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Observed OH and HO_2 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 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_2O, NO, CO, hydrocarbons, albedo and overhead ozone column. We find that the reaction $O(^1D)$ + H_2O 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_3OOH and H_2O_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 (hydroperoxyl 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 *Crosley*, 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_2O, 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 solar cycle. NO_t (=$NO+NO_2+NO_3+2N_2O_5+HNO_2+HNO_4$) 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 NO_2 photolysis rate to within 10% in all cases. Agreement with observations for photolysis of O_3 to $O(^1D)$ 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_2O_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

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state concentrations of 50 species, including HO_2, OH, $O(^1D)$, CH_3O_2, NO_y species (NO_2, NO_3, N_2O_5, HNO_2, HNO_4, HNO_3, PAN), and other photochemical intermediates, in particular formaldehyde (CH_2O) and peroxides (H_2O_2 and CH_3OOH). Problems associated with the steady state assumption for peroxides will be a focus of discussion later in this paper.

HO_x 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 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 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_x 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_x with H_2O_2, CH_3OOH, HNO_2, HNO_3, HNO_4, HOCl, and HOBr, which we assume in the model to be at steady state. Primary sources of HO_x include the $O(^1D)+H_2O$ reaction and the photolysis of acetone. Photolysis of acetone yields two HO_x molecules, and leads to production of CH_2O which can photolyze to yield additional HO_x, resulting in a total yield of about three HO_2 molecules per acetone molecule photolyzed [*Singh et al.*, 1995]. The source of HO_x from acetone photolysis shown in Figure 2 is based on this total yield as computed in the model. The secondary HO_x source from CH_2O photolysis in Figure 2 is mainly from the oxidation of CH_4 by OH; it excludes the contribution from CH_2O produced by decomposition of acetone since this contribution is accounted for as part of the primary source from acetone photolysis. Because CH_2O originates from HO_x reactions, and is at chemical steady state in the model, we view it as a secondary source of HO_x.

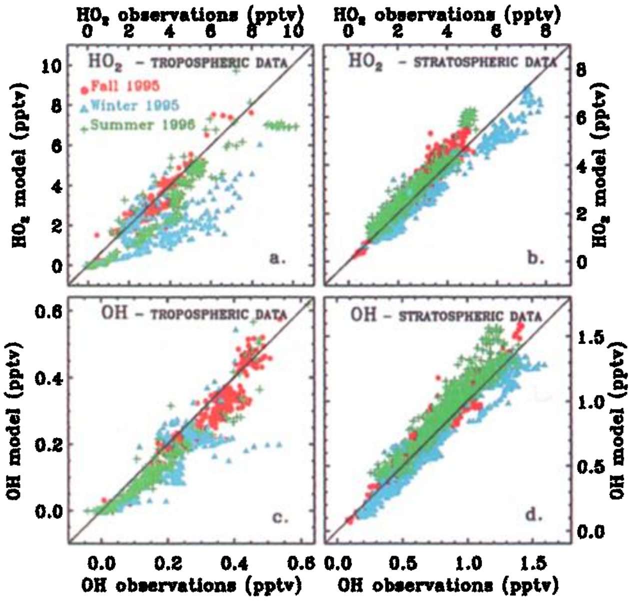

Figure 1. Simulated versus observed HO_2 and OH mixing ratios for 15 ER-2 flights between October 1995 and August 1996. The simulated values are from a diel steady state model sampled at the time of day of observations. Primary sources of HO_x in the model include $O(^1D)+H_2O$ and acetone photolysis.

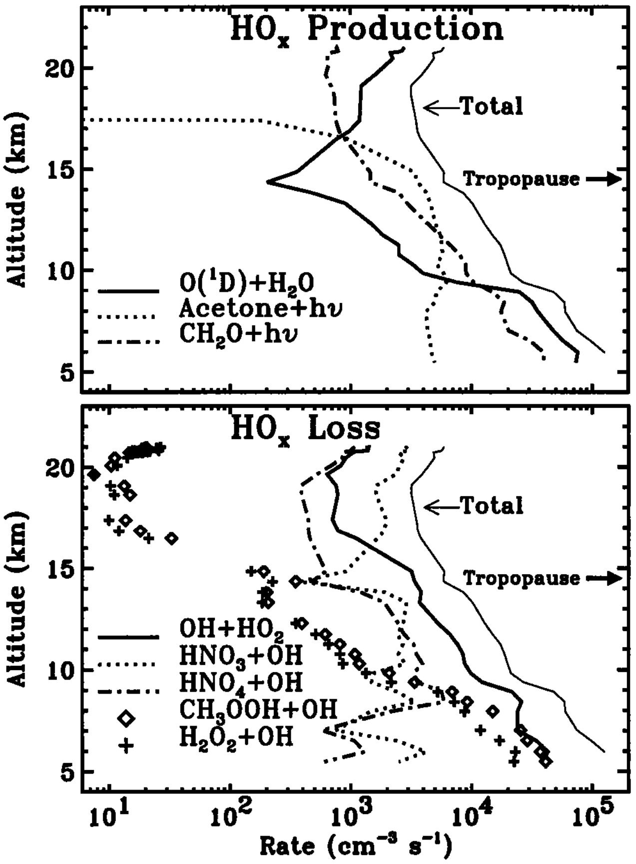

Figure 2. Production and loss rates of HO_x (24-hour averages) computed in the diel steady state model as a function of altitude for the ER-2 descent over Hawaii on November 7, 1995. See text for details on the accounting of HO_x sources and sinks. Only the major reactions are shown. All other reactions contribute individually to less than 10% of the total HO_x loss or production anywhere in the column.

A remarkable feature of Figure 2 is the relative unimportance of water vapor as a local source of HO_x 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 $O(^1D)+H_2O$ shows a pronounced minimum in the upper troposphere. By contrast, the source of HO_x from acetone photolysis shows little variation with altitude in the troposphere (Figure 2), and dominates over $O(^1D)+H_2O$ as a primary source of HO_x in the upper troposphere. Loss of HO_x is dominated by the $OH+HO_2$ reaction and is therefore quadratic which damps the response of OH and HO_2 concentrations to changes in the HO_x sources. Not including the acetone source in the upper troposphere would result in predicted HO_x 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_x 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

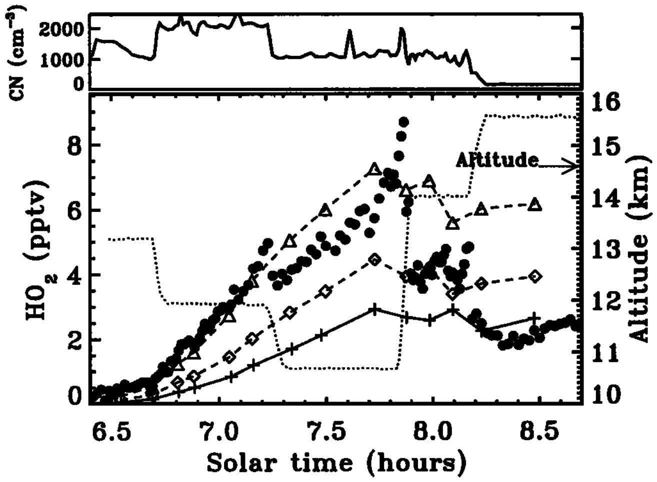

Figure 3. Sunrise flight of February 8, 1996 (Hawaii). Comparison between observations (solid circles) and diel steady state model calculations (pluses) of HO_2 mixing ratios, as a function of solar time. Also shown are results from a trajectory model assuming convective input of peroxides and CH_2O 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 CH_2O (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.

northeastern Pacific (January 29 and February 2, 1996). 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_3I. In contrast, for the flights where the diel steady state model reproduces observed HO_x 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_2 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_3I (0.15 pptv) and low levels of NO_x (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 CH_3OOH, H_2O_2, and CH_2O from the boundary layer provides a major source of HO_x in the tropical upper troposphere. H_2O_2 is expected to be scavenged by precipitation during deep convection because of its high solubility in water, but CH_3OOH and CH_2O 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 (CH_3OOH: 90 pptv; H_2O_2: 230 pptv) much lower than in the marine boundary layer (CH_3OOH: 1010 pptv; H_2O_2: 810 pptv). Enhanced concentrations of peroxides at 8-12 km altitude (mean values of 530 ± 120 pptv for CH_3OOH and 445 ± 145 pptv for H_2O_2) were observed in air of recent convective origin, as diagnosed by elevated concentrations of dimethyl sulfide (> 3 pptv). CH_2O 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_2O in deep convection similar to that for CH_3OOH, we estimate typical CH_2O 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_2O the concentrations previously mentioned for convective outflows. Concentrations of O_3, H_2O, NO_t, 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_3OOH, 590 pptv H_2O_2, and 200 pptv CH_2O; and a lower-bound case (B) with initial concentrations of 410 pptv CH_3OOH, 50 pptv H_2O_2, and 50 pptv CH_2O. Case B assumes quantitative scavenging of H_2O_2 in deep convection. Results in Figure 3 show factors of 2-5 enhancement of HO_x 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_2 after sunrise, in contrast to the diel steady state calculation. The improved simulation of the early morning rise of HO_2 reflects the enhanced concentrations of peroxides, which photolyze at longer wavelength than ($O_3 \rightarrow O(^1D)$) or acetone. Note that even if H_2O_2 were efficiently scavenged during convective pumping (case B), we find that CH_3OOH photolysis can still sustain high levels of OH and HO_2. In either case, A or B, the convected CH_2O is relatively insignificant as a source of HO_x, 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_3I decrease sharply and the diel steady state calculations are in better agreement with the observations while the trajectory calculations overpredict HO_2. 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_x in the upper troposphere depends on the characteristic decay time for the HO_x perturbation following a convective event. This characteristic time is defined by the lifetime of the chemical family HO_y (= HO_x + HNO_4 + HNO_2 + peroxides) which accounts for HO_x recycling from its short-lived reservoirs including peroxides. Figure 5 shows the evolution of HO_2, peroxides and formaldehyde obtained by the trajectory cal-

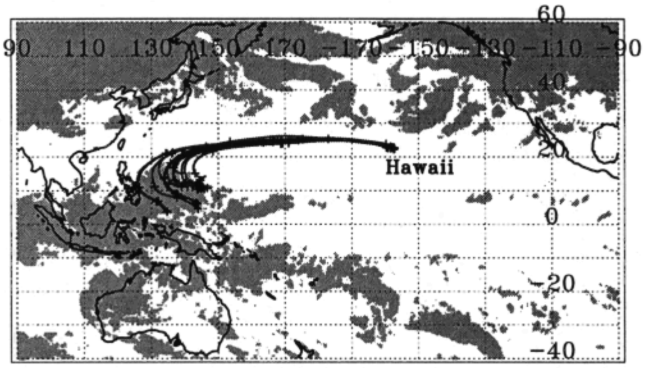

Figure 4. Five-day isentropic back-trajectories for the air sampled by the ER-2 over Hawaii on February 8, 1996. 14 trajectories are shown which were initialized along the flight track for potential temperatures between 345 and 360 K. Each tick mark represents one day. The shaded areas indicate the presence of high-altitude clouds (>11 km) based on satellite infrared brightness temperatures for the time period between February 3 and 6, 1996. In the tropics the presence of high clouds is generally associated with the occurrence of deep convection.

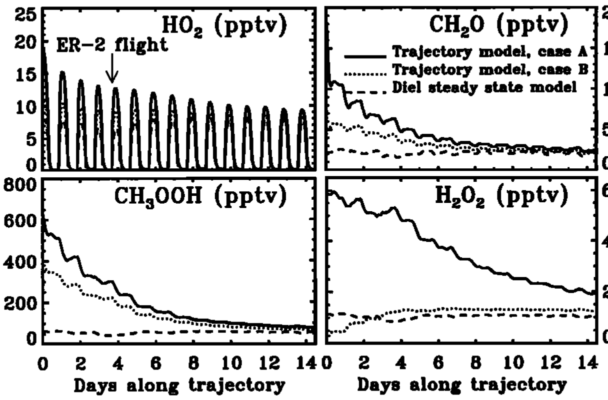

Figure 5. Simulated mixing ratios of HO_2, CH_2O, CH_3OOH and H_2O_2 in the trajectory model calculation at 11 km altitude initialized with tropical convective outflow on February 4, intercepting the ER-2 flight track 3.5 days later on February 8, and extended another 10 days at the latitude of Hawaii. 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 HO_y family is limited by the rate at which HO_y is lost via the $OH+HO_2$ and H_2O_2+OH reactions, which provide its main sinks. It takes more than 10 days after the injection of peroxides for HO_x to return to its steady state level, corresponding to the lifetime of the HO_y 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 HO_x 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 HO_x budget in the upper troposphere would take a longer time to decay at mid-latitudes reflecting the longer lifetime of the HO_y family.

Further support for our hypothesis of a major convective contribution of peroxides to HO_x levels in the upper troposphere is offered by previous observations of H_2O_2 and CH_3OOH 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 HO_2 thus indicates that convection can affect ozone production in the upper troposphere not only through the injection of NO_x and hydrocarbons [*Dickerson et al.*, 1987; *Pickering et al.*, 1993], but also by the transport of peroxides, in particular CH_3OOH. Our study points to the need for future aircraft missions to include measurements of OH, HO_2, peroxides, CH_2O and acetone in order to obtain a highly constrained analysis of the HO_x budget in the upper troposphere.

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