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Journal

Journal of Geophysical Research, 106(D23)

ISSN

0148-0227

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Publication Date

2001-12-16

DOI

10.1029/2001jd900009

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Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide (HO_x) radicals in the tropical upper troposphere

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Abstract. Concurrent measurements of OH, HO_2 , H_2O_2 , and CH_3OOH 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 HO_2 and CH_3OOH in the convective outflow were elevated by 50 and 350% relative to background, respectively, while concentrations of OH and H_2O_2 were not elevated. The high CH_3OOH concentrations in the outflow were due to convective pumping from the marine boundary layer. In contrast to CH_3OOH , H_2O_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 HO_2 enhancement in the convective outflow and attributes it to the enhanced CH_3OOH ; the calculation also reproduces the lack of OH enhancement in the outflow and attributes it to OH loss from reaction with CH_3OOH . 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 HO_2 concentrations and better closure of the chemical budgets for both CH_3OOH and H_2O_2 . The $\text{CH}_3\text{O}_2 + \text{HO}_2$ reaction then becomes the single most important loss pathway for HO_x radicals ($\text{HO}_x = \text{OH} +$ peroxy radicals) in the upper troposphere.

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Paper number 2001JD900009.
0148-0227/01/2001JD900009\$09.00

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 CH_3OOH , 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 HO_x in convective outflows [Brune *et al.*, 1998] and also for enhanced CH_3OOH [Cohan *et al.*,

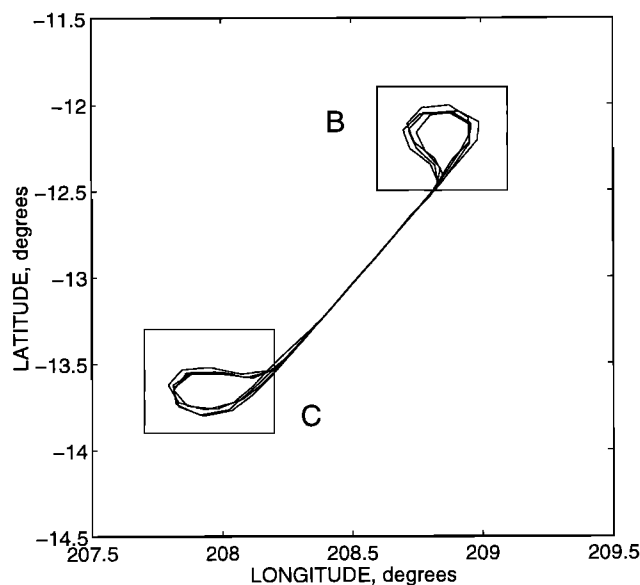


Figure 1. Back-and-forth flight track at 10 km altitude followed by the DC-8 aircraft between 5.7 and 9.7 LT on April 2, 1999 (PEM-Tropics B flight 15). Region B sampled background conditions while region C sampled an aged convective outflow (see text and Table 1).

1999]. Concurrent measurements of HO_x, 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_x [Jaeglé *et al.*, 2001]. A greater relative importance for CH₃OOH 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_x concentrations from convected CH₃OOH 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 CH₃OOH as a source of HO_x and also to analyze uncertainties in CH₃OOH chemistry. More general analyses of the HO_x 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 CH₃OOH as a major source of HO_x in the convective outflow, we also show evidence that the rate constant used in standard photochemical mechanisms for the reaction CH₃O₂ + HO₂ 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_x and NO_x 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 ₃ , ppbv	23 ± 2	29 ± 2
CO, ppbv	42 ± 3	41 ± 3
NO, pptv	32 ± 7	44 ± 19
H ₂ O, ppmv	199 ± 48	67 ± 10
Relative Humidity, %	35 ± 10	12 ± 2
CH ₃ OOH, pptv	290 ± 103	64 ± 24
H ₂ O ₂ , pptv	77 ± 21	77 ± 20
CH ₃ COCH ₃ , pptv	334 ± 15	328 ± 11
HCHO, pptv	165 ± 57	122 ± 38
SO ₂ , pptv	12 ± 1	15 ± 2
CH ₃ I, pptv	0.09 ± 0.02	0.04 ± 0.02
CHBr ₃ , pptv	0.43 ± 0.05	0.26 ± 0.04
C ₂ H ₂ , 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 ₃ production, ppbv day ⁻¹	0.99 (0.71)	0.83 (0.66)
HO _x concentration, 10 ⁷ molecules cm ⁻³	4.42 (3.36)	2.93 (2.31)
HO ₂	3.19 (2.54)	2.18 (1.77)
CH ₃ O ₂	1.14 (0.74)	0.66 (0.47)
OH	0.09 (0.08)	0.08 (0.07)
HO _x production, 10 ⁴ molecules cm ⁻³ s ⁻¹	6.1 (5.5)	3.4 (3.0)
CH ₂ O + hν	2.6 (2.0)	1.5 (1.2)
CH ₃ OOH + hν	1.5 (1.5)	0.3 (0.3)
H ₂ O ₂ + hν	0.5 (0.5)	0.5 (0.5)
O(¹ D) + H ₂ O	0.9 (0.9)	0.4 (0.4)
CH ₃ COCH ₃ + hν	0.4 (0.4)	0.4 (0.4)
HNO ₂ + hν	0.1 (0.1)	0.2 (0.1)
Others	0.1 (0.1)	0.1 (0.1)
HO _x loss, 10 ⁴ molecules cm ⁻³ s ⁻¹	6.1 (5.5)	3.4 (3.0)
OH + HO ₂	1.8 (1.3)	1.2 (0.8)
CH ₃ O ₂ + HO ₂	1.6 (2.4)	0.6 (1.1)
HO ₂ + HO ₂	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 CH₃O₂ + HO₂ 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 O₃ and NO and by higher levels of H₂O and CH₃OOH. 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, CH₃I and CHBr₃, 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 SO₂ and H₂O₂ that are scavenged efficiently during convection [Mari *et al.*, 2000]. The C₂H₂ 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 HO₂ 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 HO₂ concentrations by ~ 50% at each return of the aircraft into the convective outflow region C. These HO₂ enhancements are synchronous with CH₃OOH enhancements (Figure 3a). Unlike CH₃OOH, H₂O₂ 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 HO₂. Using a photochemical model, Cohan *et al.* [1999] previously found that a HO₂ enhancement in the upper troposphere due to convected CH₃OOH does not imply the same enhancement for OH because the added source of HO_x in the convective outflow (CH₃OOH photolysis) is balanced by the additional OH sink from oxidation of CH₃OOH. 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_x radicals and re-

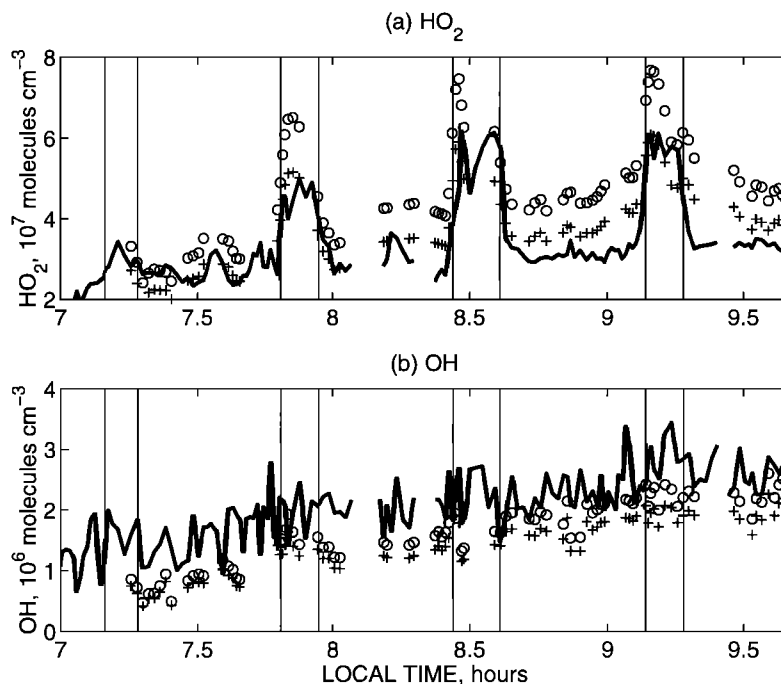


Figure 2. (a) HO₂ and (b) OH time series of concentrations between 7 and 9.7 LT on DC-8 flight 15. Observations are shown as solid lines. Circles show results from a standard photochemical calculation constrained with the ensemble of observations for other species aboard the aircraft. Crosses show the effect of increasing the rate constant for the CH₃O₂ + HO₂ 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 (O₃, CO, H₂O, NO_x, HNO₃, 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_x 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 HO₂, NO₂, NO₃, and N₂O₅, 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_x budget.

3.1. HO_x Enhancement in the Convective Outflow

Circles in Figure 2 show model results for HO₂ 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_x concentrations as the morning progresses, the HO₂ enhancement in the convective outflow region C, and the lack of a corresponding OH enhancement. However, the model is $\sim 30\%$ too high for HO₂. 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_x 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_x 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 ppbv d^{-1} versus 0.83 ppbv d^{-1}). The largest source of HO_x 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_x. (A primary source of HO_x such as the O(¹D) + H₂O reaction, or the photolysis of

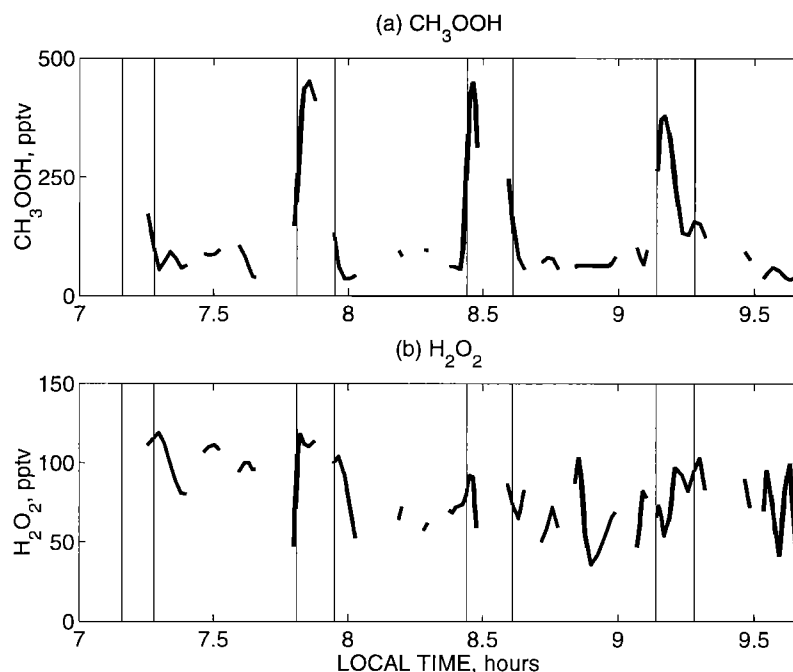


Figure 3. (a) CH₃OOH and (b) H₂O₂ mixing ratios observed between 7 and 9.7 LT on DC-8 flight 15. Vertical lines indicate when the airplane enters or exits the convective outflow (region C on Figure 1).

acetone or convected peroxides, is independent of the local HO_x concentration; the resulting HO_x leads to production of HCHO, mainly by oxidation of CH₄ by OH, and photolysis of this HCHO then provides a secondary source of HO_x 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_x source in the convective outflow is driven by CH₃OOH photolysis (5 times larger in the convective outflow). The CH₃OOH concentration in the convective outflow is 2–4 times above chemical steady state (Figure 4, discussed below) so that most of the corresponding HO_x source is due to photolysis of convected CH₃OOH rather than of CH₃OOH produced locally. Photolysis of CH₃OOH in the convective outflow is therefore mostly a primary rather than a recycling source of HO_x. The source of HO_x from ozone photolysis in the convective outflow is only 60% that from CH₃OOH photolysis. This result can be compared to the photochemical model study by Cohan *et al.* [1999] of a fresh convective outflow with 700 ppmv H₂O (82% relative humidity) in PEM-Tropics A, where ozone photolysis remained the major source of HO_x in the outflow despite the CH₃OOH enhancement. The convective outflow exam-

ined here is much drier (200 ppmv H₂O), 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 HO₂. The model reproduces this feature and it represents indeed a signature of the HO_x source from convected CH₃OOH. Although CH₃OOH photolysis yields OH as a direct product, this OH is quickly converted into HO₂ and CH₃O₂, and the OH/peroxy ratio is then controlled by cycling within the HO_x family [Jaeglé *et al.*, 2000]. Reaction of CH₃OOH with OH to form CH₃O₂ decreases the OH/peroxy ratio, compensating for the overall increase in HO_x and resulting in little change in OH concentrations in the convective outflow relative to the background atmosphere (Table 2).

3.2. Sensitivity to the CH₃O₂+HO₂ Reaction Rate Constant

As shown in Figure 2, the standard model simulation overestimates HO₂ 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 H₂O₂ and CH₃OOH constrained with the observed peroxides concentrations are not in balance in the background atmosphere: loss exceeds production for CH₃OOH, while production exceeds loss for H₂O₂, by large factors (Fig-

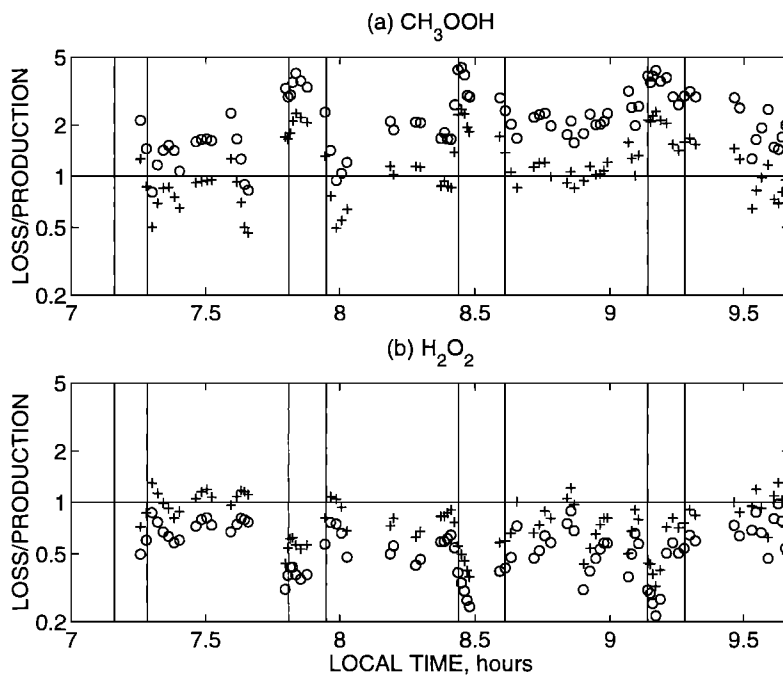


Figure 4. Ratios of chemical loss to production rates for (a) CH₃OOH and (b) H₂O₂ in the photochemical model calculation constrained with observed CH₃OOH and H₂O₂ concentrations on DC-8 flight 15. The chemical production and loss rates are computed as 24-hour averages for each point along the flight 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 CH₃O₂ + HO₂ 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 CH₃OOH in the background atmosphere, the measured peroxide concentrations are well above the detection limits (10 pptv for H₂O₂, 25 pptv for CH₃OOH [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 CH₃OOH and depleted in H₂O₂. 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 CH₃OOH, 2 days for H₂O₂) 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 CH₃O₂ + HO₂ → CH₃OOH + O₂ 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 HO₂. The reaction CH₃O₂ + HO₂ is then the largest single sink of HO_x (Table 2). Local ozone production rates decrease, amounting to 0.71 ppbv d⁻¹ in the convective

outflow and 0.66 ppbv d⁻¹ 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 CH₃OOH and H₂O₂ are brought into close balance in the background air, as increasing $k_{\text{CH}_3\text{O}_2+\text{HO}_2}$ increases the CH₃OOH production rate but decreases the H₂O₂ production rate (because of lower HO₂ concentrations). In the convective outflow, chemical loss of CH₃OOH still exceeds chemical production, while chemical production of H₂O₂ exceeds chemical loss, consistent with the expected effect of the convective transport on the peroxide budgets.

4. Conclusions

We have used concurrent observations of HO₂, OH, CH₃OOH, and H₂O₂ 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 CH₃OOH as a major primary source of HO_x 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 HO₂ were enhanced by 50% in the convective outflow, and this enhancement could be explained by the synchronous increase observed for

CH₃OOH. 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 CH₃OOH. Our results thus emphasize the need to account for convective transport of CH₃OOH in chemical models of the upper troposphere.

We found substantial evidence that the standard rate constant used in models for the reaction CH₃O₂ + HO₂ → CH₃OOH + O₂ [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, HO₂ 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 CH₃OOH and H₂O₂ 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 1.2×10^{-11} cm³ molecule⁻¹ s⁻¹ to 3.4×10^{-11} cm³ molecule⁻¹ s⁻¹) resolves these discrepancies. With the faster rate constant, the reaction CH₃O₂ + HO₂ becomes the most important HO_x radical sink (accounting for 35–45% of total HO_x 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 HO₂ 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_x concentrations in that region of the atmosphere.

Acknowledgments. This research was funded by the NASA Global Tropospheric Chemistry Program. The work of F. Ravetta was funded in part by the French Ministère des Affaires Étrangères (Bourse Lavoisier).

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(Received September 14, 2000; revised December 21, 2000; accepted January 3, 2001.)