Sources of HO_x and production of ozone in the upper troposphere over the United States

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Abstract. The sources of HO_x (OH+peroxy radicals) and the associated production of ozone at 8-12 km over the United States are examined by modeling observations of OH, HO_2, NO, and other species during the SUCCESS aircraft campaign in April-May 1996. The HO_x concentrations measured in SUCCESS are up to a factor of 3 higher than can be calculated from oxidation of water vapor and photolysis of acetone. The highest discrepancy was seen in the outflow of a convective storm. We show that convective injection of peroxides (CH_3OOH and H_2O_2) and formaldehyde (CH_2O) from the boundary layer to the upper troposphere could resolve this discrepancy. More generally, the data collected over the central United States during SUCCESS suggests that local convection was a major source of HO_x and NO_x to the upper troposphere. The OH and HO_2 observations together with the observations of NO allow us to directly calculate the ozone production in the upper troposphere and its dependence on NO_x. We find an average net ozone production of 2 ppbv day^{-1} between 8 and 12 km over the continental United States in the spring. Ozone production was NO_x-limited under essentially all the conditions encountered in SUCCESS. The high levels of HO_x present in the upper troposphere stimulate ozone production and increase the sensitivity of ozone to NO_x emissions from aircraft and other sources.

Introduction

In the troposphere, ozone is produced by oxidation of CO and hydrocarbons in the presence of nitrogen oxide radicals (NO_x=NO+NO_2) and hydrogen oxide radicals (HO_x=OH+peroxy radicals). There is at present considerable interest in understanding the effects of increasing aircraft NO_x emissions on ozone in the upper troposphere [*Schumann*, 1995; *NASA*, 1997]. Depending on the relative supply of NO_x and HO_x in the upper troposphere, an increase in NO_x may cause either an increase or a decrease in ozone [*Brasseur et al.*, 1996].

In this paper we analyze the first concurrent measurements of HO_x [*Brune et al.*, this issue] and NO_x [*Campos et al.*, this issue] made in the aircraft flight corridor over the central United States. The measurements were made during the SUCCESS (SUbsonic aircraft: Cloud and Contrail Effects Special Study) DC-8 mission [*Toon et al.*, this issue]. We examine the factors controlling HO_x concentrations in the upper troposphere by comparing a photochemical model to the SUCCESS data. We use the combination of HO_x and NO_x measurements to quantify ozone production in the upper troposphere and assess its sensitivity to anthropogenic NO_x. A companion paper [*Jaeglé et al.*, this issue] focuses on the origin and chemical cycling of NO_x.

Model description

We use the Harvard 0-D photochemical model to calculate the concentrations of radicals and other photochemical intermediates along the aircraft flight tracks [*Jacob et al.*, 1996]. The model calculations are constrained with local 1-minute averaged observations of O_3, CO, NO, H_2O, CH_4, pressure, temperature, UV ra-

diation, and aerosol surface area. Acetone was not measured in SUCCESS but is included in our calculations as a linear function of CO concentrations based on the acetone-CO correlation observed in the PEM-West B aircraft campaign over the western Pacific [*McKeen et al.*, 1997]. The resulting acetone concentrations in the upper troposphere range from 200 to 900 pptv (average of 550 pptv). The values may be too low for a continental atmosphere, as sampled in SUCCESS, considering that acetone has a shorter lifetime than CO and that the acetone-CO correlation is based on relatively old marine air. The sensitivity of model results to the assumed concentration of acetone will be discussed below.

All input quantities except NO concentrations are assumed constant over the diel cycle. Total NO_t (= $NO+NO_2+NO_3+2N_2O_5+HNO_2+HNO_4$) is also assumed constant and is calculated iteratively in the model to match the observed NO at the time of day of observations. The model calculates the diel steady state concentrations of 30 species including HO_2, OH, $O(^1D)$, CH_3O, CH_3O_2, NO_y species (NO_2, NO_3, N_2O_5, HNO_2, HNO_4, HNO_3, PAN), and other photochemical intermediates (H_2O_2, CH_3OOH, and CH_2O) along the flight track of the aircraft. "Diel steady state" is defined by the reproducibility of concentrations in the model over a 24-hour solar cycle. The corresponding 24-hour average reaction rates are also retrieved from the model output. Model calculations for a total of 2770 individual points were performed. The photochemical mechanism used in this model is the same as in *Jacob et al.* [1996], with updated rates [*DeMore et al.*, 1997]. For acetone photolysis we use recent measurements of the temperature-dependent cross-sections and pressure-dependent quantum yield [*McKeen et al.*, 1997].

The ozone column was specified from daily SBUV/2 satellite observations (A. J. Miller and C. Long, personal communication, 1996). Cloud and albedo effects are taken into account by using the NO_2 photolysis rate (JNO_2(Eppley)) derived from the Eppley UV radiometer instrument on-board the DC-8 [*Madronich*, 1987]. All the clear sky photolysis rates are scaled by JNO_2(Eppley)/JNO_2(clear), where JNO_2(clear) is the clear sky NO_2 photolysis rate computed by the radiation model at the local time of day of the observations (assuming a surface albedo of 0.1). For clear sky periods, JNO_2(Eppley) and JNO_2(clear) are within 10% of each other. Because the DC-8 often flew in the vicinity of clouds, the ratio of JNO_2(Eppley)/ JNO_2(clear) ranged between 0.5 and 2.5, the mean being 1.3.

HO_x in the Upper Troposphere

Figure 1 shows a comparison between observations and diel steady state model calculations of the OH and HO_2 mixing ratios in the upper troposphere (8-12.5 km). OH and HO_2 were detected by laser induced fluorescence with a 50% uncertainty [*Brune et al.*, this issue]. OH was measured between April 20 and May 15, 1996. Simultaneous HO_2 observations became available starting May 2. The steady state model generally underestimates the observed HO_2 and OH. The level of agreement varies on a flight to flight basis: the mean ratio of observed-to-modeled HO_2 ranged between 0.85 and 3.6. For OH this mean ratio ranged between 0.75 and 2.8. Much better agreement was found for the HO_2/OH ratio, which reflects rapid cycling between OH and HO_2 driven principally by CO and NO. Simulated HO_2/OH ratios were generally within 20-30% of the observations [*Brune et al.*, this issue]. During a few flights, air with a strong stratospheric signature was sampled (O_3 > 300 ppbv). On these occasions, observed and modeled HO_x were within 10-30% of each other.

The primary sources of HO_x in the diel steady state model include the reaction of $O(^1D)$ with water vapor and, in the upper troposphere, acetone photolysis [*Singh et al.*, 1995]. For the conditions of SUCCESS, acetone photolysis becomes an important primary source of HO_x when water vapor falls below 100 ppmv. The average water vapor mixing ratio measured above 10 km during SUCCESS was 60 ppmv. Thus, not including acetone results in even larger underpredictions of the observed HO_x than shown in Figure 1 [*Brune et al.*, this issue]. The uncertainty associated with the acetone concentrations in SUCCESS is buffered by the quadratic loss of HO_x through the reaction $OH+HO_2$. If the actual acetone concentrations were a factor of two larger than assumed (average of 1100 pptv instead of 550 pptv), the resulting HO_x concentrations would be at most 50% larger than in the calculations presented here. This would still be lower than observed.

Our analysis of the NO_x data in SUCCESS [*Jaeglé et al.*, this issue] shows that convection of boundary layer air frequently supplied fresh NO_x to the upper troposphere, resulting in observed NO_x/NO_y concentrations ratios higher than predicted from chemical steady state. Convection of boundary layer air can also supply elevated levels of peroxides (CH_3OOH and H_2O_2) and carbonyls (CH_2O) to the upper troposphere [*Prather and Jacob*, 1997]. Our previous analysis of HO_x measurements made during the STRAT campaign over the North Pacific identified convective injection of peroxides as a potential major source of HO_x in the upper troposphere [*Jaeglé et al.*, 1997].

No observations of peroxides or carbonyls were made during SUCCESS. Our model calculations, assuming these species to be in a chemical steady state defined by the primary sources of HO_x from water vapor and acetone, yield mean concentrations of H_2O_2, CH_3OOH and CH_2O at 10-12 km altitude of 135 ± 110 pptv, 40 ± 36 pptv, and 25 ± 8 pptv respectively. These values can be compared to typical boundary layer concentrations over the United States for that time of year of 400-2800 pptv H_2O_2 [*Boatman et al.*, 1989], 400-700 pptv CH_3OOH [*Hewitt and Kok*, 1991], and the 500-2700 pptv CH_2O [*Hastie et al.*, 1993; *Harris et al.*, 1989]. The boundary layer concentrations are one order of magnitude higher than the steady state model values in the upper troposphere. Convective injection of boundary layer air could thus be expected to provide a major source of peroxides and CH_2O, and consequently of HO_x, in the upper troposphere. Although H_2O_2 is highly water-soluble and would be efficiently scavenged by the precipitation associated with deep convection, CH_3OOH and CH_2O are only sparingly soluble [*Betterton*, 1992] and would escape scavenging. Using the HO_x yields per molecule calculated by *Prather and Jacob* [1997], we find that convective injection of CH_2O could be a source of HO_x comparable to CH_3OOH.

The highest levels of OH in the upper troposphere during SUCCESS were measured on the May 8 flight as the DC-8 sampled the anvil of an active convective system over Wisconsin at an altitude of 11 km. Figure 2 shows the observations of OH, HO_2, NO, NO_y, and condensation nuclei (CN) obtained for this flight as the aircraft flew in and around the anvil. Air impacted by convection is evidenced by high levels of CN (> 1000 cm^{-3}) on three occasions along the flight track: 12.9-13.05 hours, 13.7-14.1 hours, and 14.3-14.4 hours. Observations of simultaneously enhanced NO show that convection was accompanied by lightning. This is particularly evident for the second event between local times 13.7 and 14.1 hours, as the aircraft was flying above the anvil: the high levels of NO, up to 1.8 ppbv, represented most of NO_y (NO/NO_y = 0.7 mol/mol). CO was only moderately enhanced during this period (120 ppbv compared to a background of 100 ppbv), which indicates that lightning rather than convec-

tively pumped pollution was the source of elevated NO. Note the high NO_y concentrations measured between times 13.05 and 13.2 hours, with relatively low NO. Stratospheric air was sampled on that occasion: high concentrations of O_3, and low concentrations of N_2O and CH_4 were simultaneously observed.

Observed concentrations of OH and HO_2 show considerable variability along the flight track (Figure 2). Part of this variability is due to changes in NO and thus in the HO_2/OH ratio, and part of it can also be due to changes in the UV flux as the aircraft flew in the vicinity of the anvil. Also shown in the figure are the diel steady state model calculations along the flight track. While the model calculations are within 10-40% of the observations between times 13.0 and 13.7 hours, above the anvil (13.7-14.1 hours) they underestimate OH by a factor of 2 and HO_2 by a factor of 4. Adding 500-1000 pptv of $CH_3OOH+H_2O_2+CH_2O$ to the model (compared to 20-200 pptv at steady state) can reconcile model and observations. As noted earlier, observations in the boundary layer show 1300-6200 pptv of $CH_3OOH+H_2O_2+CH_2O$. Thus in order to account for the observed HO_x levels, less than a 20% fraction of these peroxides needs to have been transported to the upper troposphere through the convective event. We conclude that the frequent convective injection of peroxides and formaldehyde is a tenable explanation to account for the high levels of HO_x observed on May 8 and on other flights in SUCCESS.

Ozone Production

The net ozone production in the upper troposphere is given to a close approximation by (e.g. *Davis et al.*, 1996):

$$P(O_3)\text{-}L(O_3) = k_2\,[NO][HO_2] - \left(k_3\,[O(^1D)][H_2O] + k_4\,[HO_2][O_3] + k_5\,[OH][O_3] \right) \quad (1)$$

where k_2, k_3, k_4, and k_5 are the rate constants for the reactions

$$NO + HO_2 \rightarrow NO_2 + OH \quad (2)$$

$$O(^1D) + H_2O \rightarrow 2\,OH \quad (3)$$

$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \quad (4)$$

$$OH + O_3 \rightarrow HO_2 + O_2\,. \quad (5)$$

The source of ozone from reactions of peroxy radicals (RO_2) with NO is neglected in equation (1) because it makes only a small contribution to ozone production in the upper troposphere [*Davis et al.*, 1996]. When we compare the results from equation (1) to the more complete ozone production rates calculated in our 0-D model, we find that agreement is better than 20%. In the upper troposphere, the ozone loss from reactions (3)-(5) is generally less than 20% of the ozone production from reaction (2).

From equation (1) we calculate the instantaneous net ozone production along the SUCCESS flight tracks solely on the basis of the observed NO, HO_2, OH, O_3 and H_2O concentrations; we then scale these instantaneous rates to 24-hour average values by using the relationship between instantaneous and 24-hour average rates as calculated from the 0-D model. The resulting ozone production rates are shown in Figure 3 (red circles) as a function of the local NO_x concentrations (measured NO plus model-calculated NO_2). Observations made in fresh aircraft exhaust plumes (CO_2 > 368 ppmv and NO > 300 pptv) and in the stratosphere (N_2O < 310 ppbv and O_3 > 100 ppbv) were excluded from this figure. Ozone production rates calculated from the 0-D diel steady state model (blue pluses) are shown for comparison. The dashed line in Figure 3 (case 1) shows the calculated dependence of the net ozone production on NO_x for a set of steady state cal-

culations where all model input variables were specified from average conditions observed in SUCCESS at 11 km (O_3 = 65 ppbv; H_2O = 60 ppmv; CO = 120 ppbv; CH_4 = 1750 ppbv; temperature = 217 K). The mean acetone concentration used was 510 pptv. For comparison, we also show the net ozone production for calculations without the source of HO_x from acetone (dotted line in Figure 3, case 0).

As we saw in the previous section the 0-D model generally underestimates the HO_x observations possibly because of a missing source from convective injection of peroxides and CH_2O. The solid line in Figure 3 (case 2) shows model results for the previously described average conditions but with added convective sources of $1x10^4$ molecules $cm^{-3}s^{-1}$ H_2O_2, $4x10^4$ molecules $cm^{-3}s^{-1}$ CH_3OOH, and $4 x10^4$ molecules $cm^{-3}s^{-1}$ CH_2O. These sources result in 2000-500 pptv of H_2O_2, 1000-150 pptv of CH_3OOH, and 90-120 pptv of CH_2O, depending on the levels of NO_x. These concentrations are higher than their steady state predicted values (H_2O_2: 210-10 pptv; CH_3OOH: 130-10 pptv, and CH_2O: 10-35 pptv).

Ozone production increases with increasing NO_x (NO_x-limited regime) up to a maximum NO_x value beyond which it decreases (NO_x-saturated regime). Whether ozone production is NO_x-limited or NO_x-saturated depends on the HO_x loss pathways. For high NO_x values, loss of HO_x mainly occurs through the formation of HNO_3 and HNO_4 followed by their reaction with OH. For lower NO_x values, loss of HO_x is dominated by the reaction of OH with HO_2.

Figure 3 shows that the high levels of observed HO_x, as compared to a standard photochemical model, result in more active ozone production and a steeper increase in ozone production for a given increase in NO_x. This dependence can be reproduced in our box model calculation for average SUCCESS conditions at 11 km by assuming a convective source of peroxides and CH_2O (case 2). As a result of the elevated levels of HO_x, the NO_x-limited regime is extended from 490 pptv (case 1) to 700 pptv of NO_x (case 2). In the study by *Brasseur et al.* [1996], the turnover point for NO_x in the upper troposphere was found to be at a lower value of 280 pptv. Neither acetone nor convective injection of peroxides and carbonyls were included in that study.

The mean NO_x mixing ratio observed in the upper troposphere during SUCCESS was 70 pptv, corresponding to an average net ozone production rate of 2 ppbv/day which is twice the rate calculated with the steady state model. Ozone production was NO_x-limited under all essentially all conditions encountered in SUCCESS. When the DC-8 sampled lightning affected air on May 8, we calculate very elevated ozone production rates (>8 ppbv day^{-1}, shown by arrows in Figure 3) based on the observed HO_x and NO. For this time interval, the steady state model predicts low ozone production because of NO_x-saturated conditions. It appears that the enhanced supply HO_x from convection increases the effectiveness of lightning NO_x as a source of ozone.

A more general picture of the dependence of ozone production on NO_x and HO_x production is shown in Figure 4. This figure was constructed by varying both the NO_x concentrations and the HO_x primary sources in the steady state model applied to the average SUCCESS conditions at 11 km altitude. The primary sources of HO_x include the $O(^1D)+H_2O$ reaction and the photolysis of acetone. In addition, we have added a varying source from convective injection of peroxides and formaldehyde. All these sources have been weighted by their yield in HO_x molecules. The three curves shown in Figure 3 (cases 0, 1, and 2) are reproduced in Figure 4. The HO_x yield from acetone is a strong function of NO, while the yields from $O(^1D)+H_2O$, H_2O_2, CH_3OOH, and CH_2O are relatively independent of NO. As a result, the

HO_x source in case 1, which is dominated by acetone, varies with NO_x even though the acetone mixing ratio remains constant.

The dashed-dotted line in the Figure separates the NO_x-limited and NO_x-saturated regimes. Over the range of HO_x source rates expected in the upper troposphere (10^3-$5x10^5$ molecules $cm^{-3}s^{-1}$), the turnover point between the two regimes varies between 350 and 1200 pptv of NO_x. Aircraft observations of NO_x in the upper troposphere worldwide [*Bradshaw et al.*, 1997] are consistently lower than these turnover points, indicating that ozone production is NO_x-limited. We also see from Figure 4 that ozone production in the upper troposphere is insensitive to the supply of HO_x when NO_x is below 30 pptv. Such low values are rarely observed in the upper troposphere except in the outflow of deep marine convection in the tropics where lightning generally does not take place [*Bradshaw et al.*, 1997]. Enhancement of peroxides in the outflow of deep marine convection thus leads to little increase of ozone production [*Folkins et al.*, manuscript in preparation, 1997]. Considerable increase of ozone production may however be expected from enhanced peroxides and CH_2O in continental convection associated with lightning. Figure 4 illustrates how our ability to model the extent of human influence on ozone in the upper troposphere relies on how well we simulate the levels of both NO_x and HO_x.

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Figure 1. Comparison between observations and steady state model calculations of HO_2 and OH mixing ratios for the SUCCESS flights between April 20 and May 15, 1996 in the upper troposphere (8-12.5 km altitude). The model was sampled at the time of day of the observations. HO_2 data was only available for the May flights. Also shown are the 1:1 lines. Observations in aircraft exhaust plumes have been excluded from this figure.

Figure 2. Data from a SUCCESS flight in and around a mesoscale convective system over Wisconsin on May 8, 1996. The altitude varied between 11 and 12 km. Observations of (a) condensation nuclei, (b) NO (solid circles) and NO_y (pluses), (c) OH and (d) HO_2. are shown along the flight track as a function of local time. Steady state model calculations (solid lines) are also shown for OH and HO_2.

Figure 3. Net ozone production (24-hour average) as a function of NO_x above 8 km: comparison between steady state point model calculations (blue pluses) and observations (red solid circles). The observed rates were computed from measured concentrations of HO_2, OH, and NO, and scaled to 24-hour average

values using diel factors from the photochemical model (see text). Observations made in fresh aircraft exhaust plumes and in the stratosphere are excluded from this figure. The three curves show model calculations for average conditions during SUCCESS at 11 km, assuming different levels of HO_x source. The dashed line (case 1) assumes the peroxides and formaldehyde to be at steady state, while the solid line (case 2) assumes a convective source of peroxides and formaldehyde. The dotted line (case 0) is the same as case 1 but without production of HO_x from acetone photolysis. The NO_x concentration is the sum of observed NO and model-calculated NO_2 (chemical steady state).

Figure 4. Contour plot of 24-hour average ozone production (in ppbv day^{-1}) in the upper troposphere as a function of the NO_x concentrations and the primary HO_x production rate. Primary HO_x production includes the sources from $O(^1D)+H_2O$, acetone photolysis, and deep convective injection of peroxides and carbonyls. These sources have been weighted by their yields in HO_x molecules. The O_3 production rates were calculated from equation (1) with a 0-D model for average conditions during SUCCESS at 11 km altitude. The three model cases shown in Figure 3 are reproduced here as dotted (case 0), solid (case 1), and dashed lines (case 2). The transition between the NO_x-limited and NO_x-saturated regimes is shown by the dashed-dotted line.

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