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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 Craft 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 [Jaeglé 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 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 NOx (= NO+NOy+NO2+2N2O5 +HNO2+HNO4) 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, and other photochemical intermediates (H2O2, CH3OH, and CH4) 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.
HOx in the Upper Troposphere

Figure 1 shows a comparison between observations and diel steady state model calculations of the HOx and OH 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 HOx 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 HOx when water vapor falls below 100 ppmv. The average water vapor mixing ratio measured above 10 ppmv. Stratospheric signatures were sampled (O3 > 300 ppbv). On these occasions, observed and modeled HO2 were within 10-30% of each other.

No observations of peroxides or carbonyls were made during SUCCESS. Our previous analysis of HO2, NOx, NOy, and condensation nuclei (CN) obtained for this flight as the aircraft flew in and around the anvil [Jaegle et al., 1997]. Air impacted 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 measured NO show that convection was accompanied by lightening. This is particutafiy evident for the second event between 13.7-14.1 hours, with relatively low NO. Stratospheric air was sampled on that occasion: high concentrations of O3, and low concentrations of NOx and CH4 were simultaneously observed.
Observed concentrations of OH and HO₂ show considerable variability along the flight track (Figure 2). Part of this variability is due to changes in NO and thus in the HO₂/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 (Figure 2), they underestimate OH by a factor of 2 and HO₂ 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 calculations (blue pluses) and observations (red solid circles). The dashed-dotted line (case 1) assumes the peroxy radicals and formaldehyde to be at steady state, while the solid line (case 2) assumes a convective source of peroxy radicals and formaldehyde. The dotted line (case 0) is the same as case 1 but without production of HO₂ from acetone photolysis. The NO concentration is the sum of observed NO and model-calculated NO₂ (chemical steady state).

Ozone Production

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

\[ \text{P(} \Delta \text{O}_3) = k_1 [\text{NO}][\text{HO}_2] - (k_2 [\text{O}^{1}\text{D})][\text{H}_2\text{O}] + k_4 [\text{HO}_2][\text{O}_3] + k_5 [\text{OH}][\text{O}_3]) \]  

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

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]  

\[ \text{O}^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \]  

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2 \]  

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  

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).

From equation (1) we calculate the instantaneous net ozone production along the SUCCESS flight tracks solely on the basis of the observed NO, HO₂, OH, O₃, and H₂O concentrations (and model calculated concentrations of O(¹D)); 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 NOX concentrations (measured NO plus model-calculated NO₂). Observations made in fresh aircraft exhaust plumes (CO₂ > 368 ppmv and NO > 300 pptv) and in the stratosphere (N₂O < 310 ppbv and O₃ > 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 NOX for a set of steady state calculations where all model input variables were specified from average conditions observed in SUCCESS at 11 km (O₃ = 65 ppbv; H₂O = 60 ppmv; CO = 120 ppbv; CH₄ = 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 HO₂ from acetone (dotted line in Figure 3, case 0).

As we saw in the previous section, the 0-D model generally underestimates the HO₂ observations possibly because of a missing source from convective injection of peroxy radicals 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 1x10⁶ molecules cm⁻³ s⁻¹ H₂O₂, 4x10⁶ molecules cm⁻³ s⁻¹ CH₃OOH, and 4x10⁶ molecules cm⁻³ s⁻¹ CH₂O. These sources result in 2000-500 pptv of H₂O₂, 1000-150 pptv of CH₃OOH, and 90-120 pptv of CH₂O, 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 NO_x loss pathways. For high NO_x values, loss of NO_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 NO_x is dominated by the reaction of OH with NO_x.

Figure 3 shows the high levels of observed NO_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 NO_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 Brassere 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 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 NO_x and HO. For this time interval, the steady state model predicts low ozone production rates because of NO_x-saturated conditions. It appears that the enhanced supply of NO_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(3P)+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_x, while the yields from O(3P)+H_2O, H_2O_2, CH_3OOH, and CH_2O are relatively independent of NO_x. 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 NO_x source rates expected in the upper troposphere (10^7-5x10^7 molecules cm^-2 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 and/or injection of polluted surface air.

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