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 (NOy) 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 (HO2) also were observed in the layer. Heterogeneous reaction rate constants of chlorine nitrate (ClONO2) with hydrogen chloride (HCl) and H2O to form nitric acid (HNO3) on sulfate aerosol are enhanced in the NO removal layer by local increases in H2O and aerosol surface area. The associated conversion of NOx (= NO + NO2) to HNO3 is the most likely cause of the observed low NO and NOx/NOy values and high ClO values.

Introduction

Reactive nitrogen (NOy = NO + NO2 + NO3 + 2N2O5 + HONO + H2O2 + NOy + PAN + ClONO2 + 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 NOy 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 (NO2) and other NOy species. The NO/NO2 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 NOy 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 ClONO2. These reactions form HNO3 at rates significantly increased by a combination of high aerosol loading following the eruption of Mt. Pinatubo, high H2O 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., 1993a; 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 mixing ratio (NO2eq) to be calculated using measured ozone (O3), ClO, H2O, temperature, pressure, and a calculated NO2 photolysis rate [Kawa et al., 1992]. These steady-state NO2 values are less than the observed NO throughout the profile, and thus very low (< ~0.02 ppbv) in the removal layer. Because NO2 exceeds 2 ppbv in the removal layer, the NO2/NOx ratio is much less than typical values of 0.1 [Fahey et al., 1993], signaling an unexpectedly large re-partitioning within the lower stratospheric NOx reservoir. Expected NOy, denoted NOy*, in Figure 1, is determined from the well-established, highly compact correlation between NOy and nitrous oxide (N2O) observed in the lower stratosphere [Loewenstein et al., 1993]. Variations in NOy not associated with N2O changes are expected near the tropopause, due in part to lightning and other sources of NOy in the troposphere [Murphy et al., 1993]. NOy in excess of NOy* (~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 NOy species [Fahey et al., 1989].

Repartitioning of the NOy reservoir is likely to have an impact on other species observed in the removal layer because of the strong coupling between reactive nitrogen, chlorine,
and hydrogen photochemistry in the lower stratosphere [Wennberg et al., 1994]. Because ClONO2 is formed by the reaction of NO2 with ClO, the removal of NO, and thus NO2, 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 (Cl2) as calculated using the observed correlation with N2O [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, HO2 increases significantly upon entering the upper troposphere, increasing the HO2/OH ratio accordingly [Wennberg et al., 1995]. In the NO removal layer, lower-limit HO2 values are significantly larger than values above the layer. Figure 1 includes steady-state HO2 (HO2ss) values calculated with the relation:

$$[\text{HO}_2]_{\text{ss}} = \frac{[\text{HO}] + [\text{OH}]}{k_{[\text{HO}] + [\text{OH}]} + k_{[\text{HO}O}_2+[\text{CO}]} + k_{[\text{HO}O}_2+[\text{CO}]} + k_{[\text{HO}O}_2+[\text{NO}]}$$

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 O3 [Murphy et al., 1993], are 34 ppbv in the layer. The steady-state HO2 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 O3 exist across the tropopause region. Stratospheric CN and O3 values are 30 cm$^{-3}$ and > 350 ppbv, respectively, while tropospheric values are > 950 cm$^{-3}$ and < 100 ppbv. Because of the CN and O3 values observed in the removal layer (180 cm$^{-3}$, 290 ppbv) and the long lifetimes of O3 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.

H2O also shows a strong gradient across the tropopause, with a local maximum (~16 parts per million by volume, ppmm) 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 H2O 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 ppmm at the tropopause, remains above ambient H2O values throughout the profile in Figure 1. Saturation mixing ratios of HNO3 over the nitric acid trihydrate (NAT) phase (HNO3_sat in Figure 1) approach available HNO3 (or NO2) 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$_x$ reservoir [Fahey et al., 1993]. In particular, the dinitrogen pentoxide (N2O5) hydrolysis reaction on sulfate aerosol reduces the NO$_x$/NOy ratio in the mid-latitude stratosphere through conversion of NO$_2$ to HNO3. 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 NOx/NOy ratio remained above 0.07 as the surface area increased to over 20 $\mu$m$^2$ cm$^{-3}$. This nonlinear or saturation effect is the result of limitations in $N_2O_5$ production, which occurs primarily at night. Therefore, a process other than $N_2O_5$ hydrolysis must be the cause of low NO and NOx/NOy in the removal layer in Figure 1. This additional process must compete with NO production, which occurs through HNO3 photolysis and the reaction of OH with HNO3. For conditions in the NO removal layer, calculations of the production rate for NOx 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 HNO3 lifetime in daylight of ~50 hr.

Two heterogeneous reactions that can affect the partitioning for both the NOx and Cl$_y$ reservoirs in the stratosphere are:

\[ \text{H}_2\text{O} + \text{ClONO}_2 \rightarrow \text{HOCI} + \text{HNO}_3 \quad (R1) \]

\[ \text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad (R2) \]

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 $N_2O_5$ hydrolysis reaction at temperatures below 200 K. However, the rate constants also depend very strongly on aerosol composition, increasing exponentially with H2O weight percent (wt%). Above the removal layer, the aerosol H2O fraction calculated using an analytic ternary solution model [Carslaw et al., 1995'] and an uptake coefficient of 0.1 was used for partitioning in the mid-latitude stratosphere. In the removal layer, the value increases to over 55 wt% due to the local increase in H2O. 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, $\gamma$, 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 NOx to HNO3 by (R1) and (R2) exceeds the production rate of NOx from HNO3, thereby largely removing NOx 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 Cl$_y$ and available NO2. Since HOCI 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$_x$). 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 $N_2O_5$ hydrolysis. The Cl$_y$ profile was determined from its observed correlation with $N_2O_5$ in a manner similar to Woodbridge et al. [1995], except that Cl$_y$ was set to zero for tropospheric $N_2O_5$ 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 NOx/NOy 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 NOx to HNO3. The distinct layer in NO- and Cl$_y$-enriched data simulated 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$_x$ 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 NOx, H$_2$O, and sulfur species.

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