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Observed OH and HO$_2$ in the upper troposphere suggest a major source from convective injection of peroxides


Abstract. ER-2 aircraft observations of OH and HO$_2$ concentrations in the upper troposphere during the NASA/STRAT campaign are interpreted using a photochemical model constrained by local observations of O$_3$, H$_2$O, NO, CO, hydrocarbons, albedo and overhead ozone column. We find that the reaction O(D) + H$_2$O is minor compared to acetone photolysis as a primary source of HO$_x$ (= OH + peroxy radicals) in the upper troposphere. Calculations using a diel steady state model agree with observed HO$_x$ 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 CH$_3$OOH and H$_2$O$_2$ from the boundary layer to the upper troposphere could resolve the discrepancy. These injections of HO$_x$ reservoirs cause large HO$_x$ 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 HO$_x$ in the upper troposphere. Simultaneous measurements of peroxides, formaldehyde and acetone along with OH and HO$_2$ are needed to test our hypothesis.

Introduction

The central role of OH (hydroxyl radical) and HO$_2$ (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 Crolsey, 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 HO$_x$ (= 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 HO$_2$ 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 HO$_x$ as a test of the complex set of reactions leading to the production and loss of O$_3$ 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 HO$_x$ 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 HO$_2$ 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 HO$_2$ 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 O$_3$, H$_2$O, NO, CO, CH$_4$, 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 cycle. NO$_x$ and HO$_x$ reservoirs is assumed to be present in negligible concentrations below 30%.

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 NO$_2$ photolysis rate to within 10% in all cases. Agreement with observations for photolysis of O$_3$ to O(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 N$_2$O$_5$, BrONO$_2$, ClONO$_2$, HOCl 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...
state concentrations of 50 species, including HO2, OH, O(1D), CH2O, NOx species (NO2, NO3, N2O5, HNO3, HNO4, HNO2, PAN), and other photochemical intermediates, in particular formaldehyde (CH2O) and peroxides (H2O2 and CH3OOH). Problems associated with the steady state assumption for peroxides will be a focus of discussion later in this paper.

**HOx Budget in the Upper Troposphere**

Figure 1 compares the observed HO2 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 HO2, but not always: the mean ratios 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 HO2/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 HOx 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 HOx with H2O2, CH3OOH, HNO2, HNO3, HNO4, HOC1, and HOB, which we assume in the model to be at steady state. Primary sources of HOx include the O(1D)+H2O reaction and the photolysis of acetone. Photolysis of acetone yields two HOx molecules, and leads to production of CH2O which can photolysze to yield additional HOx, resulting in a total yield of about three HO2 molecules per acetone molecule photolyzed [Singh et al., 1995]. The source of HOx from acetone photolysis shown in Figure 2 is based on this total yield as computed in the model. The secondary HOx source from CH2O photolysis in Figure 2 is mainly from the oxidation of CH4 by OH; it excludes the contribution from CH2O produced by decomposition of acetone since this contribution is accounted for as part of the primary source from acetone photolysis. Because CH2O originates from HOx reactions, and is at chemical steady state in the model, we view it as a secondary source of HOx.

A remarkable feature of Figure 2 is the relative unimportance of water vapor as a local source of HOx 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)+H2O shows a pronounced minimum in the upper troposphere. By contrast, the source of HOx from acetone photolysis shows little variation with altitude in the troposphere (Figure 2), and dominates over O(1D)+H2O as a primary source of HOx in the upper troposphere. Loss of HOx is dominated by the OH+HO2 reaction and is therefore quadratic which damps the response of OH and HO2 concentrations to changes in the HOx sources. Not including the acetone source in the upper troposphere would result in predicted HOx 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 HOx 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 ER-2. Observations of condensation nuclei concentrations CH2O (see text for details). The dotted line shows the altitude of are shown in the upper panel.

Comparison between observations (solid circles) and diel steady state model calculations (plusses) of HO2 mixing ratios, as a function of solar time. Also shown are results from a trajectory model assuming convective input of peroxides and CH2O three days prior to the date of the flight with upper-bound (triangles; case A) and lower-bound (diamonds; case B) initial values for peroxides and CH2O (see text for details). The dotted line shows the altitude of the ER-2. Observations of condensation nuclei concentrations are shown in the upper panel.

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 CH3I. In contrast, for the flights where the diel steady state model reproduces observed HOx 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 HO2 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^{-2}, see Figure 3), relatively high levels of CH3I (0.15 pptv) and low levels of NOx (10-20 pptv) 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 ~3 days prior to sampling by the aircraft.

In a companion paper, Prather and Jacob [this issue] propose that convective injection of CH2O and CH3I from the boundary layer provides a major source of HOx in the tropical upper troposphere. H2O is expected to be scavenged by precipitation during deep convection because of its high solubility in water, but CH2O and CH3I are far less soluble [Betterton, 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 [Heikes et al., 1996]. These data at 15°N-10°S show mean concentrations at 8-12 km altitude (CH2O: 90 pptv; H2O: 230 pptv) much lower than in the marine boundary layer (CH2O: 1010 pptv; H2O: 810 pptv). Enhanced concentrations of perox-
Figure 5. Simulated mixing ratios of HO2, CH2O, CH3OOH 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).

Calculations 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, HO2, peroxides, CH2O and acetone in order to obtain a highly constrained analysis of the HOx budget in the upper troposphere.

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