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Photochemistry of NO_2 in Earth's Stratosphere: Constraints from Observations

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1. Introduction

The chemistry of nitrogen oxides has been a central theme in atmospheric chemistry since NO was identified as one of the ingredients necessary for producing photochemical smog by Haagen-Smit.[1] Later, a free radical catalytic cycle involving NO_x ($NO_x \equiv NO + NO_2$) was identified as one of the key ingredients of photochemical ozone production in urban areas. Levy demonstrated that this same mechanism applied throughout the global troposphere.[2]

Appreciation of the importance of nitrogen oxides to atmospheric chemistry grew further with the recognition that a nitrogen oxide catalytic cycle was the main natural sink of stratospheric ozone,[3,4] and that a proposed global-scale experiment—commercial supersonic aviation depositing a large mass of nitric oxide in the stratosphere—could severely deplete the stratospheric ozone layer.[3,5]

With these strong motivations, the chemistry of nitrogen oxides has been the subject of extensive research. Laboratory experiments providing detailed knowledge of absorption cross sections, quantum yields, and reaction rates and insight into chemical mechanisms are reviewed and reconciled into a reference table of recommendations by panels coordinated by JPL[6] and IUPAC.[7] There are also numerous observations of atmospheric nitrogen oxides from the ground, aircraft, and satellites.

Within the past few years, new or significantly revised textbooks by Seinfeld and Pandis,[8] Jacob,[9] Finlayson-Pitts and Pitts,[10] Warneck,[11] and Brasseur et al.[12] have been published. They are all excellent introductions and contain reviews of the subject of nitrogen oxides in the atmosphere. Kondo's chapter in the *Encyclopedia of Atmospheric Sciences* presents an overview of reactive nitrogen with an emphasis

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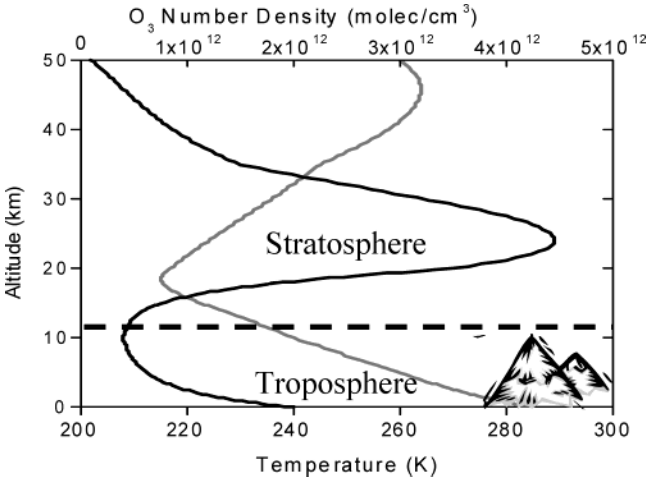

Figure 1. Schematic of the altitude dependence of O_3 (black) and temperature (gray) in the troposphere and stratosphere (Mt. Everest shown for scale).

on earth science coordinates such as altitude and latitude.[13] In addition, progress in the scientific understanding of stratospheric ozone is perhaps more routinely reviewed than any other field of chemistry. Every 3−4 years, in support of the Montreal Protocol and its amendments, the international scientific community produces a consensus scientific assessment of our knowledge of ozone depletion.[14] Other reviews that are pertinent to discussion of stratospheric nitrogen oxides include the historical perspective by Harold Johnston[15] and reviews of research on the heterogeneous chemistry of stratospheric aerosol by Molina, Molina, and Kolb[16] and by Zondlo and Tolbert,[17] on polar ozone depletion by Anderson,[18] and on mid-latitude and polar ozone by Solomon.[19,20] Holton et al.'s review of stratospheric dynamics and transport has become a singularly important reference for understanding the role of transport in setting up the distribution of long-lived species including N_2O, the main precursor of stratospheric nitrogen oxides.[21] Dessler et al. review scientific results that derive from the observations from the Upper Atmosphere Research Satellite (UARS).[22]

Rather than repeat the content of these other documents, in this review we provide our own perspective on the role of nitrogen oxides in the chemistry of Earth's stratosphere, highlighting research completed during the past 10 years or so. We focus on chemical processes as much as possible, especially on field observations that have been interpreted to provide quantitative constraints on chemical processes involving NO_2. We do not review important research associated with development of new instrumentation and on the nonchemical factors (e.g., types of sources, transport mechanisms, etc.) that affect the total amount and spatial distribution of nitrogen oxides in the stratosphere.

2. Overview of Stratospheric Chemistry

The ozone layer is essentially synonymous with the stratosphere, a region of the Earth's atmosphere ranging from about 12 to 40 km above the Earth's surface (Figure 1). This region is characterized by intense solar ultraviolet radiation, low mole fractions (2−8 ppm) of water, large mole fractions of ozone and oxygen atoms, and rapid free radical photochemistry. These elements are coupled: UV photolysis of molecular oxygen is the primary source of stratospheric ozone, and UV photolysis of other species (N_2O, chlorofluorocarbons (CFCs), O_3) is the source of free radicals. UV absorption by ozone also heats the stratosphere internally, producing a permanent global-scale temperature inversion. Vertical transport times within the stratosphere range from months to years as a consequence of this temperature inversion.

Ozone is the stratospheric chemical of primary interest because its strong UV absorption greatly reduces the flux of radiation at wavelengths short of 310 nm, where photons are capable of efficiently mutating DNA, and because of its role in atmospheric dynamics and in maintaining the atmospheric temperature structure. Interest in ozone dates to 1881, when Hartley recognized that it was the cause of solar UV absorption.[23] However, it was not until the International Geophysical Year, 1957, that a network of Dobson monitoring stations was established that led to determination of a global climatology of column ozone. A still broader interest in ozone developed in the early 1970s, following the recognition that human activities might substantially modify the ozone layer. Harold Johnston's 1971 paper[5] showed that significant global ozone reductions might be caused by emissions from a proposed commercial fleet of supersonic aircraft if this fleet flew within the stratosphere. Three years later, Mario Molina and F. Sherwood Rowland predicted that halocarbon releases at the Earth's surface would result in ozone reduction.[24] A large fleet of supersonic aircraft (100 planes or more) has not been built, although interest in the possibility continues. Recent evaluations suggest that modern technology might be able to produce an aircraft with emissions that are benign to the ozone layer;[25] however, the challenge of meeting other environmental standards, especially noise standards, has not been met. By contrast, the unintentional global-scale experiment associated with CFC emissions was already well underway when Molina and Rowland recognized its potential consequences. Emissions of CFCs and related halocarbons ultimately increased the source of reactive chlorine to the stratosphere by more than a factor of 4 over the natural background before controls became effective.[14]

Dramatic changes to polar ozone and significant changes to mid-latitude ozone have indeed resulted from these halocarbon releases at the Earth's surface. The losses in the upper stratosphere (30−40 km) are about 5%/decade since the mid-1970s,[26] similar in magnitude and location to the initial predictions of Molina and Rowland.[24] However, as a consequence of chemical mechanisms that were not understood in 1974, ozone loss occurs at lower altitudes both at the poles during the winter and spring seasons and at mid-latitudes.[14] Ozone loss within the Antarctic lower stratosphere approaches 100% each spring; losses over the Arctic during northern hemisphere spring are lower, in the range 30−60% over the past few years. The discovery of the Antarctic ozone hole sparked intense public and scientific interest in the ozone layer because it is such a clear demonstration that chemical emissions that occur one leaking air-conditioner or refrigerator at a time can have global-scale environmental consequences.

Explaining the abundance and distribution of stratospheric ozone is a long-standing challenge to physical chemists, earth and planetary scientists, and meteorologists. Chapman was the first to recognize the importance of photochemical reactions as a control over stratospheric ozone.[27] In Chapman's mechanism, proposed in 1930, ozone is produced in the stratosphere by oxygen photolysis,

$$O_2 + h\nu \rightarrow O + O \qquad (R1)$$

followed by three-body recombination of the oxygen atoms with O_2,

$$O_2 + O + M \rightarrow O_3 + M \qquad (R2)$$

and the production is balanced by the couplet

$$O_3 + h\nu \rightarrow O + O_2 \qquad (R3)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (R4)$$

$$\text{Net:}\quad O_3 + O_3 \rightarrow 3\ O_2 \qquad (1)$$

In subsequent years, as the rates of these reactions became better known, and as the dynamics of stratospheric transport became better understood, it became clear that the rate of $O + O_3$ is much too slow to explain the observations of the concentration of ozone as a function of altitude or latitude. HO_x ($\equiv$ H + OH + HO_2) catalysis was proposed to make up part of the shortfall by Bates and Nicolet.[28] However, it was not until the extraordinary papers by Crutzen, showing both that NO_x catalysis was a major fraction of the globally integrated stratospheric ozone removal processes and that stratospheric NO_x has its natural source in microbial production of N_2O in soils,[3,4] and by Johnston on the potential consequences of NO_x emitted directly into the stratosphere by a proposed fleet of supersonic aircraft,[5] that we began to reach a chemically complete representation of ozone catalysis. We now know that NO_x catalysis accounts for the majority of catalytic destruction of O_3. The recognition that halogen catalysis also plays a role followed quickly on the heels of the NO_x discoveries.[24,29,30] Crutzen, Molina, and Rowland were awarded the 1995 Nobel Prize in Chemistry for their insight into the links between surface emissions, human activity, and the sensitive chemistry of stratospheric ozone.

During the 1970s and 1980s, predictions of the free radical composition of the stratosphere and the corresponding rates for catalysis of ozone inspired significant advances in our observational capabilities. At the beginning of this period, models incorporating rate constants determined in the laboratory were far ahead of observations, in the sense that they could predict the relative abundances of all the radicals and define the key science questions. However, the models were essentially untested. In situ observations of ClO, BrO, OH, and HO_2 by Jim Anderson and his group,[31−35] and of nitrogen oxides by Ridley,[36] and remote observations of NO_2, NO, and HNO_3 pioneered by Noxon[37] and Murcray[38] were among the first observations of stratospheric free radicals and their reservoirs. As these new technologies emerged, a suite of observational "firsts" provided experimental bounds on reasonable models of the free radical composition of the stratosphere. These experiments occurred in an environment of rapid improvement in the quality of our knowledge of free radical kinetics. Some key rate constants, most of them related to HO_x kinetics, were found to be in error, one or two by orders of magnitude. At this early stage, the basic question was whether photochemical-transport models represented enough of the chemistry and physics to provide a reasonable description of the stratosphere.

By the 1990s, improvements to our understanding of chemical dynamics and atmospheric transport, to the accuracy of rate constants, and to the database of stratospheric observations led scientific questions about factors controlling the ozone column abundance to evolve into ones that are significantly more quantitative than the early studies. Today, observations of a wide-ranging suite of chemicals are required to address increasingly focused and detailed research questions posed about the rates of transport and of chemical transformations within the stratosphere.

Much of this review will focus on observations made from NASA's ER-2 aircraft because its payload is extremely comprehensive. As a result, reliance on a complicated kinetic model is not required to interpret the observations. The ER-2 payload includes instrumentation that measures all the important free radical species (OH, HO_2, NO, NO_2, ClO, and BrO) and their sources and reservoirs (CH_4, H_2O, H_2, NO_y, $ClONO_2$, ClOOCl, and HCl), dynamical tracers (N_2O and CO_2), aerosol size distributions, the radiation field, and meteorological variables. Comprehensive chemical observations have also been obtained from balloons[39] and from space,[40−44] although they are not as extensive.

3. Stratospheric NO_x

Observations and analysis show that in the lower stratosphere (12−22 km), concentrations of nitrogen oxide radicals are the primary variable controlling local ozone destruction rates.[45−48] As we indicated above, the ozone concentrations depend on transport through regions with different chemical production and loss rates. Figure 2 represents the local ozone removal rate schematically. The total ozone removal rate follows the top of the shaded area, and the different shades of gray reflect the portion of the total due to NO_x, HO_x, and halogen catalysis, respectively. The left side of the figure (low NO_x) describes a NO_x-poor region of the stratosphere. In this region, ozone catalysis is more rapid and is dominated by HO_x and halogens via catalytic cycles such as

$$O_3 + OH \rightarrow HO_2 + O_2 \quad (R5)$$

$$O_3 + HO_2 \rightarrow OH + 2O_2 \quad (R6)$$

$$\text{Net:} \quad O_3 + O_3 \rightarrow 3O_2 \quad (2)$$

$$O_3 + Cl \rightarrow ClO + O_2 \quad (R7)$$

$$O_3 + Br \rightarrow BrO + O_2 \quad (R8)$$

$$ClO + BrO \rightarrow BrCl + O_2 \quad (R9)$$

$$BrCl + h\nu \rightarrow Br + Cl \quad (R10)$$

$$\text{Net:} \quad O_3 + O_3 \rightarrow 3O_2 \quad (3)$$

The rate-determining steps in the odd hydrogen and halogen catalytic cycles depend on the abundance of HO_2 and ClO, and NO_x acts to suppress both of these species. Therefore, the rate of these cycles is inversely proportional to NO_x concentrations, and the ozone removal rate has a steep negative dependence on NO_x. If the curve were extended to the left, it would describe the chemistry of springtime polar ozone depletion. As NO_x levels approach zero, which occurs routinely during polar winter, halogen catalysis rates increase 100-fold above that shown in Figure 2. At intermediate NO_x concentrations, ozone removal rates are insensitive to changes in NO_x. Increases in NO_x (and therefore in NO_x catalysis of ozone) are almost exactly balanced by decreases in the rate of ozone catalysis by HO_x and halogens. At still higher concentrations of NO_x, NO_x catalysis dominates over all other reactions, and ozone removal rates increase linearly in proportion to NO_x.

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (R11)$$

$$O_3 + h\nu \rightarrow O + O_2 \quad (R3)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (R12)$$

$$\text{Net:} \quad O_3 + O_3 \rightarrow 3O_2 \quad (4)$$

NO_x in the lower stratosphere varies with season and latitude, and as a function of aerosol loading. On average it is NO_x poor. Small perturbations to NO_x in this region of the atmosphere will cause changes in ozone of the *same sign*. Large increases in NO_x will, however, push an increasing fraction of the lower stratosphere toward NO_x-rich chemistry. Thus, in the lower stratosphere, NO_x buffers the catalysis of hydrogen and halogen radicals: when NO_x concentrations in the lower stratosphere are low (during winter and following major volcanic eruptions), the rate of catalytic removal of ozone by HO_x and halogens in this region of the atmosphere is enhanced. When NO_x is at a maximum (in summer and during volcanically quiescent periods), the rate of catalytic removal of ozone by HO_x and halogen radicals in the lower stratosphere is suppressed. Except during polar summer, NO_x rarely reaches levels where it is the dominant sink of O_3 in the lower stratosphere. By contrast, in the upper stratosphere, an NO_x-rich situation is an excellent first approximation.

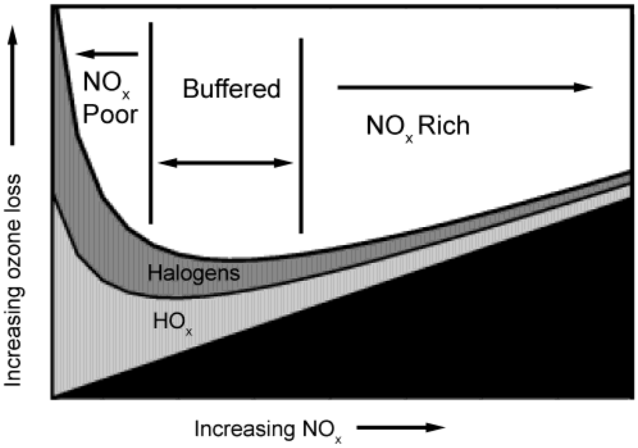

Figure 2. Ozone loss from each type of catalytic cycle as a function of NO_x abundance.

Historically (although our conceptual understanding was less clear than it is today), changes to predictions of the effects of stratospheric aircraft or halogen emissions have come about because of changes in the fraction of the model atmosphere that was NO_x poor, NO_x buffered, or NO_x rich. In the early 1970s, most of the stratosphere was thought to be NO_x rich, and supersonic transport NO_x emissions were predicted to cause significant ozone depletion, while CFCs were thought to be less damaging. Changes to reaction rates, resulting from improved laboratory techniques, have frequently altered the balance between these regimes in models.

We now have simultaneous observations of NO_x, HO_x, and halogen radicals and extensive observations of the interdependence of these radical concentrations.[39,46−49] These observations provide unequivocal evidence for the relative roles of these radicals throughout the lower stratosphere[46,50] and the middle and upper stratosphere.[39] Measurements from the ER-2 beginning in 1993 provide extensive observational constraints on the distribution of all three radical catalysts as functions of latitude (70°S−90°N), altitude (12−21 km), and season.[51−55] Measurements of radicals from a variety of remote sensing platforms provide additional information in the lower stratosphere and direct measures in the middle and upper stratosphere.[39,56]

At the poles, the direct cause of springtime ozone loss is the high concentration of chlorine and bromine radicals. To enable this catalysis, NO_x must first be driven almost entirely from the system. During the winter, NO_x is converted to HNO_3, which may be removed from the gas phase if polar stratospheric clouds (PSCs) form. When this situation persists until and beyond polar sunrise, ensuing ozone loss rates in NO_x-free air approach a few percent per day.[57−61] In a matter of weeks, nearly all of the ozone within the polar vortex can be destroyed. In the Antarctic, it frequently remains cold enough for complete loss of ozone, while in the Arctic the temperatures are more variable, and ozone loss in recent years has ranged from minimal to nearly 40%.[62,63]

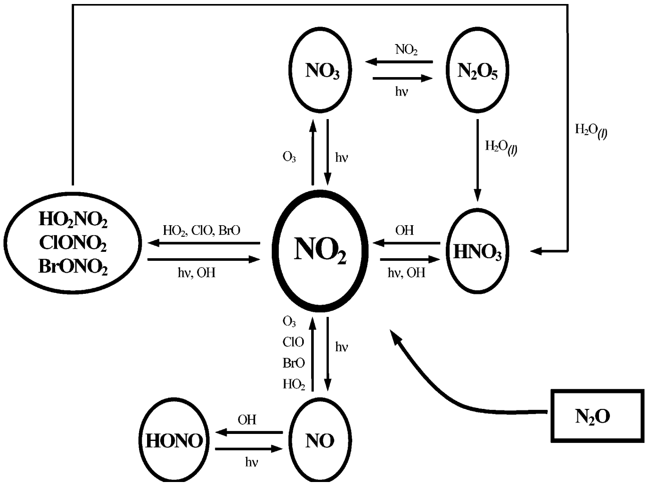

Figure 3. NO_2 plays a central role in stratospheric reactive nitrogen (NO_y).

On the basis of the overall understanding described above, it is reasonable to argue that the key variable for understanding stratospheric photochemistry, and the sensitivity of stratospheric ozone to ongoing or hypothetical perturbations, is the abundance of NO_2. NO_2 is also at the center of nearly every important transformation among stratospheric reactive nitrogen species (Figure 3). The major subject of this review is how observations test our understanding of the processes controlling stratospheric NO_2 concentrations. The sum of oxidized nitrogen in conventionally referred to as NO_y, a collection of species that can be more easily measured in situ as a group than the individual species themselves.[64] Comparison of in situ NO_y measurements and the sum of individual nitrogen oxides measured by space and balloon-borne remote sensing demonstrate the accuracy of both types of observations.[65,66]

On short time scales (100 s), NO_2 is controlled by its chemical interconversions with NO. On intermediate time scales (hours to days), NO_2 interconverts with NO_3, N_2O_5, $ClONO_2$, $BrONO_2$, and HO_2NO_2. On still longer time scales (weeks to months), conversion of HNO_3 to NO_2 sets the abundance of NO_2. Finally, on time scales of months to years, production of NO by oxidation of N_2O, mixing within the stratosphere, and transport out of the stratosphere by stratosphere–troposphere exchange and by sedimentation of HNO_3-containing particles affect NO_2. We treat the processes in order below.

3.1. Controls over the Concentration of NO_2

3.1.1. Fast Photochemistry: NO ⇔ NO_2

One of the simplest atmospheric chemical relationships is the interconversion of NO and NO_2. The reactions controlling these transformations in the lower stratosphere are

$$NO_2 + h\nu \rightarrow NO + O \tag{R13}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R11}$$

$$\text{Net:} \quad O_3 \rightarrow O + O_2 \quad \text{(null for odd oxygen)} \tag{5}$$

Other reactions affect conversion of NO to NO_2 at a level of 10% or less, including reaction of NO with ClO, BrO, and HO_2 and the reaction of NO_2 with O. Both reactions R11 and R13 have been extensively studied in the laboratory.[6] Through atmospheric observations, we would like to demonstrate that (a) laboratory measurements of the rate of each reaction rate are consistent with the rates as they occur in the atmosphere and (b) the reaction set enumerated above is complete. To accomplish this goal, in addition to measurements of the concentration of NO and NO_2, a complete test requires simultaneous measurements of temperature, the concentrations of O_3, and the 4π integral of the spectrally resolved radiation field. It also requires measurements showing that other reactants that might react with NO or NO_2 at rates fast enough to compete with R11 and R13 are not present at high enough concentration to do so. In a laboratory experiment, one would evaluate the reaction kinetics by altering the temperature, the ozone concentration, and the intensity of the light field, each over a wide range, and each while holding all of the other variables constant and with confidence that any undesirable secondary chemistry is negligible. In the atmosphere, this approach has, until recently, only rarely been adopted because simultaneous measurements of the reactants involved was not sufficiently routine to enable observations over a sufficiently wide range in any variable while holding the others constant. This approach has also been hampered by confusion over the necessary accuracy required of the measurements. Cohen et al. show that for many questions about atmospheric kinetics, we can tolerate inaccuracy of order 10–15% if the error is a single multiplicative factor to be applied uniformly to all measurements.[67]

The time scale for cycling of NO and NO_2 during daytime is about 100 s. In the stratosphere this means NO and NO_2 are virtually always in photostationary state, with the rate of production of NO by photolysis of NO_2 equal to the rate of destruction of NO by reaction with O_3.

$$J_{NO_2}[NO_2] = k[NO][O_3] \tag{6}$$

Neglecting oxidants other than O_3 (which we do for discussion, though all calculations include reactions with HO_2, ClO, and BrO as well) and rearranging eq 6 to separate quantities that are directly measurable from those that we would like to evaluate with atmospheric observations gives

$$\frac{J_{NO_2}(\int I(\sigma(T)\lambda))}{k_{NO+O3}(T)} = \frac{[NO][O_3]}{[NO_2]} \tag{7}$$

This equation isolates the "model" on the left side, which depends on the variables of temperature and wavelength. Cohen et al.[67] approximated a controlled laboratory experiment by identifying air where the radiation field was constant and temperature ranged from 215 to 233 K to evaluate the accuracy of the temperature dependence of the rate coefficient used in current models. Their results, along with those of others, are shown in Figure 4. The observations are

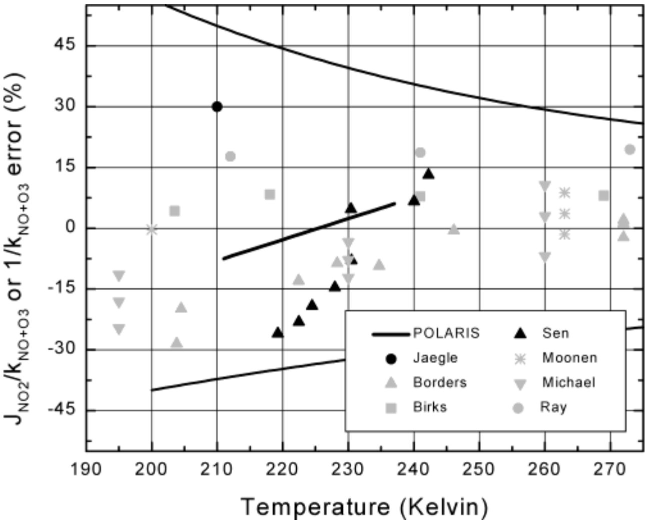

Figure 4. Percentage error in J_{NO_2}/k_{NO+O_3} versus temperature (taken from Cohen et al.[67]). Laboratory measurements are shown as gray symbols, atmospheric observations are in black, and the outer lines represent the JPL 1997 estimate of uncertainty. Reprinted with permission from ref 67. Copyright 2000 American Geophysical Union.

consistent with known kinetics to well within their combined uncertainties. There is a small difference in the temperature dependence of the observations compared with the model. The rate coefficient k_6 used in current atmospheric models is $k_6 = (3 \times 10^{-12})$ exp$(-1500/T)$. The JPL panel uses a form for the rate constant that allows for only a single exponential. The ER-2 data suggest that the activation energy in this expression is slightly too high at low temperatures (200−220 K). This is not surprising since it is well known that the NO + O_3 reaction has two product channels, one ground-state NO_2 and the other electronically excited NO_2 (chemiluminescence from the latter is the basis for most instruments designed to observe atmospheric NO), and laboratory observations have hinted at a biexponential temperature dependence for R11. Atmospheric models that use a biexponential form of the temperature dependence will have higher NO_2-to-NO ratios at low temperature and lower NO_x abundances because all NO_x loss processes pass through NO_2.

With respect to the other major parameter controlling NO_2-to-NO ratios, Cohen et al. show that there is a seasonal error in the radiation models that appears when the model measurement comparison is examined as a function of the albedo (the reflectivity of the Earth and sky below the measurement point). Gao et al. show that at constant T, the response of NO_2 and NO to changes in the distribution of the radiation field as the sun sets are accurately described,[68] indicating that the change in the radiation field during changing insolation is modeled accurately.

These analyses focus on partial derivatives, with respect to T or λ, but we are also interested in the absolute accuracy. A detailed propagation of error gives an absolute accuracy of the ratio J_{NO_2}/k_6 of 16% as derived from the observations of NO, NO_2, O_3, HO_2, ClO, BrO, T, and the radiation field.[67] This is about one-third the uncertainty recommended by the JPL panel and is an indication of the potential of ambient measurements to reduce uncertainties in models of the atmosphere. A variety of other observations support this result.[56,68,69]

While these analyses quantitatively constrain the main processes that interconvert NO and NO_2, the reaction of $NO_2 + O(^3P)$ is the rate-limiting step in the NO_x catalytic cycle (R11, R3, R12). Recent laboratory measurements of this rate[70] more firmly establish the absolute rate of O_3 catalysis.

3.1.2. Short-Lived Reservoirs: Gas-Phase Chemistry

3.1.2.1. NO_3 and N_2O_5. The reaction of NO_2 with ozone (R14) to form NO_3 has a steep temperature dependence ($E_a = 20.3$ kJ/mol). At 220 K and 10^{12} molecules/cm^3 O_3, the lifetime of NO_2 with respect to this reaction is about a week. During the day, NO_3 is rapidly ($\tau \approx 10$ s) converted back to NO_2 by photolysis, maintaining its abundance at sub-ppt mixing ratio. The minor branching ratio for production of NO and O_2 by photolysis of NO_3 occurs with a wavelength-dependent quantum yield of about 8%.[71] This process is significant in that it completes a catalytic cycle destroying ozone. At night, when there is no photolysis, NO_3 accumulates and is available to react with NO_2 ($\tau_{NO_3} \approx 100$ s for 1 ppb NO_2) to form dinitrogen pentoxide, N_2O_5. For a typical lower stratospheric scenario, about one-fourth of NO_2 is converted to N_2O_5 during a 12-h night. N_2O_5 is converted back to NO_2 during the day by photolysis ($\tau \approx 12$ h).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (R14)$$

$$NO_3 + h\nu \rightarrow NO_2 + O \qquad (R15a)$$

$$\rightarrow NO + O_2 \qquad (R15b)$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \qquad (R16)$$

$$N_2O_5 + h\nu \rightarrow NO_2 + NO_3 \qquad (R17)$$

NO_3 and N_2O_5 have been observed using limb-scanning and balloon-borne spectrometry. These observations confirm the large diurnal variation in the mixing ratio of both compounds.[72,73] Night-time observations of NO_3 have been compared to models that include reactions R14 and R16 and suggest that a slight reduction in the activation energy of k_{14} and a larger reduction in the equilibrium constant governing reaction R16 would result in a better representation of the observations.[74,75]

3.1.2.2. $ClONO_2$ and $BrONO_2$. Nitrogen oxides control the abundance of active chlorine in the stratosphere through the production of chlorine nitrate (R18) and the subsequent photolysis of $ClONO_2$.

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (R18)$$

$$ClONO_2 + h\nu \rightarrow ClO + NO_2 \qquad (R19)$$

$$\rightarrow Cl + NO_3 \rightarrow ClO + NO_2$$

The time scale for these processes to reach steady state is typically 15 min at midday, but approaches

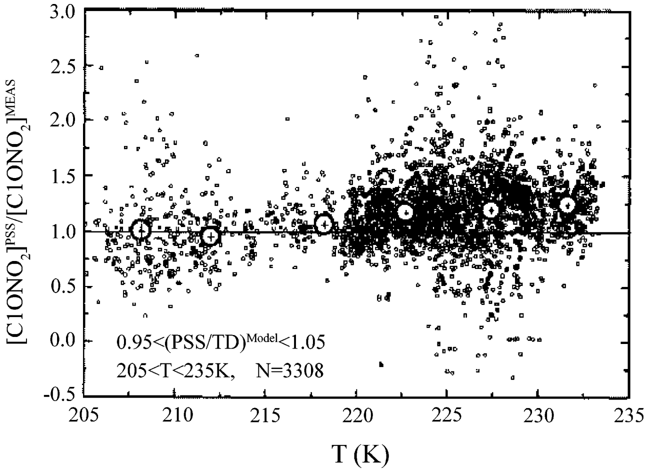

Figure 5. Ratio of modeled to measured $ClONO_2$ versus temperature, in which the circles represent averages in six equally spaced bins (taken from Stimpfle et al.[76]). Reprinted with permission from ref 76. Copyright 1999 American Geophysical Union.

hours near sunrise or sunset. Under typical conditions, about one-third of active chlorine (chlorine not attached to a CFC or a hydrochlorofluorocarbon, HCFC) is in the form of $ClONO_2$, with the balance stored as HCl. With respect to the nitrogen reservoir, $ClONO_2$ is usually a small fraction, less than 10%.

Simultaneous measurements of $ClONO_2$, NO_2, and ClO permit direct measure of the ratio of J_{12}/k_{11},

$$J_{12}/k_{11} = [ClO][NO_2]/[ClONO_2] \qquad (8)$$

as long as the steady-state conditions are met. $ClONO_2$ has been observed by thermal dissociation followed by detection of ClO from the ER-2[76] and by IR remote sensing.[77,78] Stimpfle et al. used observations to show that at temperatures between 215 and 235 K, the observed ratio $[ClO][NO_2]/[ClONO_2]$ is within 15% of the value of J_{19}/k_{18} derived from laboratory measurements. Figure 5 shows the ratio of $ClONO_2$ predicted by a steady-state model to measurements during POLARIS. The ratio is 1 at 207 K and 1.25 at 230 K. The temperature dependence of the comparison has a slope that is outside the range of expected uncertainty, indicating the need for more accurate measurements and further study of these reactions. It should be noted that the NO_3 product of $ClONO_2$ photolysis (QY = 0.6−0.9) is important because subsequent photolysis of NO_3 produces O_2, effectively completing an ozone-destroying catalytic cycle.

There are no atmospheric observations of $BrONO_2$. Although its chemistry is similar to that of $ClONO_2$, the red-shift of its absorption spectrum[79,80] results in much more rapid photolysis. Also, there is much less bromine than chlorine, making $BrONO_2$ an even smaller contributor to reactive nitrogen. Nonetheless, to the extent that it photolyzes to produce NO_3, $BrONO_2$ is a catalyst for ozone destruction.[81] Also, halogen nitrates participate in heterogeneous processes that accelerate conversion of NO_x to HNO_3 (see below).

3.1.2.3. HO_2NO_2. Peroxynitric acid is formed through the association of HO_2 and NO_2, and its lifetime is strongly temperature dependent under stratospheric conditions. It is also removed by photolysis and by reaction with OH.

$$HO_2 + NO_2 + M \leftrightarrow RO_2NO_2 + M \qquad (R20)$$

$$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2 \qquad (R21a)$$

$$\rightarrow OH + NO_3 \qquad (R21b)$$

$$HO_2NO_2 + OH \rightarrow H_2O + O_2 + NO_2 \qquad (R22)$$

Wennberg et al.[82] used observations of OH and HO_2 to infer the product of the abundance of HO_2NO_2 and the wavelength dependence of its photodissociation cross-section. These observations provided strong but indirect evidence for rapid near-IR overtone photodissociation in HO_2NO_2, as had been postulated by Donaldson.[83] Subsequent laboratory measurements confirmed that the absorption cross-section inferred from the HO_x observations is approximately correct,[84] although further experiments are required to refine the temperature and wavelength dependence of J_{14} in the near-IR. Comparison of direct measurements of HO_2NO_2 with photochemical models also confirms the importance of IR photolysis on peroxynitric acid mixing ratios.[85] Detailed tests of the type described above for $ClO/NO_2/ClONO_2$ or $O_3/NO/NO_2$ chemistry await analysis of simultaneous HO_2NO_2, HO_2, and NO_2 measurements along chemical coordinates.

3.1.3. HNO_3: The Long-Lived Reservoir

3.1.3.1. Gas-Phase Chemistry. HNO_3 usually comprises 80% or more of NO_y in the stratosphere. The lifetime of NO_2 with respect to HNO_3 is typically a couple of days, and the lifetime of HNO_3 with respect to NO_2 is usually of order 1 month. HNO_3 is formed in the gas phase by reaction of OH with NO_2.

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (R23)$$

The reaction of NO_2 with OH is unusual. The association reaction of OH + NO_2 does not reach the high-pressure limit until tens of bar total pressure,[86] as opposed to typical association reactions that reach the high-pressure limit at pressures below a few hundred millibar.

Recently, much progress has been made in understanding the kinetics and the reaction dynamics that govern the unusual behavior of these reactions. Observations in the range of temperature and pressure most relevant to the stratosphere have largely settled the question of how fast OH reacts with NO_2 and HNO_3.[87−89] For this reaction (R23), part of the complication in the dynamics is attributable to formation of a quasistable isomer of HNO_3 with the geometry HOONO. Several searches for this product were unsuccessful,[89,90] though its existence has been predicted on the basis of theoretical grounds.[91,92] Recent work by Nizkorodov and Wennberg[93] provides the first observation of HOONO. Under atmospheric conditions, it is believed that more than 90% of the reaction proceeds to form HNO_3, although the product yield remains to be more clearly established by experiment.

HNO_3 production by the reaction of OH with NO_2 is balanced by the reaction of OH with HNO_3 and by HNO_3 photolysis.

$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (R24)$$

$$HNO_3 + OH \rightarrow H_2O + NO_3(R25) \qquad (R25)$$

The reaction of OH with HNO_3 is a hydrogen abstraction reaction. Such reactions ordinarily have no pressure dependence, yet a strong pressure dependence is observed for R25. Recent experiments point to a complex mechanism involving a stable hydrogen-bonded intermediate.[94,95]

For many years, these three reactions (R23−R25) were thought to be sufficient to describe the chemistry of NO_2 and HNO_3, although often with the caveat that heterogeneous processes were being neglected. Recent observations of heterogeneous reactions converting the short-lived NO_y species (N_2O_5, $ClONO_2$ and $BrONO_2$) to HNO_3 show that these processes are too fast to be ignored in stratospheric chemistry. However, there are unique circumstances where the gas-phase reactions almost exclusively control the interconversion of NO_2 and HNO_3. Observations during the continuously sunlit period of polar summer, when NO_3 photolysis prevents formation of N_2O_5 and temperatures are too warm for significant heterogeneous processing of $ClONO_2$, show that the three gas-phase reactions (R23−R25) describe the observed ratio of HNO_3 to NO_2 to within 20%.[67,96−99] Using the rate constants derived from laboratory observations as described by Donahue, Dransfield, and Brown results in a 25% improvement in the ratio of model to measurement (the error is reduced from 35% to 10%). There is also a significant improvement in the representation of NO_2/HNO_3 as a function of the chemical coordinates, indicating that derivatives of the NO_2/HNO_3 ratio are also represented more accurately by the revised rate constants.[67] Jucks et al.[100] suggest there remain some discrepancies in the gas-phase chemistry at higher altitudes, where there appears to be an error in the relative rates of HNO_3 photolysis and the HNO_3 reaction with OH.

3.1.3.2. Heterogeneous Chemistry. Hydrolysis of N_2O_5, $ClONO_2$, and $BrONO_2$ on particle surfaces also leads to production of HNO_3.[101−109]

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (R26)$$

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \qquad (R27)$$

$$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr \qquad (R28)$$

In the stratosphere, most of the aerosol is a mixture of two-thirds sulfuric acid and one-third water, although at the cold temperatures of polar winter, this composition changes, as do the halogen replacement reactions:

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \qquad (R29)$$

$$BrONO_2 + HCl \rightarrow HNO_3 + BrCl \qquad (R30)$$

The potential for heterogeneous reactions to play an important role in atmospheric chemistry has been recognized at least since 1971,[5] with a much more thorough study by Cadle et al.[110] The ability to make reliable and reproducible measurements on analogues of atmospherically relevant surfaces and at the temperatures and pressures appropriate for atmospheric reactions moved the issue of heterogeneous chemistry from the speculative to a firm scientific basis.

All of the reactions listed above have the effect of reducing the NO_x/HNO_3 ratio by offering alternate paths for converting NO_2 to HNO_3. As a consequence of heterogeneous chemistry, NO_2 has a much lower abundance in regions of the stratosphere where aerosols are available to drive reactions rapidly. This is especially true in the lower stratosphere, where a background of aerosol accumulates from oxidation of OCS, and in the polar regions, where temperatures are low enough for cloud formation at stratospheric humidity. NO_x is affected throughout the stratosphere following massive volcanic eruptions (massive in the sense that the explosive cloud containing SO_2 is pumped directly into the stratosphere).

3.1.3.2.1. N_2O_5 Hydrolysis. Under background aerosol conditions, the surface area available for reaction is of order 1 $\mu m^2/cm^3$, but a large volcanic eruption on the scale of Pinatubo can increase the surface area 10-fold.[111] Calculations suggest that in the sunlit lower stratosphere, over 24 h, N_2O_5 hydrolysis converts NO_2 to HNO_3 at about the same rate as OH + NO_2 on the background aerosol, effectively halving the NO_2 mixing ratio. At high aerosol loading, N_2O_5 is more rapidly converted to HNO_3. A 10-fold increase is not realized because the N_2O_5 hydrolysis rate becomes fast enough to completely remove all the N_2O_5 formed at night via the sequence R14 + R16.[45] Laboratory measurements demonstrate that this reaction occurs frequently, about once in 10 collisions of N_2O_5 with an aerosol particle.[104,112,113]

Chemically complete observations capable of confirming the atmospheric rate of N_2O_5 hydrolysis have not been accomplished because there are not simultaneous measurements of NO_2, NO_3, N_2O_5, and aerosol surface area at night. However, numerous indirect pieces of evidence strongly support the idea that this reaction occurs in the stratosphere at a rate close to that used in current models.[114−116] In situ measurements by Fahey et al. before and after the Pinatubo eruption show that NO_x was strongly suppressed by volcanic aerosol.[45] Some of the most convincing data are observations of ratios of the column HNO_3 divided by the column NO_2 before and after the Mt. Pinatubo eruption in June 1991.[102] The ratio increased by between 1.6 and 1.8 following the eruption, with a decay that followed the decay of stratospheric aerosol loading. Simultaneous observations of NO_2 and HNO_3 in the stratosphere prior and subsequent to the Pinatubo eruption (Figure 6) demonstrate that nitric acid concentrations were enhanced at the expense of nitrogen dioxide.[117] Other mid-latitude measurements of individual NO_y species after Pinatubo are consistent with hydrolysis of N_2O_5 being the dominant sink of NO_x below 18 km,

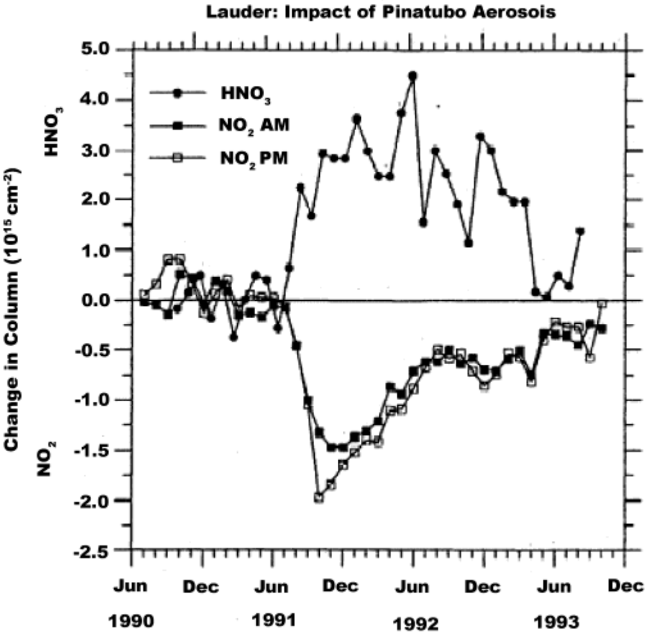

Figure 6. Deviation from the reference monthly mean column amount of observed HNO_3 (●) and observed NO_2 at sunrise (■) and sunset (□).[117] Reprinted with permission from ref 117. Copyright 1994 American Geophysical Union.

where the aerosol surface area was as high as 14 $\mu m^2/cm^3$.[73]

The complex interplay between the four processes (R23−R26) that dominate interconversion of NO_2 and HNO_3 has obscured our ability to learn about kinetics from atmospheric observations. In fact, numerous papers have been published arguing that models and observations are in “good agreement”, with the implication that the models are correct, only to have new laboratory measurements, such as the measurements of R23 by Dransfield et al., Donahue et al., and Brown et al., undermine confidence in the accuracy of the models. Many of these papers were developed using observations where N_2O_5 hydrolysis accounted for most or all of the conversion of NO_x to HNO_3. Cohen et al.[67] attempted to provide a more systematic perspective on what atmospheric observations do and do not teach us about the state of our knowledge. They develop an idea, dubbed “chemical coordinates”, to describe the information content of a set of observations and to permit clear identification of whether a new atmospheric observation does provide a new test of the models or merely repeats prior observations.

With respect to NO_2 and HNO_3, Cohen et al. define two coordinates: (1) the ratio of the 24-h integrated rate of $OH + NO_2$ to the 24-h integrated rate of N_2O_5 hydrolysis and (2) the ratio of the 24-h integrated rate of HNO_3 photolysis to the 24-h integrated rate of $HNO_3 + OH$. Viewed along chemical coordinates, the observations obtained during the POLARIS ER-2 campaign smoothly connect from those made in continuous sunlight to those where the heterogeneous reaction of N_2O_5 is 70% of the NO_2 conversion to HNO_3. This perspective provides at least partial explanation for a range of papers describing good agreement between models of NO_x and HNO_3 that were published prior to revision of the laboratory rate constant for $OH + NO_2$. Most of these papers described observations where N_2O_5 hydrolysis was the primary (probably more than 80%) NO_x sink, and so they were insensitive to whether the model accurately described the rate of $OH + NO_2$. In the second coordinate, Cohen et al. show that the observations provide little insight because there is essentially no variation in the position along this coordinate sampled by observations in the lower stratosphere. Higher altitude observations, such as those described by Jucks et al.,[100] do provide constraints along this coordinate.

3.1.3.2.2. $ClONO_2$ and $BrONO_2$ Hydrolysis. The heterogeneous reactions of halogen nitrates have been characterized in the laboratory, and observational evidence demonstrates that these reactions (R27−R30) occur in the atmosphere. There are several recent reviews of the rates of heterogeneous reactions on liquid and solid aerosol surfaces.[17,118,119] The reaction of halogen nitrates and H_2O occurs on cold stratospheric aerosol with a reaction probability highly dependent on the weight percent of H_2SO_4.[6]

At low temperatures, there is nearly complete conversion of inorganic chlorine to free radical form, with a parallel conversion of NO_x to HNO_3.[120] Reactions R27 and R29 are known to be effective in the polar vortex, but it has also been suggested that reaction R27 occurs with widespread frequency on cirrus cloud surfaces near the tropopause.[121] Enhancement in ClO mixing ratios[122,123] was reported in the lower stratosphere. In one event, a ClO increase and a corresponding reduction in NO/NO_y[124] were observed. This event occurred at low temperature and unusually high water abundance, consistent with aerosol processing of HCl and $ClONO_2$. However, analysis of extensive ER-2 observations shows no evidence that high ClO mixing ratios are a generic feature of the lower stratosphere.[125]

$BrONO_2$ can have an impact on NO_x-to-HNO_3 conversion, even under sunlit conditions and at midlatitudes. In the lower stratosphere under constant illumination, hydrolysis of bromine nitrate was estimated to account for up to 15% of the conversion of NO_x to HNO_3.[99] The strong interdependence of the radical cycles is evidenced by the fact that HO_x[126] and OClO[127] are described more accurately by models that include reaction R30. Analysis of column NO_2 from 1990 to 1995 by Slusser et al.[128] suggested that hydrolysis of $BrONO_2$ was one of the primary processes enhancing NO_x-to-NO_y conversion following the eruption of Pinatubo.

3.2. Sources and Sinks of Stratospheric NO_y

In the preceding sections we described short-term (seconds to months) factors controlling NO_2 mixing ratios. These are all reactions that interconvert NO_y species. On longer time scales, NO_2 concentrations are established by the sources and sinks of NO_y. The primary source of NO_y in the stratosphere is N_2O produced at the Earth's surface. N_2O is emitted at the surface from biological processes and, to a lesser extent, anthropogenic activity.[129] Anthropogenic N_2O emissions have increased by a factor of 5 in the past century (Figure 7), while natural sources remain in

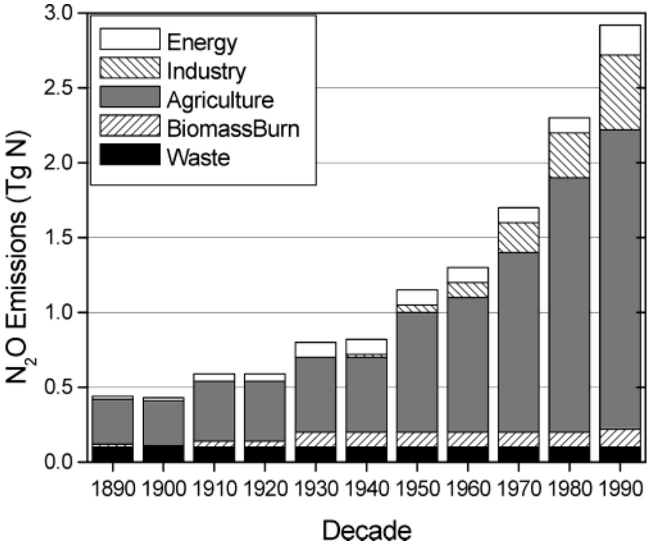

Figure 7. Anthropogenic N_2O emission sources by decade for the past century. Adapted from ref 158.

the range of 6−12 Tg N/yr. Ice core data show that surface concentrations have increased from 280 to 310 ppb during the past century.[130]

Global N_2O distributions were measured directly by the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument aboard the Upper Atmosphere Research Satellite (UARS) satellite.[131] Climatologies have been constructed from ER-2 aircraft data,[132] and observations from Atmospheric Trace Molecule Spectroscopy (ATMOS) and balloon-borne instruments provide additional information.[65,133,134]

Once in the stratosphere, N_2O is removed irreversibly by photolysis (R31) and reaction with electronically excited oxygen atoms (R32). These reactions are most rapid in the upper tropical stratosphere. One in 10 N_2O molecules are destroyed by reaction with $O(^1D)$, and of those roughly 42% form NO (R32b).

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (R31)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad (R32a)$$

$$N_2O + O(^1D) \rightarrow 2NO \qquad (R32b)$$

Because reactive nitrogen is formed in the stratosphere at the expense of N_2O, and because horizontal mixing is fast, the two species have a compact relationship.[135] Figure 8 depicts the relationship between NO_y and N_2O observed by in situ and remote spectroscopy. The NO_y/N_2O correlation becomes nonlinear at low N_2O/high altitude, reflecting additional chemical sinks via N + NO. Nevison et al.[136] describe NO_y observations and make a comparison to a 2-D chemical transport model above 30 km. Differences between this model and measurements approach 50%. In this region the chemical and transport time scales are comparable for NO_y, and errors in both are likely contributors to the discrepancy.[136,137]

At low altitudes, NO_y is removed from the stratosphere by transport into the troposphere either in gas-phase form or as solid HNO_3 incorporated in PSC. At high N_2O values, the ratio of $[NO_y]/[N_2O]$ has a global annually averaged value of about 0.07, reflecting the globally integrated stratospheric production and loss for each species.[51,138,139] Data described by Keim et al. show that the seasonal variance in the ratio is much larger in the SH than in the NH (30% vs 5%). Gravitational sedimentation of HNO_3-containing aerosol (denitrification) in the polar regions during winter, followed by transport of air with higher NO_y/N_2O ratios from upper to lower stratosphere during the remainder of the year, is consistent with a seasonal cycle in the ratio. The weaker seasonal amplitude in the NH follows, since aerosol sedimentation is less effective in the Northern Hemisphere. There are numerous observations of depressed NO_y/N_2O ratios that have been used to describe the location and timing of denitrification.[138,140−144] Santee et al. discuss the use of remote sensing to test thermodynamic theories of PSC formation from gas-phase HNO_3[145] and the difficulty in using data on this scale to observe spatially limited denitrification events.[146] Our understanding of the chemical mechanisms responsible for denitrification is evolving. Recent theoretical models[147−150] attempt to couple atmospheric temperature distributions, nucleation mechanisms that depend on water and nitric acid supersaturation, and the chemical and physical properties of pre-existing particles to account for observations of denitrification.

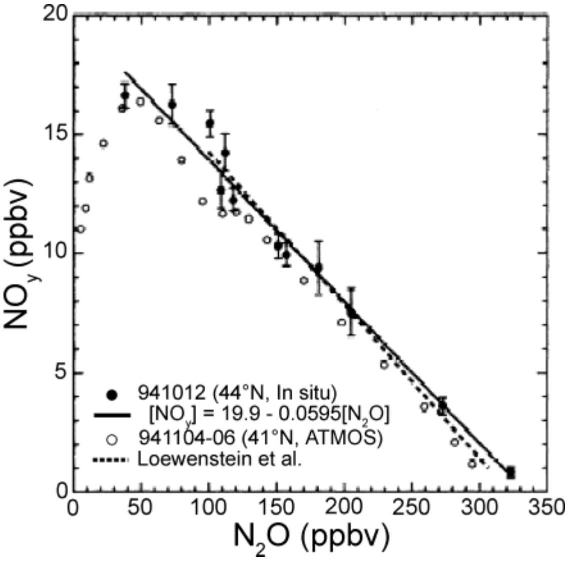

Figure 8. Compact relationship between NO_y and N_2O in the stratosphere from balloon-borne (●) and remote (○) observations, and predictions of a 2-D model (- - -).[134] Reprinted with permission from ref 134. Copyright 1996 American Geophysical Union.

In situ observations showed that HNO_3 is found in particles between 5 and 20 μm in size in the Arctic vortex.[144,151] Gravitational sedimentation of these particles could denitrify the lower stratosphere by up to 80% in regions where this process occurs. Analysis of these PSC observations by Fueglistaler et al.[152] demonstrated that the resolution afforded by a microphysical/mesoscale model is required to reproduce the spatial and temporal extent of ice and NAT clouds. Davies et al.[153] used a 3-D chemical-transport model and simultaneous measurements from the ER-2 to quantify the contribution of denitrification to ozone loss. Waibel et al.[154] and Tabazadeh et al.[155]

presented remote sensing observations of denitrification in the Arctic and Antarctic, respectively, and used microphysical models to assess the potential of future stratospheric cooling to promote widespread Arctic denitrification and therefore increased polar ozone depletion. Confirmation of the role played by NAT in denitrification was obtained by the observations by Voigt et al.[143] of large ($1-2\ \mu$m), low number density particles containing water and nitric acid in a 3:1 ratio, in locations consistent with predictions by thermodynamic models of the lower Arctic stratosphere. Data regarding the size distribution and concentration of the particles and the geographical extent of their formation offer multiple constraints for atmospheric models of PSC formation, which will improve our understanding of the process of denitrification and models of stratospheric NO_y distribution. The feedback between climate variables and the chemical mechanisms of denitrification and dehydration in combination with decreases in stratospheric chlorine levels will determine the extent of Artic polar ozone loss in the coming decades.[154−156]

4. Conclusions

With the advent of chemically comprehensive observations and the relative ease of the acquisition of large data sets spanning across season, latitude, and altitude, we have entered a new phase of stratospheric chemistry. The advances in the understanding of nitrogen oxide chemistry discussed in this review represent one part of that progress. Observations of the atmosphere can now be used to place limits on the uncertainty of kinetics (subject to the assumption that the kinetic model is complete) and to point to areas where more accurate measurements in the laboratory are needed. We can also evaluate the observations holding all but one variable constant, much as we do in the laboratory. These capabilities are resulting in tests of our understanding that have unprecedented accuracy.

In the coming decade we can expect an increase in the number of species measured in situ from aircraft in the stratosphere. At the same time, satellite-borne spectrometers—GOME (1995−1998) and SCIAMACHY(1999−2004),[157] launched by the European Space Agency, and the UARS (launched 1991) and EOS AURA (launch in 2004) NASA missions—are allowing increased global observations of reactive nitrogen and other trace species. These data will allow new tests of chemical models and a clearer understanding of the geophysical context in which the chemistry occurs.

We can also expect that the knowledge we have gained about how to dissect the chemistry of the stratosphere will be extended to the lower altitudes of the troposphere. By comparison to the troposphere, the chemistry of the stratosphere is relatively simple, because the only hydrocarbon of significance is CH_4. The chemistry of stratospheric NO_2 is also more straightforward because of simpler transport and the fact that NO_y is generally a conserved species over the time scale of stratospheric transport. New experiments studying the troposphere may take advantage of this fact and use observations within the stratosphere as a common reference point, or standard control experiment. Then, with knowledge that they have observed the simpler part of the atmosphere, the experiments will move lower, examining the deviation of a model−measurement comparison, if any, as altitude decreases and measurements enter the more complex chemical environment of the troposphere.

While we gain confidence that our understanding of most of the individual chemical processes that govern stratospheric ozone photochemistry is quite accurate, observations of the atmosphere can begin to reduce uncertainties reported for laboratory data. However, we still cannot completely explain the chemical or dynamical origin of the observed losses of mid-latitude ozone over the past 30 years.[14] Also, the scientific community is routinely asked to make projections of ozone for the next 50 years, as halogen concentrations in the stratosphere are expected to decrease to nearly pre-industrial levels. On such long time scales, even small uncertainties can propagate. Tracking the changes in ozone and evaluating how accurately we understand the perturbation due to halogens from the observations is an enormous and exciting challenge, especially since, as is typical in the Earth system, more than one interesting variable will be changing during the course of the experiment. In this case, climate change is affecting the composition, temperature, and circulation within the stratosphere, and increasing emissions of N_2O associated with industrial fertilizer use will also continue, slowly raising nitrogen oxide concentrations.

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