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# Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide ( $\text{HO}_x$ ) radicals in the tropical upper troposphere

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**Abstract.** Concurrent measurements of OH,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{CH}_3\text{OOH}$  concentrations were made during an aircraft flight over the tropical South Pacific that followed a back-and-forth pattern at constant 10 km altitude for 4 hours. One end of the pattern sampled an aged convective outflow, while the other end sampled the background atmosphere. Concentrations of  $\text{HO}_2$  and  $\text{CH}_3\text{OOH}$  in the convective outflow were elevated by 50 and 350% relative to background, respectively, while concentrations of OH and  $\text{H}_2\text{O}_2$  were not elevated. The high  $\text{CH}_3\text{OOH}$  concentrations in the outflow were due to convective pumping from the marine boundary layer. In contrast to  $\text{CH}_3\text{OOH}$ ,  $\text{H}_2\text{O}_2$  was not enhanced in the outflow because its high water solubility allows efficient scavenging in the convective updraft. A photochemical model calculation constrained with the ensemble of aircraft observations reproduces the  $\text{HO}_2$  enhancement in the convective outflow and attributes it to the enhanced  $\text{CH}_3\text{OOH}$ ; the calculation also reproduces the lack of OH enhancement in the outflow and attributes it to OH loss from reaction with  $\text{CH}_3\text{OOH}$ . Further analysis of model results shows substantial evidence that the rate constant used in standard mechanisms for the  $\text{CH}_3\text{O}_2 + \text{HO}_2$  reaction is about a factor of 3 too low at the low temperatures of the upper troposphere. A sensitivity simulation using a value of  $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 233 K for this rate constant yields better agreement with observed  $\text{HO}_2$  concentrations and better closure of the chemical budgets for both  $\text{CH}_3\text{OOH}$  and  $\text{H}_2\text{O}_2$ . The  $\text{CH}_3\text{O}_2 + \text{HO}_2$  reaction then becomes the single most important loss pathway for  $\text{HO}_x$  radicals ( $\text{HO}_x = \text{OH} +$  peroxy radicals) in the upper troposphere.

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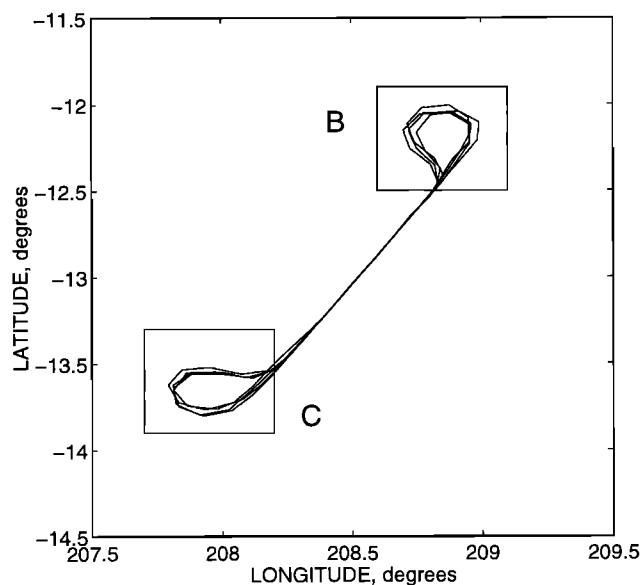
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## 1. Introduction

It is well known that deep convection impacts the radical chemistry of the upper troposphere by supplying nitrogen oxide radicals ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) from combustion and lightning [Pickering *et al.*, 1996; Crawford *et al.*, 1997; Jaeglé *et al.*, 1998b]. More recently, model studies have proposed that deep convective transport of peroxides and aldehydes from the lower troposphere could provide a major source of hydrogen oxide radicals ( $\text{HO}_x = \text{OH} +$  peroxy radicals) to the upper troposphere [Jaeglé *et al.*, 1997; Prather and Jacob, 1997; Crawford *et al.*, 1999; Müller and Brasseur, 1999]. Particular attention in these studies has focused on  $\text{CH}_3\text{OOH}$ , which is present at ppbv levels in the lower troposphere, and can be transported to the upper troposphere in deep convection without scavenging on account of its low solubility in water [Mari *et al.*, 2000]. Aircraft observations in the upper troposphere have shown evidence for enhanced  $\text{HO}_x$  in convective outflows [Brune *et al.*, 1998] and also for enhanced  $\text{CH}_3\text{OOH}$  [Cohan *et al.*,



**Figure 1.** Back-and-forth flight track at 10 km altitude followed by the DC-8 aircraft between 5.7 and 9.7 LT on April 2, 1999 (PEM-Tropics B flight 15). Region B sampled background conditions while region C sampled an aged convective outflow (see text and Table 1).

1999]. Concurrent measurements of HO<sub>x</sub>, peroxides, and HCHO in the upper troposphere were first made during the SONEX aircraft mission over the North Atlantic, but the convective outflows sampled in this mission contained sufficient water vapor to dominate the supply of HO<sub>x</sub> [Jaeglé *et al.*, 2001]. A greater relative importance for CH<sub>3</sub>OOH might be expected in the tropical upper troposphere, where water vapor mixing ratios in convective outflows are less because of the lower temperatures [Jaeglé *et al.*, 1997; Wennberg *et al.*, 1998].

We present here the first direct observational evidence of enhanced HO<sub>x</sub> concentrations from convected CH<sub>3</sub>OOH in the tropical upper troposphere. Our analysis is based on data from an aircraft flight at 10 km altitude over the South Pacific during the NASA Pacific Exploratory Mission–Tropics B (PEM–Tropics B). That flight featured repeated sampling of an aged convective outflow and of the neighboring background from sunrise to midmorning. Through photochemical modeling of the difference between these two air masses, we are able to isolate the role of convected CH<sub>3</sub>OOH as a source of HO<sub>x</sub> and also to analyze uncertainties in CH<sub>3</sub>OOH chemistry. More general analyses of the HO<sub>x</sub> concentrations measured in PEM–Tropics B are presented by Tan *et al.* [this issue].

The observations are presented in section 2, and the photochemical model analysis is discussed in section 3. In that section we not only demonstrate the importance of convected CH<sub>3</sub>OOH as a major source of HO<sub>x</sub> in the convective outflow, we also show evidence that the rate constant used in standard photochemical mechanisms for the reaction CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> is too low. Conclusions are in section 4.

## 2. Observations

The PEM–Tropics B aircraft mission took place in March–April 1999 to investigate tropospheric chemistry related to ozone and aerosol formation over the tropical Pacific [Raper *et al.*, this issue]. We focus here on flight 15 of the DC-8 aircraft, which took place northwest of Tahiti on April 2, 1999. The goal of this flight was to study the evolution of HO<sub>x</sub> and NO<sub>x</sub> radicals in the upper troposphere across sunrise and into the morning hours. The aircraft flew a back-and-forth pattern at

**Table 1.** Air Composition Observed at 10 km altitude on PEM–Tropics B DC-8 Flight 15

	Convective Outflow (Region C)	Background Troposphere (Region B)
O <sub>3</sub> , ppbv	23 ± 2	29 ± 2
CO, ppbv	42 ± 3	41 ± 3
NO, pptv	32 ± 7	44 ± 19
H <sub>2</sub> O, ppmv	199 ± 48	67 ± 10
Relative Humidity, %	35 ± 10	12 ± 2
CH <sub>3</sub> OOH, pptv	290 ± 103	64 ± 24
H <sub>2</sub> O <sub>2</sub> , pptv	77 ± 21	77 ± 20
CH <sub>3</sub> COCH <sub>3</sub> , pptv	334 ± 15	328 ± 11
HCHO, pptv	165 ± 57	122 ± 38
SO <sub>2</sub> , pptv	12 ± 1	15 ± 2
CH <sub>3</sub> I, pptv	0.09 ± 0.02	0.04 ± 0.02
CHBr <sub>3</sub> , pptv	0.43 ± 0.05	0.26 ± 0.04
C <sub>2</sub> H <sub>2</sub> , pptv	13 ± 1	11 ± 1

Observations reported here were made at 10 km altitude over the South Pacific in an aged convective outflow (region C) and in the neighboring background atmosphere (region B) from 7 to 9.7 local time (Figure 1). Pressure was 260 hPa and temperature was 233 K. Relative humidity is defined with respect to ice. The table gives means and standard deviations of concentrations computed from a database of 1-min average measurements ( $n = 40$  in region B,  $n = 36$  in region C).

**Table 2.** Model Results for Convective Outflow and Background Conditions

	Convective Outflow	Background Troposphere
HCHO, pptv	88 (69)	51 (40)
Net O <sub>3</sub> production, ppbv day <sup>-1</sup>	0.99 (0.71)	0.83 (0.66)
HO <sub>x</sub> concentration, 10 <sup>7</sup> molecules cm <sup>-3</sup>	4.42 (3.36)	2.93 (2.31)
HO <sub>2</sub>	3.19 (2.54)	2.18 (1.77)
CH <sub>3</sub> O <sub>2</sub>	1.14 (0.74)	0.66 (0.47)
OH	0.09 (0.08)	0.08 (0.07)
HO <sub>x</sub> production, 10 <sup>4</sup> molecules cm <sup>-3</sup> s <sup>-1</sup>	6.1 (5.5)	3.4 (3.0)
CH <sub>2</sub> O + hν	2.6 (2.0)	1.5 (1.2)
CH <sub>3</sub> OOH + hν	1.5 (1.5)	0.3 (0.3)
H <sub>2</sub> O <sub>2</sub> + hν	0.5 (0.5)	0.5 (0.5)
O( <sup>1</sup> D) + H <sub>2</sub> O	0.9 (0.9)	0.4 (0.4)
CH <sub>3</sub> COCH <sub>3</sub> + hν	0.4 (0.4)	0.4 (0.4)
HNO <sub>2</sub> + hν	0.1 (0.1)	0.2 (0.1)
Others	0.1 (0.1)	0.1 (0.1)
HO <sub>x</sub> loss, 10 <sup>4</sup> molecules cm <sup>-3</sup> s <sup>-1</sup>	6.1 (5.5)	3.4 (3.0)
OH + HO <sub>2</sub>	1.8 (1.3)	1.2 (0.8)
CH <sub>3</sub> O <sub>2</sub> + HO <sub>2</sub>	1.6 (2.4)	0.6 (1.1)
HO <sub>2</sub> + HO <sub>2</sub>	1.7 (1.1)	0.8 (0.6)
Others	1.0 (0.7)	0.8 (0.5)

Values are 24-hour averages for the standard model calculation conducted for the mean compositions of regions B and C (Table 1). Values in parentheses are from a sensitivity calculation with the rate constant for the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction increased by a factor of 3.

a constant 10 km altitude from 5.7 to 9.7 LT, over a track extending 2° in a SW-NE axis centered at 13S, 208.5W (Figure 1). This track was intended to sample a uniform air mass over the 4-hour sampling period so that solar elevation would be the only changing variable. In fact, one end of the flight track (C in Figure 1) sampled an aged convective outflow while the rest of the track sampled typical background conditions. Table 1 gives the chemical composition for the air masses after sunrise at the two ends of the flight track, B (background) and C (convective outflow). The two air masses were sampled repeatedly as the aircraft conducted the back-and-forth pattern. Their chemical compositions remained remarkably constant, as shown by the small standard deviations in Table 1.

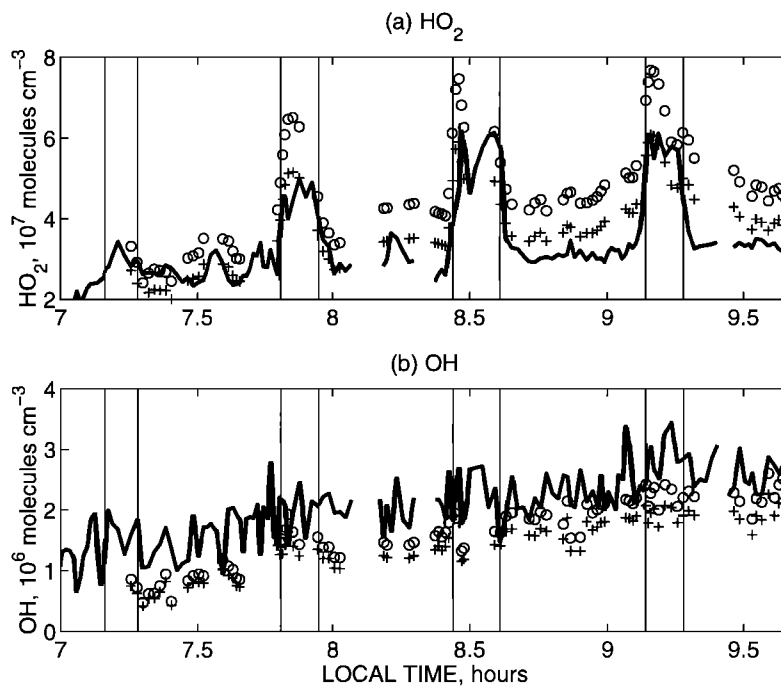
Compared to region B, region C is characterized by lower levels of O<sub>3</sub> and NO and by higher levels of H<sub>2</sub>O and CH<sub>3</sub>OOH. Given the vertical distributions of those species in the tropics [O'Sullivan *et al.*, 1997; Schultz *et al.*, 1999] and more specifically for this campaign, this difference is consistent with an air mass convected from the marine boundary layer to the upper troposphere. Indeed, CH<sub>3</sub>I and CHBr<sub>3</sub>, two tracers of marine convection, have significantly larger concentrations in the convective outflow (region C) than in the background upper troposphere (region B). No difference is seen for water-soluble species such as SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> that are scavenged efficiently during convection [Mari *et al.*, 2000]. The C<sub>2</sub>H<sub>2</sub> and CO mixing ratios are low in both air masses and characteristic of clean southern hemispheric air. The water vapor concentration in region C is 3 times higher than in region B, but the

relative humidity is still only 35%. According to the classification of Cohan *et al.* [1999], the air sampled in region C is characteristic of an aged convective outflow having subsided over the flight track.

The time series of HO<sub>2</sub> and OH concentrations (Figure 2) show increases during the morning hours driven by the increasing solar elevation. We focus on the measurements after sunrise (between 7 and 9.7 local time). Superimposed on the diurnal increase in Figure 2 are enhancements of HO<sub>2</sub> concentrations by ~ 50% at each return of the aircraft into the convective outflow region C. These HO<sub>2</sub> enhancements are synchronous with CH<sub>3</sub>OOH enhancements (Figure 3a). Unlike CH<sub>3</sub>OOH, H<sub>2</sub>O<sub>2</sub> is efficiently scavenged in the precipitation associated with deep convection [Cohan *et al.*, 1999], and no enhancement is observed for this peroxide in the convective outflow (Figure 3b). Enhancements of OH concentrations in the convective outflow are hardly detectable from the noise of the instrument (Figure 2) and are in any case much less than for HO<sub>2</sub>. Using a photochemical model, Cohan *et al.* [1999] previously found that a HO<sub>2</sub> enhancement in the upper troposphere due to convected CH<sub>3</sub>OOH does not imply the same enhancement for OH because the added source of HO<sub>x</sub> in the convective outflow (CH<sub>3</sub>OOH photolysis) is balanced by the additional OH sink from oxidation of CH<sub>3</sub>OOH. We will come back to that point in section 3.

### 3. Photochemical Model Analysis

We use the Harvard photochemical point model [Jacob *et al.*, 1996; Jaeglé *et al.*, 1998a; Schultz *et al.*, 1999] to simulate the concentrations of HO<sub>x</sub> radicals and re-



**Figure 2.** (a) HO<sub>2</sub> and (b) OH time series of concentrations between 7 and 9.7 LT on DC-8 flight 15. Observations are shown as solid lines. Circles show results from a standard photochemical calculation constrained with the ensemble of observations for other species aboard the aircraft. Crosses show the effect of increasing the rate constant for the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction by a factor of 3 in that calculation. Vertical lines indicate when the airplane enters or exits the convective outflow (region C of Figure 1).

lated species along the track of flight 15. The model is constrained with observed 1-min averages of the concentrations of long-lived chemical species (O<sub>3</sub>, CO, H<sub>2</sub>O, NO<sub>x</sub>, HNO<sub>3</sub>, peroxyacetylnitrate, alkylnitrates, peroxides, acetone, methanol, methane, ethane). Concentrations of radicals and other photochemical intermediates including HCHO are calculated by imposing a 1-day periodicity for model results (diurnal steady state). The NO<sub>x</sub> concentration is assumed constant over the diurnal cycle and is adjusted to match the observed NO concentration at the time of day of observation. The overhead ozone column for photolysis calculations is specified using daily Total Ozone Mapping Spectrometer (TOMS) observations. Modeled clear-sky photolysis frequencies are scaled to observations aboard the aircraft [Lefer *et al.*, this issue] to take into account cloud scattering and absorption. The chemical mechanism is based on the compilations of DeMore *et al.* [1997] and Atkinson *et al.* [1997]. Four heterogeneous reactions are included to describe aerosol uptake of HO<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub>, using reaction probabilities from Jacob [2000]. Aerosol surface areas measured on flight 15 were  $\sim 3.5 \mu\text{m}^2 \text{cm}^{-3}$ , sufficiently small that heterogeneous chemistry did not play a significant role in the HO<sub>x</sub> budget.

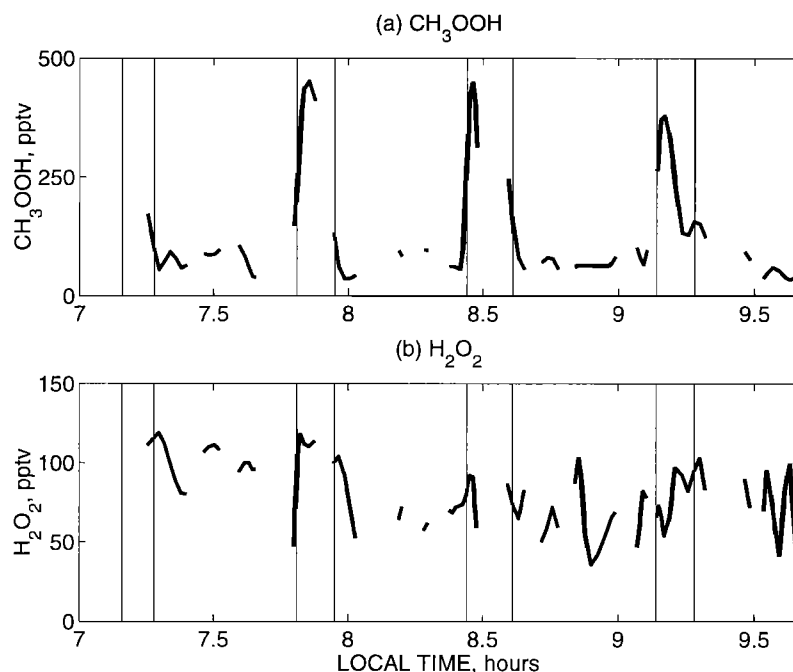
### 3.1. HO<sub>x</sub> Enhancement in the Convective Outflow

Circles in Figure 2 show model results for HO<sub>2</sub> and OH concentrations. Gaps in model results are mainly

due to missing NO measurements. The model captures the general shape of the increase in the HO<sub>x</sub> concentrations as the morning progresses, the HO<sub>2</sub> enhancement in the convective outflow region C, and the lack of a corresponding OH enhancement. However, the model is  $\sim 30\%$  too high for HO<sub>2</sub>. Model-calculated concentrations of OH are systematically smaller than measured ones, but the difference could reflect an instrument artifact of  $\sim 0.5 \times 10^6 \text{ molecules cm}^{-3}$  (W.H. Brune, personal communication, 2001).

We examine further the HO<sub>x</sub> enhancement in convective outflow by focusing on two point simulations representative of the convective outflow and background chemical environments sampled by the aircraft. The average compositions given for each environment in Table 1 are used to constrain the model, except for HCHO computed at chemical steady state.

Table 2 gives the 24-hour average HO<sub>x</sub> concentrations, sources, and sinks for these two points, along with local 24-hour average ozone production rates and HCHO mixing ratios. Concentrations of peroxy radicals are  $\sim 50\%$  larger in the convective outflow than in the background troposphere, and the ozone production rate is correspondingly larger ( $0.99 \text{ ppbv d}^{-1}$  versus  $0.83 \text{ ppbv d}^{-1}$ ). The largest source of HO<sub>x</sub> in both cases is HCHO photolysis, but since HCHO in the model is specified from chemical steady state it does not provide a primary source of HO<sub>x</sub>. (A primary source of HO<sub>x</sub> such as the O(<sup>1</sup>D) + H<sub>2</sub>O reaction, or the photolysis of



**Figure 3.** (a) CH<sub>3</sub>OOH and (b) H<sub>2</sub>O<sub>2</sub> mixing ratios observed between 7 and 9.7 LT on DC-8 flight 15. Vertical lines indicate when the airplane enters or exits the convective outflow (region C on Figure 1).

acetone or convected peroxides, is independent of the local HO<sub>x</sub> concentration; the resulting HO<sub>x</sub> leads to production of HCHO, mainly by oxidation of CH<sub>4</sub> by OH, and photolysis of this HCHO then provides a secondary source of HO<sub>x</sub> that amplifies the primary source [Jaeglé *et al.*, 1997, 2001].) The HCHO concentrations simulated by the model at chemical steady state underestimate the observed values by 80 pptv both in the background and in the convective outflow (compare Table 1 and Table 2). This problem is a common feature of upper tropospheric chemistry models [Jaeglé *et al.*, 2001], although the bias here is close to the detection limit of the HCHO instrument (50 pptv; Raper *et al.* [this issue]).

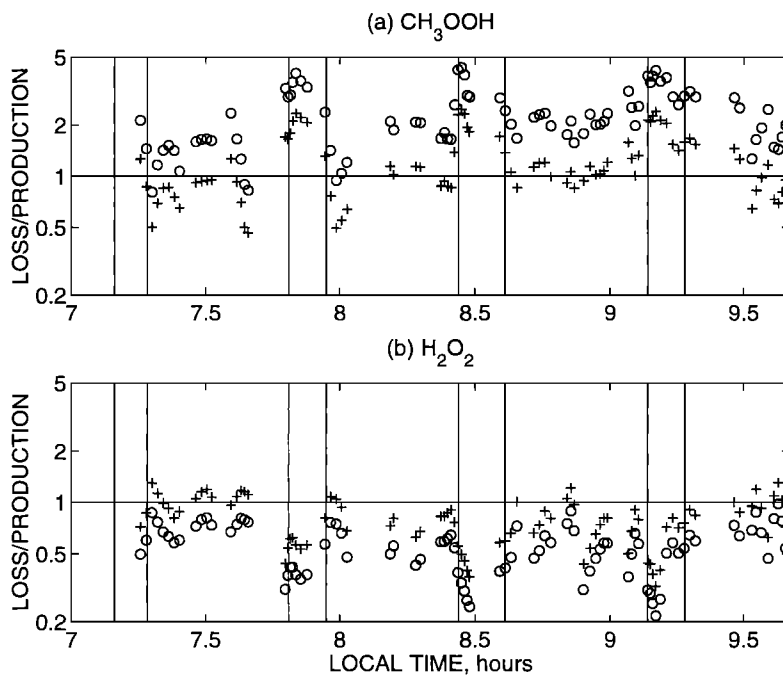
As seen in Table 2, the increase in the primary HO<sub>x</sub> source in the convective outflow is driven by CH<sub>3</sub>OOH photolysis (5 times larger in the convective outflow). The CH<sub>3</sub>OOH concentration in the convective outflow is 2–4 times above chemical steady state (Figure 4, discussed below) so that most of the corresponding HO<sub>x</sub> source is due to photolysis of convected CH<sub>3</sub>OOH rather than of CH<sub>3</sub>OOH produced locally. Photolysis of CH<sub>3</sub>OOH in the convective outflow is therefore mostly a primary rather than a recycling source of HO<sub>x</sub>. The source of HO<sub>x</sub> from ozone photolysis in the convective outflow is only 60% that from CH<sub>3</sub>OOH photolysis. This result can be compared to the photochemical model study by Cohan *et al.* [1999] of a fresh convective outflow with 700 ppmv H<sub>2</sub>O (82% relative humidity) in PEM-Tropics A, where ozone photolysis remained the major source of HO<sub>x</sub> in the outflow despite the CH<sub>3</sub>OOH enhancement. The convective outflow exam-

ined here is much drier (200 ppmv H<sub>2</sub>O), reflecting an origin at higher altitudes followed by subsidence along the flight track. (Water vapor mixing ratios in convective outflows decrease rapidly with outflow altitude because of the temperature dependence of the water saturation vapor pressure.)

A remarkable feature of observations in the convective outflow is the lack of OH enhancement, in contrast to HO<sub>2</sub>. The model reproduces this feature and it represents indeed a signature of the HO<sub>x</sub> source from convected CH<sub>3</sub>OOH. Although CH<sub>3</sub>OOH photolysis yields OH as a direct product, this OH is quickly converted into HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>, and the OH/peroxy ratio is then controlled by cycling within the HO<sub>x</sub> family [Jaeglé *et al.*, 2000]. Reaction of CH<sub>3</sub>OOH with OH to form CH<sub>3</sub>O<sub>2</sub> decreases the OH/peroxy ratio, compensating for the overall increase in HO<sub>x</sub> and resulting in little change in OH concentrations in the convective outflow relative to the background atmosphere (Table 2).

### 3.2. Sensitivity to the CH<sub>3</sub>O<sub>2</sub>+HO<sub>2</sub> Reaction Rate Constant

As shown in Figure 2, the standard model simulation overestimates HO<sub>2</sub> concentrations by ~ 30% in both the background atmosphere and in the convective outflow. Another deficiency in the simulation is that computed chemical production and loss rates of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH constrained with the observed peroxides concentrations are not in balance in the background atmosphere: loss exceeds production for CH<sub>3</sub>OOH, while production exceeds loss for H<sub>2</sub>O<sub>2</sub>, by large factors (Fig-



**Figure 4.** Ratios of chemical loss to production rates for (a) CH<sub>3</sub>OOH and (b) H<sub>2</sub>O<sub>2</sub> in the photochemical model calculation constrained with observed CH<sub>3</sub>OOH and H<sub>2</sub>O<sub>2</sub> concentrations on DC-8 flight 15. The chemical production and loss rates are computed as 24-hour averages for each point along the flight track from 7 to 9.7 LT. Circles show results from the standard photochemical calculation, while crosses show results from a sensitivity calculation with the rate constant for the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction increased by a factor of 3. Vertical lines indicate when the airplane enters or exits the convective outflow (region C on Figure 1).

ure 4). Except for CH<sub>3</sub>OOH in the background atmosphere, the measured peroxide concentrations are well above the detection limits (10 pptv for H<sub>2</sub>O<sub>2</sub>, 25 pptv for CH<sub>3</sub>OOH [Raper *et al.*, 2001]). Such imbalances between peroxide production and loss rates might be expected in the convective outflow, as the convective updraft supplies air enriched in CH<sub>3</sub>OOH and depleted in H<sub>2</sub>O<sub>2</sub>. It should not be present in the background upper troposphere, as the lifetimes of the peroxides against photolysis and reaction with OH are sufficiently short (1 day for CH<sub>3</sub>OOH, 2 days for H<sub>2</sub>O<sub>2</sub>) that chemical steady state should be approached.

One possible explanation that could resolve all these model deficiencies is that the low-temperature rate constant used for the reaction CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> → CH<sub>3</sub>OOH + O<sub>2</sub> may be too low. The compilation of DeMore *et al.* [1997] gives a rate constant  $k_{\text{CH}_3\text{O}_2+\text{HO}_2} = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 233 K, which we use in the standard simulation. However, the compilation also estimates a factor of 2.9 uncertainty for the rate constant at that temperature. We conducted a sensitivity simulation for flight 15 with  $k_{\text{CH}_3\text{O}_2+\text{HO}_2} = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , corresponding to the upper end of the estimated uncertainty. As seen in Figure 2a (crosses), this change largely corrects the overestimate of HO<sub>2</sub>. The reaction CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> is then the largest single sink of HO<sub>x</sub> (Table 2). Local ozone production rates decrease, amounting to 0.71 ppbv d<sup>-1</sup> in the convective

outflow and 0.66 ppbv d<sup>-1</sup> in the background. The simulated OH concentrations decrease, (Figure 2b) but the change is small and as mentioned previously a measurement offset could possibly account for the model underestimate. Photochemical production and loss rates of CH<sub>3</sub>OOH and H<sub>2</sub>O<sub>2</sub> are brought into close balance in the background air, as increasing  $k_{\text{CH}_3\text{O}_2+\text{HO}_2}$  increases the CH<sub>3</sub>OOH production rate but decreases the H<sub>2</sub>O<sub>2</sub> production rate (because of lower HO<sub>2</sub> concentrations). In the convective outflow, chemical loss of CH<sub>3</sub>OOH still exceeds chemical production, while chemical production of H<sub>2</sub>O<sub>2</sub> exceeds chemical loss, consistent with the expected effect of the convective transport on the peroxide budgets.

#### 4. Conclusions

We have used concurrent observations of HO<sub>2</sub>, OH, CH<sub>3</sub>OOH, and H<sub>2</sub>O<sub>2</sub> concentrations from an aircraft flight at 10 km altitude over the South Pacific to provide the first direct experimental evidence for the role of convective transport of CH<sub>3</sub>OOH as a major primary source of HO<sub>x</sub> in the tropical upper troposphere. The aircraft flew a back-and-forth pattern in and out of an aged convective outflow from sunrise to midmorning. Concentrations of HO<sub>2</sub> were enhanced by 50% in the convective outflow, and this enhancement could be explained by the synchronous increase observed for

CH<sub>3</sub>OOH. No significant enhancement of OH was observed in the outflow, and this could be explained by an increase in the OH sink from reaction with CH<sub>3</sub>OOH. Our results thus emphasize the need to account for convective transport of CH<sub>3</sub>OOH in chemical models of the upper troposphere.

We found substantial evidence that the standard rate constant used in models for the reaction CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> → CH<sub>3</sub>OOH + O<sub>2</sub> [DeMore *et al.*, 1997] is too low by about a factor of 3 at the low temperatures of the upper troposphere. In our standard simulation, HO<sub>2</sub> concentrations are too high by ~ 30%, both in the background upper troposphere and in the convective outflow. In addition, the computed chemical production and loss rates of CH<sub>3</sub>OOH and H<sub>2</sub>O<sub>2</sub> are out of balance in the background atmosphere, whereas one would expect chemical steady state. A sensitivity simulation with  $k_{\text{CH}_3\text{O}_2+\text{HO}_2}$  at 233 K increased by a factor of 3 (from  $1.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> to  $3.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) resolves these discrepancies. With the faster rate constant, the reaction CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> becomes the most important HO<sub>x</sub> radical sink (accounting for 35–45% of total HO<sub>x</sub> loss) both for background conditions and in the convective outflow. Laboratory studies are needed to reduce the uncertainty on the rate constant of this reaction.

An unresolved problem in our modeling analysis is the poor agreement between simulated and observed concentrations of HCHO in the upper troposphere. Modeled values at chemical steady state are too low and the point to point correlation is poor. This problem is apparent in the ensemble of the PEM-Tropics B data (including flight 15) [Tan *et al.*, this issue], as well as in data from previous missions [Schultz *et al.*, 1999; Jaeglé *et al.*, 2000]. In the present study we constrained HCHO concentrations from chemical steady state. Constraining them with observations would cause an overestimate of HO<sub>2</sub> concentrations (F. Ravetta *et al.*, manuscript in preparation, 2001). Resolution of this long-standing discrepancy between models and observations of HCHO in the upper troposphere is crucial for gaining confidence in our understanding of the processes controlling HO<sub>x</sub> concentrations in that region of the atmosphere.

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