Ozone production and loss rate measurements in the middle stratosphere

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Abstract

We present the first simultaneous measurements of HO_x, NO_x, and Cl_x radicals in the middle stratosphere obtained during a balloon flight at 34°N in September 1989, along with calculations from a photochemical model, to show that NO_x catalytic cycles dominate loss of ozone (O_3) for altitudes between 24 and 38 km; the observed abundance of ClO is lower than that expected for altitudes above 30 km on the basis of models using recommended rates and cross sections, reducing the relative importance of the Cl_x catalytic cycles for loss of O_3; and removal rates of O_3 derived from observed concentrations of rate limiting HO_x, NO_x, and Cl_x radicals balance computed production rates for altitudes between 32 and 38 km, a region where ozone is expected to be regulated primarily by photochemical processes.

1. Introduction

Understanding the rate of removal of stratospheric ozone through catalytic cycles involving HO_x (HO_2 and OH), NO_x (NO_2 and NO), and halogen (ClO and BrO) radicals is essential for assessing the response of ozone to anthropogenic and natural perturbations such as industrial release of chlorofluorocarbons (CFCs) and halons, emission of nitrogen oxides from subsonic and supersonic aircraft, rising levels of N_2O and CH_4, and enhanced levels of sulfate aerosols following volcanic eruptions [*World Meteorological Organization (WMO)*, 1991; *Stolarski and Wesoky*, 1993; *Rodriguez et al.*, 1994].

Recent calculations from models of the midlatitude stratosphere give the following theoretical results: first, catalytic cycles involving NO_x radicals are expected to dominate ozone destruction from about 22 to 45 km, while HO_x cycles dominate both above and below [*McElroy et al.*,1992; *Rodriguez et al.*, 1994]; and second, modeled photochemical loss of ozone exceeds calculated production by 10%–50% in the upper stratosphere [*Eluszkiewicz and Allen*, 1993; *Minschwaner et al.*, 1993; *Crutzen et al.*, 1995; *Siskind et al.*, 1995]. The latter result has been termed the "ozone deficit" problem, because at these altitudes, ozone is expected to be in photochemical equilibrium (production equaling loss), since the photochemical lifetime of ozone is much shorter than transport replacement times [*Ko et al.*, 1989; *Perliski et al.*, 1989].

The first theoretical result has recently been tested below 21 km by using in situ aircraft measurements of HO_x, NO_x, and Cl_x radicals [*Wennberg et al.*, 1994]. These measurements, made under conditions of high aerosol loading as a result of the eruption of Mt. Pinatubo, are in good agreement with models that include the heterogeneous hydrolysis reaction of N_2O_5 on sulfate aerosols [*Fahey et al.*, 1993; *Salawitch et al.*, 1994].

The ozone deficit problem in the middle and upper stratosphere has been studied recently with the use of Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) measurements of O_3, nitrogen oxides, and other trace gases [*Minschwaner et al.*, 1993], HAlogen Occultation Experiment (HALOE) measurements of O_3, NO_2, and HCl [*Crutzen et al.*, 1995], and a combination of Microwave Limb Sounder (MLS) measurements of O_3 and ClO and Cryogenic Limb Atmospheric Limb Sounder (CLAES) measurements of NO_2 [*Dessler et al.*, 1996]. *Minschwaner et al.* [1993] concluded that production and loss of O_3 are in balance near 40 km altitude, provided models allow for production of HCl from a branch of the reaction of ClO+OH, as suggested by theoretical studies constrained by ATMOS measurements of HCl and $ClONO_2$ [*McElroy and Salawitch*, 1989] and submillimeter heterodyne measurements of ClO and HCl [*Stachnik et al.*, 1992]. *Crutzen et al.* [1995] concluded production and loss of O_3 were in closer balance than was suggested by other analyses of satellite data [*Eluszkiewicz and Allen*, 1993; *Siskind et al.*, 1995], but their conclusions are affected by the use of O_3 from HALOE, which is systematically lower than O_3 measured by MLS. *Dessler et al.* [1996] concluded ozone production and loss rates constrained by measured ClO, NO_2, and O_3 from MLS are nearly in balance at 40 km. All previous studies lack direct, simultaneous measurements of HO_x, Cl_x, and NO_x radicals.

In this paper we use the the first simultaneous measurement of concentrations of HO_x, NO_x, Cl_x, and radical precursors throughout the middle stratosphere [*Chance et al.*, 1996] to calculate the photochemical removal rate of ozone between 20 and 38 km. Our analysis uses simultaneous measurements of a complete set of radicals to determine experimentally the ordering of the loss cycles of ozone in the middle stratosphere and to study the ozone deficit problem.

Diurnally averaged photochemical removal rates of O_3 by each family of radicals are determined in two ways: from direct measurements of radical concentrations (radical method) and from radical concentrations calculated by a photochemical model constrained by measurements of radical precursors (precursor method). The radical method is used to derive empirical measures of the total loss rate of ozone as well as the relative removal rate by each family of radicals that regulate the abundance of ozone in the middle stratosphere. The precursor method provides a basis for comparing the empirical loss rates to theoretical rates constrained by appropriate environmental conditions, represented by the observed concentrations of long-lived radical precursors. Empirical loss rates found by using the radical method demonstrate that catalytic cycles involving NO_x radicals dominate photochemical removal of O_3 in the middle stratosphere, consistent with theoretical predictions using the precursor method. Our measurements demonstrate that production and loss rates of ozone (found by using both methods) balance to within the uncertainty of measurement (10%) for altitudes between 31 and 38 km. This finding, which reconciles a long-standing discrepancy in stratospheric chemistry, is due primarily to our observation of a lower abundance of ClO than that calculated by models that allow for production of HCl only from reaction of Cl and hydrocarbons and HO_2 [*Chance et al.*, 1996].

2. Measurements and Model

Descriptions of the measurement technique and analysis methods [*Traub et al.*, 1991; *Johnson et al.*, 1995; *Waters et al.*, 1984] have been published previously; thus only a brief summary is given here. Data were acquired on a balloon flight launched from Ft. Sumner, New Mexico (34°N, 104° W), from 1714 UT on September 26, 1989, until 1832 UT on September 27, 1989, with the exception of a 4-hour telemetry gap prior to sunrise on September 27. Concentrations of ClO were measured at midday between altitudes of 20 and 40 km with the Jet Propulsion Laboratory (JPL) Balloon Microwave Limb Sounder (BMLS), which senses microwave emission from the limb. Concentration profiles of OH, HO_2, H_2O_2, HOCl, HCl, NO_2, HNO_3, N_2O, H_2O, O_3, and temperature were measured throughout a diurnal cycle with the Smithsonian Astrophysical Observatory (SAO) far-infrared Fourier transform spectrometer (FIRS 2), which detects atmospheric thermal emission in a limb-viewing geometry.

The constrained photochemical model used in our analysis balances, over a 24-hour period, the production and loss of 35 reactive gases for the temperature, pressure, and latitude at which the observations were obtained [*Salawitch et al.*, 1994]. Standard reaction rates and absorption cross sections were used [*DeMore et al.*, 1994], except that photolysis cross sections for H_2O_2 and HNO_4 were extrapolated to longer wavelengths to accurately represent photolysis of these molecules at large solar zenith angles. A reaction probability of 0.1 was used for the heterogeneous hydrolysis of N_2O_5 [*DeMore et al.*, 1994]. The altitude profile for the surface area density of sulfate aerosols was adopted from Stratospheric Aerosol and Gas Experiment (SAGE) II extinction measurements for this time period [*WMO*, 1991]. The heterogeneous hydrolysis of $ClNO_3$ and $BrNO_3$ was included [*Hanson and Ravishankara*, 1994, 1995; *Hanson and Lovejoy*, 1995] but have a negligible effect on model results for the temperatures and aerosol loading of these observations. Other inputs to the constrained photochemical model include profiles of temperature, O_3, and H_2O measured by FIRS 2. Profiles of CH_4, odd nitrogen ($NO_y = NO + NO_2 + NO_3 + 2\times N_2O_5 + HNO_2 + HNO_3 + HNO_4 + ClNO_3 + BrNO_3$), inorganic chlorine ($Cl_y = HCl + ClNO_3 + ClO + HOCl + Cl + OClO + 2xCl_2O_2 + ClOO$), and inorganic bromine ($Br_y = HBr + BrONO_2 + BrO + HOBr + BrCl$) have been inferred from the FIRS 2 measurement of N_2O by using relations derived from previous satellite [*Gunson et al.*, 1990] and in situ observations [*Fahey et al.*, 1990; *Woodbridge et al.*, 1995; *Schauffler et al.*, 1993]. The maximum Br_y at high altitude is assumed to be 21 pptv.

3. Comparison of Measurements and Model

Chance et al. [1996] have presented a detailed discussion of model uncertainties, as well as a comparison between measurements of HO_x, NO_x, and Cl_x radicals and profiles calculated by using the model presented here. We summarize below the main conclusions of *Chance et al.* [1996] as they apply to the analysis to follow.

Calculated concentrations of OH and HO_2 are in satisfactory agreement with observations throughout the observed altitude range, 20 to 38 km, with the exception that the observed abundances of OH exceed calculations by more than 20%, the 2σ measurement uncertainty, at 38 km. The NO_2 and HNO_3 measurements are also in good agreement with theoretical profiles except at 24 km (near the peak mixing ratio of HNO_3), where measured concentrations of HNO_3 exceed calculated values by about 15%, larger than the 1-sigma uncertainty of the measurement. Above 30 km the measurements of Cl_y species (ClO, HCl, and HOCl) are not in agreement with the values calculated assuming a conventional set of reactions, which assumes the only sources of HCl are the reactions of Cl with hydrocarbons and HO_2 (a typical assumption of current multidimensional models of atmospheric photochemistry and transport [*Prather and Remsberg*, 1993]). The conventional model tends to overpredict the reactive chlorine (ClO and HOCl) while it underpredicts HCl. The measured concentrations of Cl_y species are in good agreement with a second model that includes the additional production of HCl by the reaction of ClO with OH with a 10% branching ratio. *DeMore et al.* [1994] suggest a lower limit of 0%, and an upper limit of 14%, for production of HCl from the ClO+OH reaction. Laboratory measurements of the production of HCl from this reaction, which would involve breaking and reforming multiple chemical bonds, give ambiguous results. While this reaction is not the only pathway for additional production of HCl that might be consistent with the simultaneous measurement of ClO, HOCl, and HCl, it is the only pathway within the recommended uncertainties of current kinetic measurements [*DeMore et al.*, 1994].

There are large uncertainties in many important reaction rates used by the photochemical model, which when considered collectively may account for the differences between the measured and modeled Cl_y partitioning. However, because the model shows reasonable agreement with the measured HO_x and NO_y species, only the uncertainties in rates for reactions that directly involve Cl_y partitioning need to be considered in discussing the overprediction of ClO by the conventional model. Specifically, the rates of the reactions in which HCl is created (Cl +

$CH_4 \rightarrow$ HCl + CH_3) or destroyed (HCl + OH $\rightarrow$ H_2O + Cl) will have the most direct impact on the partitioning of Cl_y species. *DeMore et al.* [1994] list uncertainties for these reactions at 250 K of about 21% and 28%, respectively. The extreme value for the rate of both reactions is required to account for the differences between the measurements and the conventional reaction set. *Michelsen et al.* [1996] present a thorough investigation of the kinetics of these reactions and conclude that the partitioning of Cl_y measured by the ATMOS and Millimeter-wave Atmospheric Sounder (MAS) instruments during the ATLAS 2 and ATLAS 3 space shuttle missions cannot be explained unless an additional source of HCl, not present in the conventional reaction set, is allowed.

A further source of uncertainty in the model is the estimation of Cl_y, NO_y, and CH_4 from relationships with N_2O. These relationships have been well established throughout the altitude range of these measurements by using observations from ATMOS at midlatitudes [*Gunson et al.*, 1990]. The uncertainties in those quantities are proportional to the measurements of N_2O, about 10%, and are affected by the amount that the air being measured deviates from midlatitude conditions. *Chance et al.* [1996] eliminated the effect of uncertainties in Cl_y by examining comparisons between theory and observations for the ratios [ClO]/[HCl] and [HOCl]/ [HCl]. Uncertainties in CH_4, whose oxidation provides a minor source of HO_x radicals, have only a minor impact on our photochemical simulations. Corroborating evidence for the existence of such an additional pathway for production of HCl is provided by Upper Atmosphere Research Satellite (UARS) measurements of O_3, H_2O, HCl, ClO, and $ClNO_3$ [*Eckman et al.*, 1995; *Dessler et al.*, 1996].

4. O_3 Photochemical Loss and Production Rates

Ozone and atomic oxygen (O), together defined as odd oxygen (O_x), are in rapid photochemical steady state via the reactions O_3 + $h\nu \rightarrow$ O + O_2 and O + O_2 + M $\rightarrow$ O_3 + M. Throughout the stratospheric altitude range discussed in this paper, O_3 represents more than 99% of total odd oxygen, and thus a change in the abundance of odd oxygen is considered as equivalent to a change in the abundance of O_3. Oxides of hydrogen, nitrogen, chlorine, and bromine regulate the abundance of O_x in the middle stratosphere through a variety of reactions that catalyze the self-reaction of O_3 or the reaction of O_3 and O. Since each reaction sequence listed below accounts for the loss of two molecules of O_x, the net loss rates are determined by doubling the diurnally averaged rate of the limiting step of each cycle. The rate-limiting steps for each cycle are indicated by the number label.

The role of HO_x radicals in regulating the abundance of odd oxygen was first noted by *Bates and Nicolet* [1950]. The important cycles are

$$\begin{aligned} \mathrm{OH}+\mathrm{O_3} &\rightarrow \mathrm{HO_2}+\mathrm{O_2}, \\ \mathrm{HO_2}+\mathrm{O_3} &\rightarrow \mathrm{OH}+\mathrm{O_2}+\mathrm{O_2}, \qquad (1) \\ \mathrm{Net:}\ 2\mathrm{O_3} &\rightarrow 3\mathrm{O_2}; \end{aligned}$$

which is significant in the lower stratosphere and

$$\begin{aligned} \mathrm{OH}+\mathrm{O_3} &\rightarrow \mathrm{HO_2}+\mathrm{O_2}, \\ \mathrm{HO_2}+\mathrm{O} &\rightarrow \mathrm{OH}+\mathrm{O_2}, \qquad (2) \\ \mathrm{Net:}\ \mathrm{O_3}+\mathrm{O} &\rightarrow 2\mathrm{O_2}; \end{aligned}$$

with other cycles accounting for less than 5% of ozone loss by HO_x species between 35 and 40 km and less than 1% below 35 km.

Crutzen [1970] and *Johnston* [1971] established the importance of removal of odd oxygen by cycles involving NO_x:

$$\begin{aligned} \mathrm{NO}+\mathrm{O_3} &\rightarrow \mathrm{NO_2}+\mathrm{O_2}, \\ \mathrm{NO_2}+\mathrm{O} &\rightarrow \mathrm{NO}+\mathrm{O_2}, \qquad (3) \\ \mathrm{Net:}\ \mathrm{O_3}+\mathrm{O} &\rightarrow 2\mathrm{O_2}; \end{aligned}$$

$$\begin{aligned} \mathrm{NO}+\mathrm{O_3} &\rightarrow \mathrm{NO_2}+\mathrm{O_2}, \\ \mathrm{NO_2}+\mathrm{O_3} &\rightarrow \mathrm{NO_3}+\mathrm{O_2}, \qquad (4) \\ \mathrm{NO_3}+h\nu &\rightarrow \mathrm{NO}+\mathrm{O_2}, \\ \mathrm{Net:}\ 2\mathrm{O_3} &\rightarrow 3\mathrm{O_2}; \end{aligned}$$

where only 10% of NO_3 photolysis produces NO to complete this cycle.

Molina and Rowland [1974] and *Stolarski and Cicerone* [1974], and *Wofsy et al.* [1975] drew attention to removal of odd oxygen by chlorine and bromine radicals, respectively. Loss occurs primarily through the cycles

$$\begin{aligned} Z\mathrm{O}+\mathrm{O} &\rightarrow Z+\mathrm{O_2}, \qquad (5) \\ Z+\mathrm{O_3} &\rightarrow Z\mathrm{O}+\mathrm{O_2}, \\ \mathrm{Net:}\ \mathrm{O_3}+\mathrm{O} &\rightarrow 2\mathrm{O_2}; \end{aligned}$$

$$\begin{aligned} \mathrm{HO_2}+Z\mathrm{O} &\rightarrow \mathrm{HO}Z+\mathrm{O_2}, \qquad (6) \\ \mathrm{HO}Z+h\nu &\rightarrow \mathrm{OH}+Z, \\ Z+\mathrm{O_3} &\rightarrow Z\mathrm{O}+\mathrm{O_2}, \\ \mathrm{OH}+\mathrm{O_3} &\rightarrow \mathrm{HO_2}+\mathrm{O_2}, \\ \mathrm{Net:}\ 2\mathrm{O_3} &\rightarrow 3\mathrm{O_2}; \end{aligned}$$

where Z = Cl or Br, as well as through the cycle

$$\begin{aligned} BrO + ClO &\rightarrow Br + Cl + O_2, \quad (7) \\ Br + O_3 &\rightarrow BrO + O_2, \\ Cl + O_3 &\rightarrow ClO + O_2, \\ \mathrm{Net}: 2O_3 &\rightarrow 3O_2; \end{aligned}$$

which is a major loss cycle for O_3 in the Antarctic spring [*McElroy et al.*, 1986].

Loss of odd oxygen proceeds also by the reaction [*Chapman*, 1930]

$$O + O_3 \rightarrow 2O_2, \quad (8)$$

which is a minor sink in the middle stratosphere. Odd oxygen is produced by photolysis of O_2 at wavelengths shorter than 242 nm, with a small contribution from the reaction of CH_3O_2 and NO [*Wennberg et al.*, 1994].

The precursor method uses a photochemical model, constrained by our measurements of O_3, H_2O, N_2O, and temperature, to predict the abundances of O, HO_2, OH, NO_2, ClO, and BrO over a 24-hour period. These abundances are used to calculate the rates of reactions (1)–(8). The loss rates of O_3 are integrated over 24 hours, by using reaction rate constants from *DeMore et al.* [1994], and summed to evaluate the the rates of the HO_x (rate-limiting reactions (1) and (2)), NO_x (reactions (3) and (4)), halogen (reactions (5), (6), and (7)), and O+O_3 (reaction (8)) loss cycles.

The radical method uses direct measurements of HO_2, OH, NO_2, and ClO to calculate the rates of reactions (1)–(8). The measurements are interpolated onto a finer time grid by normalizing the abundances calculated by the constrained photochemical model for each of these molecules to best fit the data throughout the 24-hour cycle. This process is shown in Figure 1 for a representative altitude of 32 km with concentrations that have been adapted from the model and measurement results presented by *Chance et al.* [1996]. We show the 1σ uncertainties in the observations which include systematic uncertainties. We note that the model is in excellent agreement with the data even before scaling for HO_2 and NO_2, while the ClO measurement is significantly lower than the results from the conventional photochemical model.

Figure 2 compares the removal rate of odd oxygen from the radical and precursor methods, partitioned into each radical family as described in the cycles listed above. The uncertainties listed here include the 1σ uncertainties from the measurements plus any residuals between the observed and normalized concentrations. The precursor method calculations are based on the results from the constrained

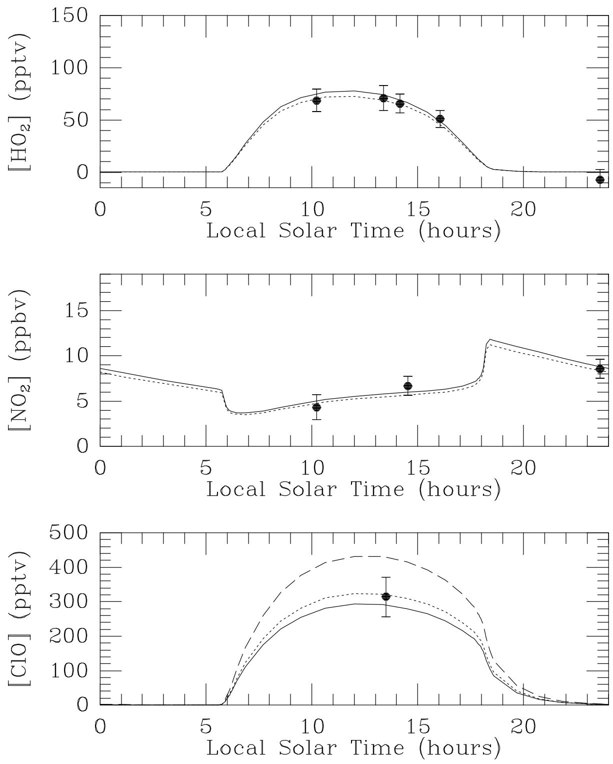

Figure 1. Individual concentration measurements (solid circles) along with the modeled diurnal concentrations (solid curves) and the corresponding scaled concentrations (dotted curves) for HO_2, NO_2, and ClO at 32 km. The 1σ uncertainties are dominated by random measurement errors but include estimated systematic errors. The modeled ClO has two curves, one including (solid curve) and one not including (dashed curve) production of HCl from the ClO+OH reaction. For this altitude the average integration time for each measurement is 22, 42, and 50 min for HO_2, NO_2, and ClO, respectively; each integration comprises several shorter observations spread over average corresponding intervals of 2, 5.5, and 6 hours, respectively (see *Chance et al.* [1996] for details).

photochemical model, whose uncertainties were discussed in some detail earlier and by *Chance et al.* [1996]. The loss rate uncertainties from the radical method depend also on the uncertainty of the rate of the limiting steps. At the lower altitudes of this study the measurement uncertainties dominate the overall uncertainty. At the higher altitudes, where the measurement uncertainties are smaller, the dominant odd oxygen loss cycles involve reactions (2), (3), (5) and (8). Reaction (5) is dominated by the ClO cycle, which is more than 2 orders of magnitude more effec-

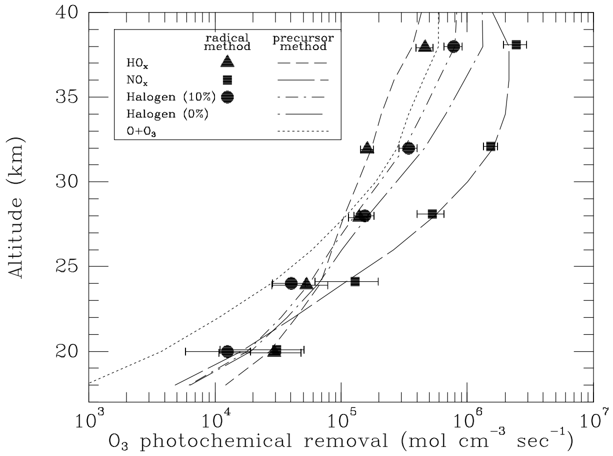

Figure 2. HO_x (solid triangles), NO_x (solid squares), and halogen (solid circles) catalyzed loss rates of O_3 inferred from radical method and calculated by using the precursor method (curves). Two halogen catalyzed precursor method loss calculations are illustrated: one assuming HCl production only from Cl reacting with hydrocarbons and one with additional production of HCl from a 10% branch of the OH + ClO reaction (see text). The O+O_3 reaction curve can be considered to represent both the radical and precursor methods since O is inferred directly from measurements of O_3, which is the precursor for O. The symbols are offset in altitude for clarity.

tive than the BrO reaction at destroying odd oxygen above 30 km. As a result, uncertainties in the loss rate of O_3 at these altitudes due to the use of calculated profiles for BrO are small compared to other sources of error. Using the average measured temperature of 240 K for these altitudes, the uncertainties in the rate constants for reactions (2), (3), (5), and (8) are 30%, 21%, 27%, and 40%, respectively [*DeMore et al.*, 1994]. Because these uncertainties will systematically affect the rates from both the radical and precursor methods and will not affect the comparisons of the two quantities, they are not included in Figure 2. This figure illustrates that the general behavior of the removal rates of odd oxygen inferred from the observed concentration of radicals is in agreement with theory for the HO_x and NO_x families of radicals. Above 32 km the lower abundance of ClO calculated by the second model gives removal rates of ozone by halogens that are reduced by as much as 40% compared to the values calculated by using the conventional set of reactions. This difference is larger than the uncertainty in the rate constant for reaction (5).

The fractional contribution of each radical family to loss of odd oxygen is shown in Figure 3. Cycles involv-

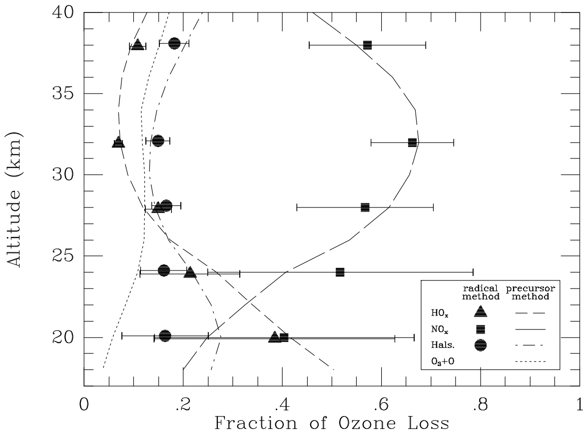

Figure 3. Fractional total loss of odd oxygen from the HO_x, NO_x, and halogen catalytic cycles shown as a function of altitude, as inferred from the radical method, using measurements of HO_2, NO_2, ClO, and O_3 (symbols) and from the precursor method (curves). The curves for the precursor method use the model that assumes additional HCl production from a 10% branch of the OH + ClO reaction.

ing NO_x radicals dominate the loss of ozone between altitudes of 24 and 38 km, contributing a maximum of 66% to the total loss rate at 32 km. In contrast to observations obtained during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) [*Wennberg et al.*, 1994], our measurements also suggest that loss of odd oxygen due to NO_x cycles is comparable to loss due to halogen cycles near 20 km. The SPADE measurements showed loss of odd oxygen due to NO_x cycles to be a factor of 2-4 slower than loss due to halogen and HO_x cycles. However, the large uncertainties of our measurements at these altitudes make it difficult to determine precisely the ordering of the loss cycles. The balloon-borne observations were obtained in 1989, when concentrations of Cl_y were approximately 14% lower than contemporary levels [*Elkins et al.*, 1993] and sulfate aerosol loading was about a factor of 5 less than values encountered during SPADE, which were elevated due to the eruption of Mt. Pinatubo in the summer of 1991. Both factors contribute to a larger relative contribution by NO_x cycles to odd oxygen removal in the lower stratosphere during 1989.

Figure 4 illustrates diurnally averaged total loss rates for odd oxygen inferred from both the radical and precursor methods, as well as production rates from photolysis of O_2 calculated by using a radiative transfer model that includes Rayleigh and aerosol scattering [*Prather*, 1981;

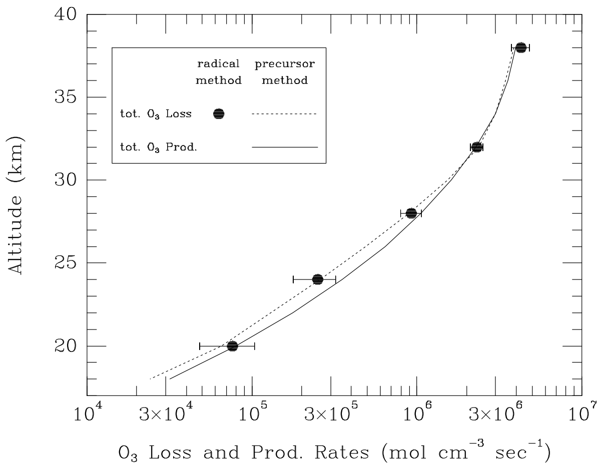

Figure 4. Loss rates of ozone calculated with the radical method (see text) from direct measurements of HO_2, NO_2, ClO, and O_3 (solid circles), loss rates calculated by using the precursor method using a model that assumes HCl production from a 10% branch of the ClO + OH reaction (dotted curve), and production rates of O_3 (solid curve) calculated primarily from photodissociation of O_2 (see text) and constrained by measurements of O_3 and temperature.

Minschwaner et al., 1993]. The error bars are derived from the uncertainties presented in Figure 2 for each of the radical families added in quadrature. Three conclusions can be drawn from this figure. First, total odd oxygen loss rates inferred from the observed concentrations of radicals (radical method) agree with theoretical loss rates (precursor method) to within the measurement uncertainty at all altitudes. Second, between 31 and 38 km, where the photochemical lifetime of ozone is short compared to transport timescales, we find that production and loss rates of odd oxygen calculated by using both methods balance to within the uncertainty of the measurements of the radicals (approximately 10%), in contrast to previous studies (which lacked simultaneous measurements of HO_2, NO_2, and ClO) that reported loss rates up to 50% greater than production rates [*Crutzen and Schmailzl*, 1983; *Froidevaux et al.*, 1985; *Jackman et al.*, 1986; *McElroy and Salawitch*, 1989; *Eluszkiewicz and Allen*, 1993]. Third, rates of production below 31 km exceed by 30% to 40% the loss rates calculated by using both methods, indicating that this region is a net photochemical source region for O_3. This imbalance is consistent with results of two-dimensional photochemical transport models that show net ozone production from this region [*Jackman et al.*, 1986; *Perliski et al.*, 1989].

At the altitudes at which we measure a balance between production and loss of odd oxygen, 32 and 38 km, the dominant odd oxygen loss cycles are the same as those discussed for Figure 2, with reaction (3) contributing more than 60% to the total odd oxygen loss. By weighting the uncertainties of these reaction rates by the relative contributions from each of these cycles we calculate a net reaction rate uncertainty of 23% in the calculated total loss rate for the radical method. This value is of the order of the estimated uncertainty (20%) in the production of O_3 [*Minschwaner et al.*, 1993] and is larger than the uncertainties (10%) in the loss rates due to the uncertainty of the measurements of the radicals at these altitudes.

5. Discussion

Our finding that production and measured loss of of odd oxygen balance for altitudes between 31 and 38 km differs from the results of previous studies for two reasons: (1) we observe lower concentrations of ClO at these altitudes than are predicted by those models which assume that production of HCl occurs only by reaction of Cl with hydrocarbons and HO_2 [*Chance et al.*, 1996], as illustrated in Figure 1, and (2) we use a formulation for photolysis of O_2 that results in deeper penetration of ultraviolet radiation [*Minschwaner et al.*, 1993], and better agreement with measured transmittances, than is found by using the formulation recommended by *WMO* [1986]. Including the additional source of HCl lowers the total modeled loss rate of odd oxygen by about 17% near 38 km (see Figures 2 and 4), resulting in close agreement between production and loss of ozone found by using the precursor method. Although this difference is less than the combined uncertainties in the production and loss rates stated above, the comparisons between the measured radicals involved in the rate limiting steps for the ozone loss cycles and the photochemical model presented here and by *Chance et al.* [1996] show that observed concentrations of HO_2 and NO_2 are well simulated, while ClO (and hence its contribution to loss of O_3) is overestimated by the conventional model.

Most current models used to assess the impact of anthropogenic emission of halogens on ozone overestimate the abundance of ClO in the upper stratosphere by neglecting the possibility of an additional pathway for production of HCl [*Prather and Remsberg*, 1993]. Our observations demonstrate that these models overestimate the relative contribution of halogen cycles to the removal rate of odd oxygen at altitudes near 40 km. The predicted decrease in ozone near 40 km resulting from the buildup of halogens during the past several decades is mitigated by 50%, if an additional pathway for production of HCl is included in models, resulting in closer agreement between observed and predicted trends in O_3 at these altitudes [*Chandra et al.*, 1993]. Above 45 km, HO_x catalyzed cycles dominate ozone loss, with the importance of halogen cycles decreasing with increasing altitude into the mesosphere. Inclusion of an additional source of HCl may not be sufficient to solve the imbalance between modeled production and loss at altitudes at which reaction (2) dominates loss of odd oxygen [*Crutzen and Schmailzl*, 1983; *Froidevaux et al.*, 1985; *Eluszkiewicz and Allen*, 1993]. New observations of HO_x radicals, measured simultaneously with O_3, NO_2, and ClO, will be necessary to advance our understanding of the budget of O_3 at altitudes higher than 38 km.

Numerous recent atmospheric observations are consistent with our findings that ClO is overpredicted by models. The study of *Minschwaner et al.* [1993] concludes, on the basis of constraints imposed by ATMOS measurements of O_3, NO, NO_2, N_2O_5, HNO_3, $ClNO_3$, HCl, H_2O, and CH_4, that production and loss of odd oxygen will balance near 40 km if a minor branch of the reaction of ClO with OH results in production of HCl. The more recent study of ATMOS and MAS (ClO) data by *Michelsen et al.* [1996] adds further support for an additional production channel for HCl. Similar conclusions were reached by *Chandra et al.* [1993], who found that submillimeter heterodyne measurements of ClO and HCl [*Stachnik et al.*, 1992] and the observed abundance and seasonal variation of O_3 near 40 km were better simulated by allowing for the additional pathway for production of HCl.

A more recent theoretical study [*Crutzen et al.*, 1995] on the balance of production and loss of odd oxygen based on constraints provided by HALOE measurements of HCl, NO_2, H_2O, and O_3 found that production usually exceeds loss in the middle and upper stratosphere, especially above 45 km. The study of *Dessler et al.* [1996] took the analysis of UARS data one step further by incorporating MLS measurements of ClO and O_3 and CLAES observations of NO_2 at 40 and 46 km, using the diurnal variation of the radicals, to discuss production and loss of O_3. Their model overestimates the measured ClO by an amount consistent with that shown in our study and use of the measured ClO brought their modeled production and loss of ozone into near balance. The Dessler et al. study further states that by considering MLS measurements of O_3 instead of HALOE values, the O_3 surplus found by Crutzen et al. would instead be a deficit.

6. Conclusions

We have used the first set of simultaneous measurements of the radicals that dominate loss of ozone in the middle stratosphere to test our understanding of the partitioning of these radicals and to determine the relative contribution of each radical family to loss of ozone. The accuracy of this set of radical measurements is sufficient to demonstrate that (1) NO_x loss cycles dominate ozone loss between 24 and 38 km, as predicted by models; (2) modeled NO_x and HO_x catalyzed loss rates of ozone are consistent with the measurements; (3) Cl_x loss rates are measured to be about a factor of 2 slower than the calculated rates above 30 km; (4) the measured total loss rates of ozone balance production rates at 32 and 38 km; and (5) inclusion of a channel for extra production of HCl in the photochemical model results in a balance between production and loss of O_3 above 31 km and agreement between observed and calculated ClO, HOCl, and HCl. These conclusions demonstrate that our first-order understanding of processes that regulate the partitioning of radicals is correct and that models, provided they allow for production of HCl either by the reaction of ClO and OH or by some other currently unknown process that results in a similar partitioning of inorganic chlorine species should provide a realistic description of the relative rate of removal of odd oxygen in the lower and middle stratosphere by each of the major catalytic cycles.

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