Observed OH and HO2 in the upper troposphere suggest a major source from convective injection of peroxides

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Abstract. ER-2 aircraft observations of OH and HO2 concentrations in the upper troposphere during the NASA/STRAT campaign are interpreted using a photochemical model constrained by local observations of O3, H2O, NO, CO, hydrocarbons, albedo and overhead ozone column. We find that the reaction O1(D) + H2O is minor compared to acetone photolysis as a primary source of HOx (= OH + peroxy radicals) in the upper troposphere. Calculations using a diel steady state model agree with observed HOx concentrations in the lower stratosphere and, for some flights, in the upper troposphere. However, for other flights in the upper troposphere, the steady state model underestimates observations by a factor of 2 or more. These model underestimates are found to be related to a recent (< 1 week) convective origin of the air. By conducting time-dependent model calculations along air trajectories determined for the STRAT flights, we show that convective injection of CH3OOH and H2O2 from the boundary layer to the upper troposphere could resolve the discrepancy. These injections of HOx reservoirs cause large HOx increases in the tropical upper troposphere for over a week downwind of the convective activity. We propose that this mechanism provides a major source of HOx in the upper troposphere. Simultaneous measurements of peroxides, formaldehyde and acetone along with OH and HO2 are needed to test our hypothesis.

Introduction

The central role of OH (hydroxyl radical) and HO2 (hydroperoxy radical) in the troposphere has long been recognized [Levy, 1972; Crutzen, 1973; Logan et al., 1981], however it is only in recent years that direct measurements of these short-lived molecules have been made [see review by Clessey, 1995]. In the troposphere, OH is the key agent in the atmosphere's oxidizing capacity, regulating the lifetime of a large number of anthropogenic and natural compounds [Thompson, 1992]. In the upper troposphere, knowledge of the factors controlling HOx (= OH + peroxy radicals) concentrations is critical for assessing the effects of aircraft on ozone [Brasseur et al., 1996], and the resulting greenhouse radiative forcing [Lacis et al., 1990].

In this paper we present a photochemical model analysis of the first measurements of OH and HO2 concentrations in the upper troposphere. These measurements were obtained as part of the STRAT (Stratospheric Tracers of Atmospheric Transport) ER-2 mission. We compare model and observations of HOx as a test of the complex set of reactions leading to the production and loss of O3 in the upper troposphere and contrast the upper troposphere to the lower stratosphere. Following the idea presented in Prather and Jacob [this issue], and previously proposed by Chatfield and Crutzen [1984], we examine the impact of deep convective transport of peroxides as a source of HOx in the upper troposphere.

Aircraft Mission and Photochemical Model

The STRAT mission took place in five successive deployments between 1995 and 1996 out of northern California and Hawaii. In the flights discussed here, NASA's ER-2 aircraft sampled the atmosphere between 4 and 21 km, the majority of observations being in the 8-21 km altitude range. Extensive measurements of OH and HO2 were obtained in the upper troposphere and lower stratosphere using laser induced fluorescence [Wennberg et al., 1995], with a measurement uncertainty of about 30%.

In this study, we compare the observed OH and HO2 concentrations to results from the Harvard 0-D photochemical model applied to diel steady state calculations and to initial-value calculations along trajectories. The model is constrained with local observations (averaged over 1-minute intervals) of O3, H2O, NO, CO, CH4, ethane, propane, butane, aerosol surface area, ozone column, albedo, temperature and pressure along the ER-2 flight track (see Fahey et al. [1995] for a description of the ER-2 payload). "Diel steady state" is defined by reproducibility of concentrations in the model over a 24-hour solar cycle. NOx (NO+NO2+NO3+2N2O5+HNO2+HNO3) is assumed to be constant during the day and is adjusted such that the model matches the observations of NO at the time of day of the observations. When no measurements are available for the hydrocarbons, observed correlations between CO and these hydrocarbons from other flights are used. Acetone was not measured during STRAT and is specified in the troposphere from its correlation with CO observed during the DC-8 mission PEM-West B [McKeen et al., this issue] over the Pacific between 4 and 12 km. In the lower stratosphere, at altitudes for which CO values are below 20 ppbv, acetone is assumed to be present in negligible concentrations because of its relatively short lifetime (10-15 days).

Photolysis rates are computed using a six-stream radiative transfer model for the Rayleigh scattering atmosphere constrained with the observed ozone column and albedo. The model reproduces the on-board radiometer observations [McElroy, 1995] of the NO2 photolysis rate to within 10% in all cases. Agreement with observations for photolysis of O3 to O1(D) is generally within 30%.

The Harvard photochemical model includes comprehensive descriptions of tropospheric and stratospheric chemistry. Bromine and chlorine chemistry are taken into account, as well as heterogeneous chemistry of N2O5, BrONO2, ClONO2, HOCI and HCl. The chemical mechanism is described in Jacob et al. [1996] and Michelsen et al. [1996]. The photolysis of acetone is computed using recent measurements of the temperature-dependent cross-sections and pressure-dependent quantum yield [McKeen et al., this issue]. The model calculates the diel steady...
state concentrations of 50 species, including HO$_2$, OH, O(¹D), CH$_2$O, NO$_3$, species (NO$_2$, NO, N$_2$O$_5$, HNO$_3$, HNO$_4$, HNO$_2$, PAN), and other photochemical intermediates, in particular formaldehyde (CH$_2$O) and peroxides (H$_2$O$_2$ and CH$_3$OOH). Problems associated with the steady state assumption for peroxides will be a focus of discussion later in this paper.

**HO$_2$ Budget in the Upper Troposphere**

Figure 1 compares the observed HO$_2$ and OH mixing ratios to diel steady state model results for 15 flights in the upper troposphere and the lower stratosphere. Tropopause heights are based on temperature profiles measured from the ER-2 (B. Gary, personal communication), and range between 12 km (mid-latitudes) and 16 km (tropics). In the lower stratosphere, the model calculations are consistently within the uncertainties of the measurements (Figure 1, panels b and d). In the upper troposphere the model generally underestimates the observed HO$_2$, but not always: the mean ratio of observed to simulated mixing ratios for individual flights vary from 0.9 to 2.5 (mean of 1.5 for all flights). For some individual points, the model underestimates the observations by as much as a factor of 5. The ratio of HO$_2$/OH is well reproduced by the model (within 10-15% of observations) both in the troposphere [Hanisco et al., manuscript in preparation, 1997] and stratosphere [Cohen et al., 1994], indicating that the rapid interchange between these short-lived radicals is well understood.

Figure 2 shows the main reactions controlling production and loss of HO$_2$ in the upper troposphere for a flight on November 7, 1995, when the diel steady state model reproduces the observations well. We have excluded from this Figure the reactions cycling HO$_2$ with H$_2$O, CH$_3$OOH, HNO$_3$, HNO$_4$, HOCI, and HOBr, which we assume in the model to be at steady state. Primary sources of HO$_2$ include the O(¹D)+H$_2$O reaction and the photolysis of acetone. Photolysis of acetone yields two HO$_2$ molecules, and leads to production of CH$_2$O which can photolyze to yield additional HO$_2$, resulting in a total yield of about three HO$_2$ molecules per acetone molecule photolyzed [Singh et al., 1995]. The source of HO$_2$ from acetone photolysis shown in Figure 2 is based on this total yield as computed in the model. The secondary HO$_2$ source from CH$_2$O photolysis in Figure 2 is mainly from the oxidation of CH$_4$ by OH; it excludes the contribution from CH$_2$O produced by decomposition of acetone since this contribution is accounted for as part of the primary source from acetone photolysis. Because CH$_2$O originates from HO$_2$ reactions, and is at chemical steady state in the model, we view it as a secondary source of HO$_2$.

A remarkable feature of Figure 2 is the relative unimportance of water vapor as a local source of HO$_2$ in the upper troposphere. The upper troposphere is characterized by low humidity compared to the lower troposphere, and by low ozone levels compared to the lower stratosphere. As a result, the rate of O(¹D)+H$_2$O shows a pronounced minimum in the upper troposphere. By contrast, the source of HO$_2$ from acetone photolysis shows little variation with altitude in the troposphere (Figure 2), and dominates over O(¹D)+H$_2$O as a primary source of HO$_2$ in the upper troposphere. Loss of HO$_2$ is dominated by the OH+HO$_2$ reaction and is therefore quadratic which damps the response of HO$_2$ to changes in the HO$_2$ sources. Not including the acetone source in the upper troposphere would result in predicted HO$_2$ concentrations a factor of two lower than those shown in Figure 1. Further discussion of the importance of acetone is given by McKeen et al. [this issue].

**The Influence of Convection**

Data for some flights in Figure 1 show major discrepancies between observed HO$_2$ concentrations and diel steady state model results. Isentropic back-trajectories using GEOS-1 assimilation data [Schoeberl et al., 1991] show that the flights with the largest discrepancies sampled air a few days downstream of either deep convective complexes over the western tropical Pacific (February 8 and August 3, 1996) or mid-latitude cyclonic storms over the
The presence of these systems is evident in GOES-9/GMS-5 infrared satellite images. The recent boundary layer origin of the air on these flights is also evident from high levels of condensation nuclei (CN), low levels of ozone, and enhanced concentrations of CH$_3$I. In contrast, for the flights where the diel steady state model reproduces observed HO$_3$ concentrations to within measurement uncertainty (October 31, November 5, and November 7, 1995; February 13 and July 30, 1996) isentropic back-trajectories and the satellite images show no recent storm disturbances for the air sampled by the aircraft.

The largest discrepancy is found for the February 8, 1996 sunrise flight over Hawaii. Figure 3 shows the evolution of the observed concentrations of HO$_3$ as a function of solar time. The diel steady state model values are 3-5 times too high. Five-day isentropic back-trajectories for the February 8 flight are shown in Figure 4 together with the GOES-9/GMS-5 data. The air sampled by the ER-2 originated from a region of intense convective activity over the western equatorial Pacific about 3 days before the observation time. The low mixing ratios of ozone measured on this flight between 11 and 14 km (20 ppbv), combined with elevated concentrations of CN (1000-2000 cm$^{-3}$, see Figure 3), relatively high levels of CH$_3$I (0.15 ppbv) and low levels of NO$_3$ (10-20 ppbv) identify a recent marine boundary layer origin for the air. Water vapor was relatively low (30-50 ppmv), as would be expected if the air had been pumped to the tropical tropopause and then subsided over the $\sim$3 days prior to sampling by the aircraft.

In a companion paper, Prather and Jacob [this issue] propose that convective injection of CH$_3$OOH, H$_2$O$_2$, and CH$_2$O from the boundary layer provides a major source of HO$_3$ in the tropical upper troposphere. H$_2$O$_2$ is expected to be scavenged by precipitation during deep convection because of its high solubility in water, but CH$_3$OOH and CH$_2$O are far less soluble [Bettermore, 1992] and should escape scavenging.

Measurements of peroxides over the western equatorial Pacific were taken in February 1994 during the PEM-West B mission, which used a DC-8 aircraft with a ceiling of 12 km altitude [Heiker et al., 1996]. These data at 15$^\circ$N-10$^\circ$S show mean concentrations at 8-12 km altitude (CH$_3$OOH: 90 ppbv; H$_2$O$_2$: 230 pptv) much lower than in the marine boundary layer (CH$_3$OOH: 1010 pptv; H$_2$O$_2$: 810 pptv). Enhanced concentrations of peroxides at 8-12 km altitude (mean values of 530 $\pm$ 120 pptv for CH$_3$OOH and 445 $\pm$ 145 pptv for H$_2$O$_2$) were observed in air of recent convective origin, as diagnosed by elevated concentrations of dimethyl sulfide (> 3 pptv). CH$_2$O was not measured during PEM-West B, but data collected in the marine tropical boundary layer indicate levels of 100-400 pptv [Arlander et al., 1990]. Assuming a dilution factor for CH$_2$O in deep convection similar to that for CH$_3$OOH, we estimate typical CH$_2$O concentrations of 50-200 pptv in outflow from deep convection in the tropics.

We conducted time-dependent 0-D model calculations for individual air parcels traveling along the isentropic trajectories of Figure 4, using as initial conditions for peroxides and CH$_2$O the concentrations previously mentioned for convective outflows. Concentrations of O$_3$, H$_2$O, NO$_3$, CO, and acetone were conserved along the trajectories and assigned on the basis of the ER-2 observations. We considered an upper-bound case (A) with initial concentrations of 650 pptv CH$_3$OOH, 590 pptv H$_2$O$_2$, and 200 pptv CH$_2$O; and a lower-bound case (B) with initial concentrations of 410 pptv CH$_3$OOH, 50 pptv H$_2$O$_2$, and 50 pptv CH$_2$O. Case B assumes quantitative scavenging of H$_2$O$_2$ in deep convection. Results in Figure 3 show factors of 2-5 enhancement of HO$_3$ concentrations in the trajectory model relative to the diel steady state model values after 3 days of aging in the upper troposphere. The trajectory calculations for cases A and B bracket the observations and capture the steep rise in HO$_3$ after sunrise, in contrast to the diel steady state calculation. The improved simulation of the early morning rise of HO$_3$ reflects the enhanced concentrations of peroxides, which photolyze at longer wavelengths than O$_3$ ($\rightarrow$O(1D)) or acetone. Note that even if H$_2$O$_2$ were efficiently scavenged during convective pumping (case B), we find that CH$_3$OOH photolysis can still sustain high levels of OH and HO$_3$. In either case, A or B, the convected CH$_2$O is relatively insignificant as a source of HO$_3$, in accord with the calculations of Prather and Jacob [this issue].

Once the aircraft climbs above 14 km (after 8 solar time), water vapor, CN (top panel in Figure 3) and CH$_3$I decrease sharply and the diel steady state calculations are in better agreement with the observations while the trajectory calculations overpredict HO$_3$. The very different tracer levels suggest a different origin for the air above 14 km, not affected by convection.

The potential importance of convective injection of peroxides as a global source of HO$_3$ in the upper troposphere depends on the characteristic decay time for the HO$_3$ perturbation following a convective event. This characteristic time is defined by the lifetime of the chemical family HO$_y$ (= HO$_3$ + HNO$_4$ + HNO$_3$ + peroxides) which accounts for HO$_3$ recycling from its short-lived reservoirs including peroxides. Figure 5 shows the evolution of HO$_3$, peroxides and formaldehyde obtained by the trajectory calculations.
Figure 5. Simulated mixing ratios of HO2, CH2O, CHOOH and H2O2 in the trajectory model calculation at 11 km altitude initialized with tropical convective outflow on February 4, intercepting the ER-2 flight track 3.5 days later on February 8, and extended another 10 days at the latitude of Hawaii. Simulations assuming upper-bound (solid line; case A) or lower-bound (dotted line; case B) enhancements of peroxide in the outflow are compared to a simulation where the peroxides are in diel steady state (dashed line).

culations starting on February 4 (3.5 days before the intercept with the ER-2) and ending 14 days later. The relaxation time for the HOx family is limited by the rate at which HOx is lost via the OH+HO2 and H2O2+OH reactions, which provide its main sinks. It takes more than 10 days after the injection of peroxides for HOx to return to its steady state level, corresponding to the lifetime of the HOx family (6 days) which is much longer than the individual lifetimes of the peroxides (1-3 days). Because this long relaxation time is comparable to the ten-day overturning rate of the tropical upper troposphere [Prather and Jacob, this issue], we conclude that convective injection of peroxides is globally important as a source of HOx in the upper troposphere. In addition to tropical deep convection, synoptic storms at mid-latitudes can play a similar role in supplying peroxides to the upper troposphere. Although the frequency of such disturbances would be lower than in the tropics, the perturbation to the HOx budget in the upper troposphere would take a longer time to decay at mid-latitudes reflecting the longer lifetime of the HOx family.

Further support for our hypothesis of a major convective contribution of peroxides to HOx levels in the upper troposphere is offered by previous observations of H2O2 and CH3OOH concentrations over the South Tropical Atlantic during TRACE-A [Jacob et al., 1996]. Diel steady state model calculations underestimated these two peroxides in the upper troposphere (8-12 km) by mean factors of 1.8 and 3.6 respectively, while agreement was much better at lower altitudes. A convective source for peroxides could account for this discrepancy. As in PEM-West B, particularly high concentrations of peroxides were measured during TRACE-A in deep convective outflows [Pickering et al., 1996].

Analysis of STRAT observations for OH and HOx thus indicates that convection can affect ozone production in the upper troposphere not only through the injection of NOx and hydrocarbons [Dickerson et al., 1987; Pickering et al., 1993], but also by the transport of peroxides, in particular CH3OOH. Our study points to the need for future aircraft missions to include measurements of OH, HOx, peroxides, CH2O and acetone in order to obtain a highly constrained analysis of the HOx budget in the upper troposphere.

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