction in k_1 for the sensitivity of stratospheric O_3 to various anthropogenic perturbations, such as emissions of NO_x and sulfate aerosol from a proposed fleet of supersonic aircraft [e.g., Gao *et al.*, 1999].

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Figure 1. MkIV observations of the NO_x/NO_y ratio at sunrise and on ascent, as indicated, for balloon flights in the Arctic on 970508 and 970708. Model calculations of NO_x/NO_y (see text) for the solar zenith angle of the observations are also shown.

Figure 2. Same as Figure 1, for the NO₂/HNO₃ ratio measured by MkIV.

Figure 3. (Left panel) Percentage difference between measured NO_x/NO_y and values from each of the model calculations for the 970508 flight. (Right panel) 24 hour average rates for the sources and sinks of NO_x as well as the total NO_x loss rate, calculated using the JPL97 model for the 970508 flight. Loss of NO_x by all heterogeneous reactions are summed in the "Het. Loss" curve.

Figure 4. (Left panel) MkIV observations of the individual NO_y gases at sunrise and calculated values for the 970508 flight. (Right panel) MkIV observations of sunrise N₂O₅ on 970508 at 65-70°N and on 930926 at 35°N compared to model profiles. For clarity, only the Model B calculation is shown for 930926.

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