Observations of large reductions in the NO/NO$_y$ ratio near the mid-latitude tropopause and the role of heterogeneous chemistry

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Abstract. During the 1993 NASA Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE), anomalously low nitric oxide (NO) was found in a distinct sunlit layer located above the mid-latitude tropopause. The presence of a significant amount of reactive nitrogen (NO$_y$) in the layer implies the systematic removal of NO, which is without precedent in stratospheric *in situ* observations. Large increases in measured chlorine monoxide (ClO) and the hydroperoxyl radical (HO$_2$) also were observed in the layer. Heterogeneous reaction rate constants of chlorine nitrate (ClONO$_2$) with hydrogen chloride (HCl) and H$_2$O to form nitric acid (HNO$_3$) on sulfate aerosol are enhanced in the NO removal layer by local increases in H$_2$O and aerosol surface area. The associated conversion of NO$_x$ (= NO + NO$_2$) to HNO$_3$ is the most likely cause of the observed low NO and NO$_x$/NO$_y$ values and high ClO values.

Introduction

Reactive nitrogen (NO$_y$ = NO + NO$_2$ + NO$_3$ + 2N$_2$O$_5$ + HONO + HO$_2$NO$_2$ + HNO$_3$ + PAN + ClONO$_3$ + aerosol nitrate + ...) species play an important role in the photochemistry of the troposphere and stratosphere. NO is an important indicator of the partitioning within the NO$_y$ reservoir and can be used to infer and limit the abundance of the higher nitrogen oxides [*Kawa et al.*, 1992]. During the day, NO is produced by the photolysis of nitrogen dioxide (NO$_2$) and other NO$_y$ species. The NO/NO$_2$ ratio requires only minutes in the sunlit atmosphere to reach steady state [*Kawa et al.*, 1992]. We describe here a distinct layer encountered at mid-latitudes above the sunlit tropopause during the spring of 1993 in which NO approached values near zero (< 0.02 parts per billion by volume, ppbv) and NO$_y$ values were large (~2 ppbv). This partitioning is consistent with the effects of heterogeneous reactions in the layer involving the inorganic chlorine species HCl and ClONO$_2$. These reactions form HNO$_3$ at rates signifi-

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cantly increased by a combination of high aerosol loading following the eruption of Mt. Pinatubo, high H$_2$O mixing ratios, and low temperatures near the tropopause.

Observations of Radical Species

The observations reported here were obtained with instruments onboard the NASA ER-2 high-altitude aircraft during its descent into Moffett Field, CA (38°N, 122°W) on 30 April 1993. The ER-2 payload included a suite of instruments designed for *in situ* measurements of a wide variety of reactive and long-lived species and aerosol parameters [*Fahey et al.*, 1995a; b]. Figure 1 displays vertical profiles of observations and calculated parameters for the near-tropopause portion of the descent. The profile range represents ~250 s of flight time close to 1500 hr local time. Based on the minimum in the temperature profile, the tropopause is located near 12.5 km at a temperature of ~205 K. The NO removal layer is defined by the region above the tropopause between 12.7 and 13.2 km where NO mixing ratios are near the detection limit of 0.01 to 0.02 ppbv. Below this layer and spanning the tropopause, NO has higher values of 0.20 ± 0.05 ppbv. Based on the ER-2 observation dataset, NO values of 0.10 to 0.30 ppbv are typically found just above the tropopause, smoothly decreasing with altitude to values < 0.10 ppbv in the upper troposphere. The removal layer also was observed during ascent on this flight (~1300 hr), and a less distinct removal layer was observed during ascent on 1 May (~0900 hr).

The measurements shown in Figure 1 were acquired in sunlight (solar zenith angle of 31°), allowing the steady-state NO$_2$ mixing ratio (NO$_{2ss}$) to be calculated using measured ozone (O$_3$), ClO, HO$_2$, temperature, pressure, and a calculated NO$_2$ photolysis rate [*Kawa et al.*, 1992]. These steady-state NO$_2$ values are less than the observed NO throughout the profile, and thus very low (< ~0.02 ppbv) in the removal layer. Because NO$_y$ exceeds 2 ppbv in the removal layer, the NO$_x$/NO$_y$ ratio is much less than typical values of 0.1 [*Fahey et al.*, 1993], signaling an unexpectedly large repartitioning within the lower stratospheric NO$_y$ reservoir. Expected NO$_y$, denoted NO$_y$* in Figure 1, is determined from the well-established, highly compact correlation between NO$_y$ and nitrous oxide (N$_2$O) observed in the lower stratosphere [*Loewenstein et al.*, 1993]. Variations in NO$_y$ not associated with N$_2$O changes are expected near the tropopause, due in part to lightning and other sources of NO$_y$ in the troposphere [*Murphy et al.*, 1993]. NO$_y$ in excess of NO$_y$* (~1 ppbv in the removal layer) could be caused at least in part by enhanced sampling of sulfate aerosol particles containing a significant fraction of condensed NO$_y$ species [*Fahey et al.*, 1989].

Repartitioning of the NO$_y$ reservoir is likely to have an impact on other species observed in the removal layer because of the strong coupling between reactive nitrogen, chlorine,
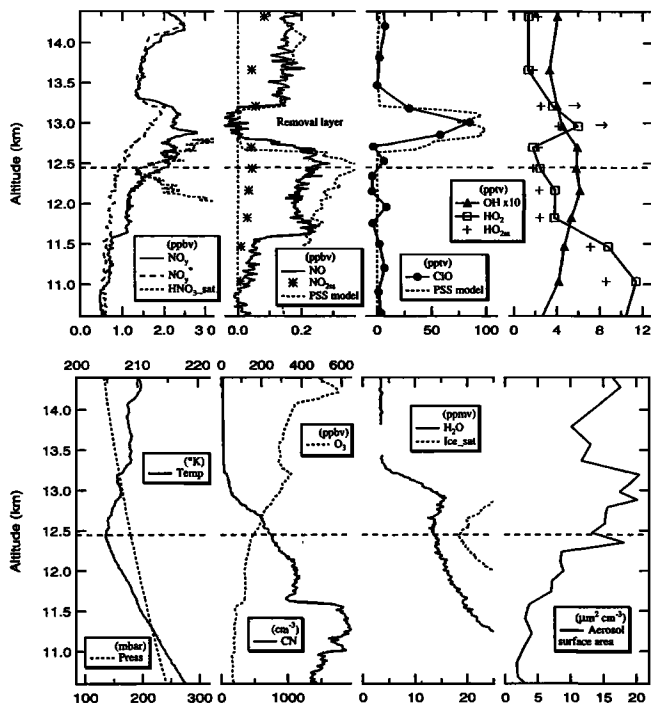
Figure 1. Observations and calculated parameters during descent on the flight of 30 April 1993. Units are noted in the legends. Measurement uncertainties are included in Fahey et al. [1995 a; b]. The tropopause is shown as a horizontal dashed line. NO$_{2ss}$ and HO$_{2ss}$ are calculated using steady-state relations. Ice_sat and HNO$_3$_sat are calculated equilibrium saturation mixing ratios of H$_2$O over ice and HNO$_3$ over NAT, respectively. NO$_y^*$ is the expected amount of stratospheric NO$_y$ determined from observed N$_2$O and the NO$_y$/N$_2$O correlation. NO$_y^*$ values in the troposphere reflect the intercept of the fit to stratospheric observations. The arrows indicate lower limit HO$_2$ values.

and hydrogen photochemistry in the lower stratosphere [Wennberg et al., 1994]. Because ClONO$_2$ is formed by the reaction of NO$_2$ with ClO, the removal of NO, and thus NO$_x$, is likely to be associated with increased ClO. In Figure 1, ClO values < 10 parts per trillion by volume (pptv) near the removal layer are typical for midday conditions at mid-latitudes [Salawitch et al., 1994]. However, ClO increases to over 90 pptv in the removal layer, corresponding to ~25% of the available inorganic chlorine (Cl$_y$) as calculated using the observed correlation with N$_2$O [Woodbridge et al., 1995]. These unexpectedly high values of ClO corroborate the NO removal layer as a region in the mid-latitude stratosphere with an unexpected photochemical balance.

The hydroxyl radical (OH) shows a largely invariant vertical profile across the tropopause in Figure 1. In contrast, HO$_2$ increases significantly upon entering the upper troposphere, increasing the HO$_2$/OH ratio accordingly [Wennberg et al., 1995]. In the NO removal layer, lower-limit HO$_2$ values are significantly larger than values above the layer. Figure 1 includes steady-state HO$_2$ (HO$_{2ss}$) values calculated with the relation:

$$[HO_2]_{ss} = \frac{[OH]\left(k_{OH+O_3}[O_3] + k_{OH+CO}[CO]\right)}{k_{HO_2+NO}[NO] + k_{HO_2+O_3}[O_3] + k_{HO_2+ClO}[ClO] + k_{HO_2+BrO}[BrO]} \quad (1)$$

where k denotes the associated rate constant [Cohen et al., 1994; Wennberg et al., 1994]. In the near-tropopause region, the bromine monoxide (BrO) term can be neglected. Average

carbon monoxide (CO) values, as estimated using the correlation observed with O$_3$ [Murphy et al., 1993], are 34 ppbv in the layer. The steady-state HO$_2$ values, which increase in the removal layer primarily because of the reduction in NO, are comparable to the lower-limit observed values.

Observations of Tracers, Aerosols, and Meteorological Parameters

Large and opposing vertical gradients of condensation nuclei (CN) and O$_3$ exist across the tropopause region. Stratospheric CN and O$_3$ values are 30 cm^{-3} and > 350 ppbv, respectively, while troposphere values are > 950 cm^{-3} and < 100 ppbv. Because of the CN and O$_3$ values observed in the removal layer (180 cm^{-3}, 290 ppbv) and the long lifetimes of O$_3$ and CN (weeks to months), only a small fraction of the air in the removal layer could have been recently transported from the free troposphere where NO values are also very low.

H$_2$O also shows a strong gradient across the tropopause, with a local maximum (~16 parts per million by volume, ppmv) occurring in the center of the NO removal region. A similar maximum was observed in all three profiles showing evidence of an NO removal layer. Values of H$_2$O significantly greater than 4 ppmv are not unusual just above the tropopause at mid-latitudes [Foot, 1984]. These high values are attributed to air parcels crossing the tropopause in the extratropics [Dessler et al., 1995]. The ice saturation mixing ratio, which reaches a minimum near 20 ppmv at the tropopause, remains above ambient H$_2$O values throughout the profile in Figure 1. Saturation mixing ratios of HNO$_3$ over the nitric acid trihydrate (NAT) phase (HNO$_3$_sat in Figure 1) approach available HNO$_3$ (or NO$_y$) only in a narrow layer centered at the tropopause [Fahey et al., 1989]. This suggests that NAT particles are not present in the removal layer and are unlikely to be involved in its formation.

In addition to CN, aerosol spectrometer measurements provided surface area as a sum over discrete particles in sizes ranging from 0.1 to 20 μm in diameter. Based on a derived size distribution, the area associated with particles outside this size range is negligible. Surface area values in the lower stratosphere are near 1 μm^2 cm^{-3} during nonvolcanic periods [Hofmann and Solomon, 1989]. Larger values in Figure 1 reflect aerosol particles produced in the stratosphere after the eruption of Mt. Pinatubo in June 1991 [Trepte et al., 1993]. Near the NO removal layer, the surface area shows a corresponding layer feature with maximum values of 20 μm^2 cm^{-3}, primarily associated with particle diameters between 1 and 4 μm.

The recent history of air parcels near the tropopause was examined using isentropic trajectory calculations based on assimilated winds and temperatures from the National Meteorological Center [Newman et al., 1993]. The 10-day back trajectories show that air parcels just above, in, and just below the removal layer had very similar trajectories and experienced no significant latitude excursions after the first three days. The lowest temperature (~208 K) for the removal layer parcel occurred on 30 April, while the 10-day temperature ranges for parcels above and below the removal layer were 206 to 216 K and 208 to 225 K, respectively.

Discussion

Previous in situ measurements have established the role of heterogeneous reactions in the partitioning of the stratospheric NO$_y$ reservoir [Fahey et al., 1993]. In particular, the dinitrogen pentoxide (N$_2$O$_5$) hydrolysis reaction on sulfate aerosol reduces the NO$_x$/NO$_y$ ratio in the mid-latitude stratosphere through conversion of NO$_x$ to HNO$_3$. The accommoda-

tion coefficient of this reaction is large and nearly independent of temperature and aerosol composition in the lower stratosphere. However, in these previous in situ measurements, the NO$_x$/NO$_y$ ratio remained above 0.07 as the surface area increased to over 20 μm^2 cm^{-3}. This nonlinear or saturation effect is the result of limitations in N$_2$O$_5$ production, which occurs primarily at night. Therefore, a process other than N$_2$O$_5$ hydrolysis must be the cause of low NO and NO$_x$/NO$_y$ in the removal layer in Figure 1. This additional process must compete with NO$_x$ production, which occurs through HNO$_3$ photolysis and the reaction of OH with HNO$_3$. For conditions in the NO removal layer, calculations of the production rate for NO$_x$ using a photochemical steady-state (PSS) model [Salawitch et al., 1994] yield a value of 8.8 x 10^3 molecules cm^{-3} s^{-1}, corresponding to an HNO$_3$ lifetime in daylight of ~30 hr.

Two heterogeneous reactions that can affect the partitioning for both the NO$_y$ and Cl$_y$ reservoirs in the stratosphere are:

$$H_2O + ClONO_2 \rightarrow HOCl + HNO_3 \qquad (R1)$$

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3 \qquad (R2)$$
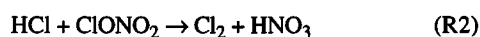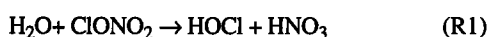
These reactions can take place on solid and liquid stratospheric particles such as NAT, ice, and sulfate aerosols. Normally, the partitioning in the mid-latitude stratosphere is not affected by these reactions due to their large temperature dependence, with rates that only become comparable to the N$_2$O$_5$ hydrolysis reaction at temperatures below 200 K. However, the rate constants also depend very strongly on aerosol composition, increasing exponentially with H$_2$O weight percent (wt%). Above the removal layer, the aerosol H$_2$O fraction calculated using an analytic ternary solution model [Carslaw et al., 1995; Del Negro et al., 1996] is 35 wt%, a value that is typical for the stratosphere. In the removal layer, the value increases to over 55 wt% due to the local increase in H$_2$O. This change in aerosol composition corresponds to an increase in the water activity of ~10 [Ravishankara and Hanson, 1996], with a corresponding 50-fold increase in the reactive uptake coefficient, γ, for (R1) [Hanson and Ravishankara, 1994]. The lifetime of ClONO$_2$ for the combination of (R1) and (R2) decreases from more than 30 days above the removal layer to 0.5 day or less in the layer. Thus, the conversion rate of NO$_x$ to HNO$_3$ by (R1) and (R2) exceeds the production rate of NO$_x$ from HNO$_3$, thereby largely removing NO$_x$ within a diurnal cycle. NO removal requires both (R1) and (R2): (R2) to increase the Cl$_y$ fraction available to form ClONO$_2$ (HCl reformation is slow) and (R1) to remove ClONO$_2$ formed with ClO and available NO$_2$. Since HOCl in (R1) reforms ClO through photolysis and reaction with O$_3$, ClONO$_2$ will continue to form and undergo conversion provided NO$_2$ is available. This cycle will maintain low levels of NO$_x$ as long as the rate constants of (R1) and (R2) are sufficiently enhanced.

Figure 1 shows that observed profiles of ClO and NO are well reproduced by the PSS model [Salawitch et al., 1994] when constrained by measured values of long-lived radical precursors (e.g., O$_3$, H$_2$O, CH$_4$, NO$_y$). The Ravishankara and Hanson [1996] formulation was used for the rate constants of (R1) and (R2), and an uptake coefficient of 0.1 was used for N$_2$O$_5$ hydrolysis. The Cl$_y$ profile was determined from its observed correlation with N$_2$O in a manner similar to Woodbridge et al. [1995], except that Cl$_y$ was set to zero for tropospheric N$_2$O values. The upper edge of the NO removal layer is caused by the sharp increase in ClONO$_2$ reactivity as the H$_2$O mixing ratio increases, and the lower edge is caused by concentrations of available Cl$_y$ that approach zero at the tropopause.

Summary and Implications

Anomalously low NO was observed in sunlight in a 0.5-km layer located above the tropopause at mid-latitudes. The NO$_x$/NO$_y$ partitioning is shifted to significantly lower values than normally observed in the mid-latitude stratosphere. Simultaneous measurements of ClO and HO$_2$ are enhanced when NO is low. In the layer, temperatures are low (~206 K) and aerosol surface area and H$_2$O values are enhanced above stratospheric values found away from the tropopause. Consequently, rate constants increase for heterogeneous reactions involving ClONO$_2$ which effectively convert NO$_x$ to HNO$_3$. The distinct layers in NO and ClO are well simulated by the PSS model in which the upper and lower edges of the layer are controlled primarily by the availability of H$_2$O and Cl$_y$, respectively. The combination of observations and interpretation presented here provide strong evidence that the roles of (R1) and (R2) in the stratosphere are consistent with laboratory measurements. Because of low NO and enhanced ClO and HO$_2$ values, 24-hr average removal rates of O$_3$ in the removal layer increase to values of ~0.2 ppbv hr^{-1}, much larger than in adjacent regions. These observations show that NO$_y$ and Cl$_y$ partitioning and O$_3$ destruction in the lower stratosphere near the tropopause are sensitive to increases in H$_2$O concentrations, particularly during periods of high aerosol loading. Consequently, the heterogeneous processes and controlling parameters that cause these important photochemical changes should be represented accurately in models of global change. Of specific interest will be assessments of the global effects of continued aircraft emissions of NO$_x$, H$_2$O, and sulfur species.

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