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


Abstract. The sources of HOx (OH+peroxy radicals) and the associated production of ozone at 8-12 km over the United States are examined by modeling observations of OH, HO2, NO, and other species during the SUCCESS aircraft campaign in April-May 1996. The HOx 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 (CH3OOH and H2O2) and formaldehyde (CH2O) from the boundary layer to the upper troposphere could resolve this discrepancy. More generally, the data collected over the central United States during SUCCESS suggest that local convection was a major source of HOx and NOx to the upper troposphere. The OH and HO2 observations together with the observations of NO allow us to directly calculate the ozone production in the upper troposphere and its dependence on NOx. 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 NOx-limited under essentially all the conditions encountered in SUCCESS. The high levels of HOx present in the upper troposphere stimulate ozone production and increase the sensitivity of ozone to NOx 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 (NOx=NO+NO2) and hydrogen oxide radicals (HOx=OH+peroxy radicals). There is at present considerable interest in understanding the effects of increasing aircraft NOx emissions on ozone in the upper troposphere [Schumann, 1995; National Aeronautics and Space Administration, 1997]. Depending on the relative supply of NOx and HOx in the upper troposphere, an increase in NOx may cause either an increase or a decrease in ozone [Brasseur et al., 1996].

In this paper we analyze the first concurrent measurements of HOx [Brune et al., this issue] and NOx [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 HOx concentrations in the upper troposphere by comparing a photochemical model to the SUCCESS data. We use the combination of HOx and NOx measurements to quantify ozone production in the upper troposphere and assess its sensitivity to anthropogenic NOx. A companion paper [Jaegle et al., this issue] focuses on the origin and chemical cycling of NOx.

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 O3, CO, NO, H2O, CH4, pressure, temperature, UV radiation, 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 ppbv (average of 550 ppbv). 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 NOx (= NO+NO2+NOy+2NOy+HNO2+2NOy+HNO3) is also assumed constant and is calculated iteratively in the model to match the observed NO at the time of day of the observations. The model calculates the diel steady state concentrations of 30 species including HO2, OH, O(D), CH3O, CH2O, NO, NO2, NO3, HNO2, HNO3, HNO4, PAN, and other photochemical intermediates (H2O, CH2OH, and CH2O) 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 NO2 photolysis rate (JNO2(Eppley)) derived from the Eppley UV radiometer instrument on-board the DC-8 [Madronich, 1987]. All the clear sky photolysis rates are scaled by JNO2(Eppley)/JNO2(clear), where JNO2(clear) is the clear sky NO2 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, JNO2(Eppley) and JNO2(clear) are within 10% of each other. Because the DC-8 often flew in the vicinity of clouds, the ratio of JNO2(Eppley)/JNO2(clear) ranged between 0.5 and 2.5, the mean being 1.3.
HO₂ in the Upper Troposphere

Figure 1 shows a comparison between observations and diel steady state model calculations of the OH and HO₂ mixing ratios in the upper troposphere (8-12.5 km). OH and HO₂ 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 HO₂ observations became available starting May 2. The steady state model generally underestimates the observed HO₂ and OH. The level of agreement varies on a flight to flight basis: the mean ratio of observed-to-modeled HO₂ 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 HO₂/OH ratio, which reflects rapid cycling between OH and HO₂ driven principally by CO and NO. Simulated HO₂/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 (O₃ > 300 ppbv). On these occasions, observed and modeled HO₂ were within 10-30% of each other.

The primary sources of HO₂ 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 HO₂ 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 HO₂ 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 HO₂ through the reaction OH + HO₂ → H₂O + O. If the actual acetone concentrations were a factor of two larger than assumed (average of 1100 pptv instead of 550 pptv), the resulting HO₂ concentrations would be at most 50% larger than in the calculations presented here. This would still be lower than observed.

Our analysis of the NO₃ data in SUCCESS [Jaegle et al., this issue] shows that convection of boundary layer air frequently supplied fresh NO₃ to the upper troposphere, resulting in observed NO₃/NOₓ concentrations ratios higher than predicted from chemical steady state. Convection of boundary layer air can also supply elevated levels of peroxydes (CH₃OOH and H₂O₂) and carbonyls (CH₂O) to the upper troposphere [Prather and Jacob, 1997]. Our previous analysis of HO₂ measurements made during the STRAT campaign over the North Pacific identified convective injection of peroxydes as a potential major source of HO₂ in the upper troposphere [Jaegle et al., 1997].

No observations of peroxydes 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 HO₂ from water vapor and acetone, yield mean concentrations of H₂O₂, CH₃OOH and CH₂O 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 H₂O₂ [Boatman et al., 1989], 400-700 pptv CH₃OOH [Hewitt and Kok, 1991], and the 500-2700 pptv CH₂O [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 peroxydes and CH₂O, and consequently of HO₂, in the upper troposphere. Although H₂O₂ is highly water-soluble and would be efficiently scavenged by the precipitation associated with deep convection, CH₃OOH and CH₂O are only sparingly soluble [Bertlton, 1992] and would escape scavenging. Using the HO₂ yields per molecule calculated by Prather and Jacob [1997], we find that convective injection of CH₂O could be a source of HO₂ comparable to CH₃OOH.

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, HO₂, NO, NOₓ, 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 NOₓ (NO/NOₓ ≈ 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 convectively pumped pollution was the source of elevated NO. Note the high NO, NOₓ concentrations measured between times 13.05 and 13.2 hours, with relatively low NO. Stratospheric air was sampled on that occasion: high concentrations of O₃, and low concentrations of N₂O and CH₄ were simultaneously observed.
Figure 3. Net ozone production (24-hour average) as a function of NOx above 8 km: comparison between steady state point model calculations (blue plus) and observations (red solid circles). The observed rates were computed from measured concentrations of HO2, OH, NOx, and H2O 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 NOx 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 HOx from acetone photolysis. The NOx concentration is the sum of observed NO and model-calculated NO2 (chemical steady state).

Observed concentrations of OH and HOx show considerable variability along the flight track (Figure 2). Part of this variability is due to changes in NO and thus in the HOx/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 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 HOx by a factor of 4. Adding 500-1000 pptv of CH3OOH+H2O2+CH2O 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 CH3OOH+H2O2+CH2O. Thus in order to account for the observed HOx levels, less than 20% 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 HOx 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):

\[
P(O_2)-L(O_2) = k_2[NO][H_2O] - (k_3[O(D)][H_2O] + k_4[HO_2][O_3] + k_5[OH][O_3]) \tag{1}
\]

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

\[
\begin{align*}
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \tag{2} \\
\text{O}_3(\text{D}) + \text{H}_2\text{O} & \rightarrow 2 \text{OH} \tag{3} \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2 \text{O}_2 \tag{4} \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \tag{5}
\end{align*}
\]

The source of ozone from reactions of peroxy radicals (RO2) 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).

The solid line in Figure 3 (case 1) shows the calculated dependence of the net ozone production on NOx for a set of steady state calculations where all model input variables were specified from average conditions observed in SUCCESS at 11 km \((\text{O}_3 = 65 \text{ ppbv}; \text{H}_2\text{O} = 60 \text{ ppmv}; \text{CO} = 120 \text{ ppbv}; \text{CH}_4 = 1750 \text{ ppbv}; \text{temperature} = 217 \text{ K})\). The mean acetone concentration used was 310 pptv. For comparison, we also show the net ozone production for calculations without the source of HOx from acetone (dotted line in Figure 3, case 0).

As we saw in the previous section, the 0-D model generally underestimates the HOx observations possibly because of a missing source from convective injection of peroxides and CH2O. The solid line in Figure 3 (case 2) shows model results for the previously described average conditions but with added convective sources of \(1 \times 10^8\) molecules cm\(^{-3}\) s\(^{-1}\) \(\text{H}_2\text{O}_2\), \(4 \times 10^8\) molecules cm\(^{-3}\) s\(^{-1}\) \(\text{CH}_3\text{OOH}\), and \(4 \times 10^8\) molecules cm\(^{-3}\) s\(^{-1}\) \(\text{CH}_2\text{O}\). These sources result in 2000-5000 pptv of \(\text{H}_2\text{O}_2\), 1000-1500 pptv of \(\text{CH}_3\text{OOH}\), and 90-120 pptv of \(\text{CH}_2\text{O}\), depending on the levels of...
NO	extsubscript{x}. These concentrations are higher than their steady state predicted values (H	extsubscript{2}O: 210-10 pptv; CH	extsubscript{3}OOH: 130-10 pptv, and CH	extsubscript{2}O: 10-35 pptv).

Ozone production increases with increasing NO	extsubscript{x} (NO	extsubscript{x}-limited regime) up to a maximum NO	extsubscript{x} value beyond which it decreases (NO	extsubscript{x}-saturated regime). Whether ozone production is NO	extsubscript{x}-limited or NO	extsubscript{x}-saturated depends on the NO	extsubscript{x} loss pathways. For high NO	extsubscript{x} values, loss of HO	extsubscript{x} mainly occurs through the formation of HONO and HNO	extsubscript{2} followed by their reaction with OH. For lower NO	extsubscript{x} values, loss of HO	extsubscript{x} is dominated by the reaction of OH with HO	extsubscript{2}.

Figure 3 shows that the high levels of observed HO	extsubscript{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	extsubscript{x}. This dependency can be reproduced in our box model calculation for average SUCCESS conditions at 11 km by assuming a convective source of peroxides and CH	extsubscript{2}O (case 2). As a result of the elevated levels of NO	extsubscript{x}, the NO	extsubscript{x}-limited regime is extended from 490 pptv (case 1) to 700 pptv of NO	extsubscript{x} (case 2). In the study by Brasseur et al. [1996], the turnover point for NO	extsubscript{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	extsubscript{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	extsubscript{x}-limited under essentially all conditions encountered in SUCCESS. When the DC-8 sampled lightning affected air on May 8, we calculated a very elevated ozone production rates (>8 ppbv day	extsuperscript{-1}, shown by arrows in Figure 3) based on the observed HO	extsubscript{x} and NO	extsubscript{x}. For this time interval, the steady state model predicts low ozone production rates because of NO	extsubscript{x}-saturated conditions. It appears that the enhanced supply HO	extsubscript{x} from convection increases the effectiveness of lightning NO	extsubscript{x} as a source of ozone.

A more general picture of the dependence of ozone production on NO	extsubscript{x} and HO	extsubscript{x} production is shown in Figure 4. This figure was constructed by varying both the NO	extsubscript{x} concentrations and the HO	extsubscript{x} primary sources in the steady state model applied to the average SUCCESS conditions at 11 km altitude. The primary sources of HO	extsubscript{x} include the O(1D)+H	extsubscript{2}O 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	extsubscript{x} molecules. The three curves shown in Figure 3 (cases 0, 1, and 2) are reproduced in Figure 4. The HO	extsubscript{x} yield from acetone is a strong function of NO	extsubscript{x}, while the yields from O(1D)+H	extsubscript{2}O, H	extsubscript{2}O	extsubscript{2}, CH	extsubscript{3}OOH, and CH	extsubscript{2}O are relatively independent of NO	extsubscript{x}. As a result, the HO	extsubscript{x} source in case 1, which is dominated by acetone, varies with NO	extsubscript{x} even though the acetone mixing ratio remains constant.

The dashed-dotted line in the Figure separates the NO	extsubscript{x}-limited and NO	extsubscript{x}-saturated regimes. Over the range of NO	extsubscript{x} source rates expected in the upper troposphere (10	extsuperscript{3}-5x10	extsuperscript{7} molecules cm	extsuperscript{-2} s	extsuperscript{-1}), the turnover point between the two regimes varies between 350 and 1200 pptv of NO	extsubscript{x}. Aircraft observations of NO	extsubscript{x} in the upper troposphere worldwide [Bradshaw et al., 1997] are consistently lower than these turnover points, indicating that ozone production is NO	extsubscript{x}-limited. We also see from Figure 4 that ozone production in the upper troposphere is insensitive to the supply of HO	extsubscript{x} when NO	extsubscript{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	extsubscript{2}O in continental convection associated with lightning and/or injection of polluted surface air.

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