

# Ozone production efficiencies of acetone and peroxides in the upper troposphere

Ian Folkins

Atmospheric Science Program, Departments of Physics and Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada

R. Chatfield, H. Singh, Y. Chen

Earth Science Division, NASA Ames Research Center, Moffett Field, CA

B. Heikes

Center for Atmospheric Chemistry Studies, Graduate School of Oceanography, University of Rhode Island, Narragansett

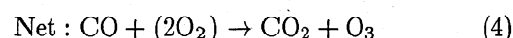
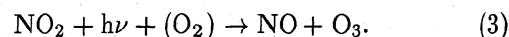
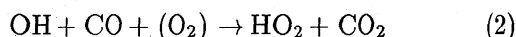
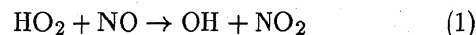
**Abstract.**  $\text{HO}_x$  concentrations in the upper tropical troposphere can be enhanced by the presence of acetone and the convective injection of peroxides. These enhancements in  $\text{HO}_x$  might be expected to increase ozone production by increasing the rate of the  $\text{HO}_2 + \text{NO}$  reaction. We show however that the convective enhancements of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ) above steady state during the PEM West B campaign were largely restricted to air parcels of marine boundary layer origin in which the mean NO concentration was 8 pptv. The ozone production efficiencies of the two peroxides at such low NO concentrations are very small. Their impact on the ozone budget of the upper tropical troposphere during PEM West B was therefore probably modest. Unlike the peroxides, acetone in the upper tropical troposphere during PEM West B exhibited a positive correlation with NO. It also has a much larger ozone production efficiency than either  $\text{H}_2\text{O}_2$  or  $\text{CH}_3\text{OOH}$ . It therefore has a much greater potential for significantly increasing ozone production rates in the upper tropical troposphere.

## 1. Introduction

Recent measurements are giving rise to new insights in our understanding of the radical chemistry of the upper tropical troposphere. Singh *et al.* [1995] showed that acetone ( $\text{CH}_3\text{COCH}_3$ ) concentrations in the upper tropical troposphere were large enough to make acetone photolysis a significant source of  $\text{HO}_x$  ( $= \text{OH} + \text{HO}_2$ ). Direct measurements of OH and  $\text{HO}_2$  appear to confirm the importance of acetone photolysis as a  $\text{HO}_x$  source [Wennberg *et al.*, 1998, McKee *et al.*, 1997]. There are however some cases in which observed OH and  $\text{HO}_2$  concentrations are larger than can be explained by invoking acetone photolysis in addition to the standard

$\text{HO}_x$  sources. Jaeglé *et al.* [1997] have argued that these cases can be explained by the convective transport, and subsequent photolysis, of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ) from the boundary layer into the upper tropical troposphere. This appears to confirm an earlier suggestion by Chatfield *et al.* [1984].

There are a number of reasons for wanting to improve our understanding of the radical chemistry of the upper tropical troposphere. The OH radical is the main oxidant of the troposphere, and as such, plays an important role in determining its chemical composition.  $\text{HO}_x$  radicals also play a pivotal role in the catalytic cycle which produces ozone from carbon monoxide (CO) oxidation.

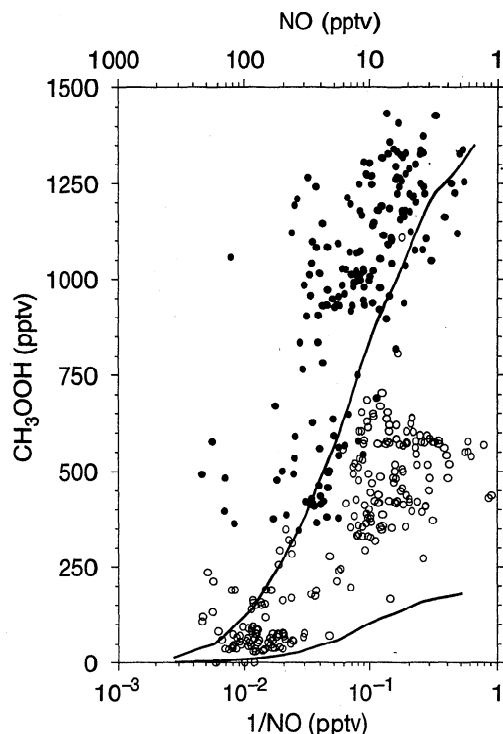


The rate of ozone production from this cycle can be increased by the presence of additional  $\text{HO}_x$  sources [Folkins *et al.*, 1997, Wennberg *et al.*, 1998]. The large scale increases in ozone production associated with acetone and the convective injection of boundary layer peroxides into the upper tropical troposphere have been estimated by Prather and Jacob [1997].

The ozone producing cycle given above (Reactions (1) - (4)) requires the participation of  $\text{NO}_x$  ( $= \text{NO} + \text{NO}_2$ ). This suggests that the amounts of ozone produced by  $\text{HO}_x$  precursors such as acetone and the peroxides will depend on the ambient  $\text{NO}_x$  concentration. In Figure 1,  $\text{CH}_3\text{OOH}$  is plotted against  $1/\text{NO}$  using measurements from the 1994 Pacific Exploratory Mission (PEM) West B campaign [Hoell *et al.*, 1997]. We have restricted attention to tropical (within  $20^\circ$  of the equator), and daylight (solar zenith angle less than  $80^\circ$ ) conditions. The solid circles were taken from near the surface (0-2 km), while the open circles were taken from the upper troposphere (9-12 km).  $\text{CH}_3\text{OOH}$  is anticorrelated with

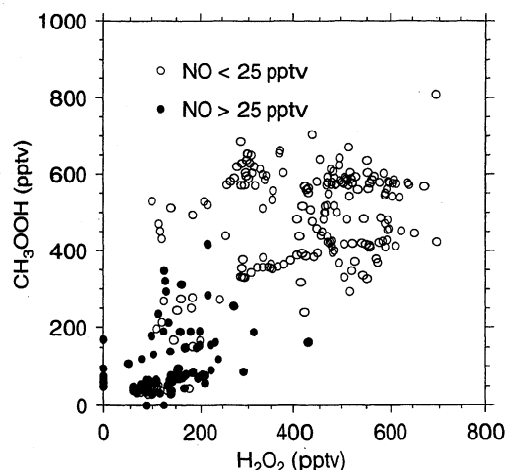
Copyright 1998 by the American Geophysical Union.

Paper number 98GL01030.  
0094-8534/98/98GL-01030\$05.00



**Figure 1.**  $\text{CH}_3\text{OOH}$  vs  $1/\text{NO}$  (pptv) from PEM West B between  $20^\circ\text{S}$  and  $20^\circ\text{N}$ , with solid (9–12 km) and open (0–2 km). The upper (1 km) and lower (10 km) curves represent the dependence of  $\text{CH}_3\text{OOH}$  on  $\text{NO}$  from a photochemical box model. Model  $\text{NO}$  refers to a day average (between sunrise and sunset) of the last day of a 10 day run.

$\text{NO}$  in both altitude intervals. The most likely origin of the anticorrelation in the upper troposphere is rapid convective transport of air from the boundary layer, in which there is a pre-existing anticorrelation driven by *in situ* chemistry. The upper curve in Figure 1 shows the predicted dependence of  $\text{CH}_3\text{OOH}$  on  $1/\text{NO}$  at 1 km from a photochemical model [Chatfield *et al.*, 1996]. The model was run for 10 days, long enough to allow  $\text{CH}_3\text{OOH}$  to reach steady state. The initial mixing ratios of  $\text{O}_3$ , acetone, PAN, CO,  $\text{CH}_4$ ,  $\text{HNO}_3$ , DMS,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  were 25 ppbv, 500 pptv, 20 pptv, 75 ppbv, 1.665 ppmv, 100 pptv, 5 pptv, 500 pptv, and 50 pptv respectively. The mixing ratios of  $\text{O}_3$ ,  $\text{NO}_x$ , and  $\text{NO}_y$  were held fixed during the 10 day simulations. The temperature was 290 K, the relative humidity 50 percent, the latitude  $15^\circ\text{N}$ , the surface albedo 0.1, and the date March 31. Although the upper 1 km model curve tends to underestimate  $\text{CH}_3\text{OOH}$  somewhat, (due probably to insufficient hydrocarbons), it roughly captures the decrease of the 0–2 km  $\text{CH}_3\text{OOH}$  measurements toward higher  $\text{NO}$  mixing ratios. The lower curve was run for the same conditions as the upper curve, but at an altitude of 10 km. It consistently substantially underestimates the observed 9–12 km  $\text{CH}_3\text{OOH}$  concentrations (open circles). This is in agreement with previous work demonstrating that peroxide concentrations in the up-



**Figure 2.** A scatterplot of  $\text{CH}_3\text{OOH}$  versus  $\text{H}_2\text{O}_2$ . Data is taken from the PEM West B campaign, 9–12 km, between  $20^\circ\text{S}$  and  $20^\circ\text{N}$ , and solar zenith angles less than  $80^\circ$ .

per tropical troposphere are underestimated by steady state models [Jacob *et al.*, 1996].

Figure 2 is a scatterplot of  $\text{CH}_3\text{OOH}$  versus  $\text{H}_2\text{O}_2$ , selected from upper tropospheric (9–12 km) PEM West B measurements using the same criteria as given above. Solid circles denote data points whose simultaneous  $\text{NO}$  mixing ratios were greater than 25 pptv, while open circles denote points with an  $\text{NO}$  mixing ratio of less than 25 pptv. Almost all high  $\text{NO}$  points have  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  less than 200 pptv, while almost all low  $\text{NO}$  points have both species larger than 200 pptv. This figure again suggests that the largest convective enhancements in the two peroxides during PEM West B occurred in low  $\text{NO}_x$  air parcels originating from the clean tropical marine boundary layer, where *in situ* chemistry most strongly favors peroxide formation.

Table 1 gives mean mixing ratios for various species in the low  $\text{NO}$  ( $\leq 25$  pptv with a mean of 8.5 pptv) “marine” and high  $\text{NO}$  ( $\geq 25$  pptv with a mean of 90.1 pptv) “continental” categories. Methyl iodide ( $\text{CH}_3\text{I}$ ), considered a tracer of marine boundary layer air, is twice as high in low  $\text{NO}$  “marine” than high  $\text{NO}$  “continental” air. Both  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  are four times higher in the low  $\text{NO}$  category. Acetone has a mildly positive correlation with  $\text{NO}$ , being 17 percent higher in “continental” air.

## 2. Ozone Production Efficiency

In order to investigate the impact of the anticorrelation between the peroxides and  $\text{NO}$  on the amount of ozone produced by the peroxides, we use the concept of ozone production efficiency (OPE). As originally introduced by Liu *et al.* [1987], it refers to the number of ozone molecules produced per emitted molecule of  $\text{NO}_x$ . Its remarkable feature is its dependence on the ambient  $\text{NO}_x$  concentration. When a  $\text{NO}_x$  molecule is

**Table 1.** Chemical characteristics of marine ( $\text{NO} < 25$  pptv) and continental ( $\text{NO} \geq 25$  pptv) upper tropical tropospheric air from the PEM West-B campaign. Latitude  $20^\circ\text{S}$  to  $20^\circ\text{N}$ , height 9–12 km, and solar zenith angle  $\leq 80^\circ$  only. All mean mixing ratios in pptv unless otherwise noted.

|                         | $\text{NO} < 25$ pptv |       | $\text{NO} \geq 25$ pptv |       |
|-------------------------|-----------------------|-------|--------------------------|-------|
|                         | Points                | Mean  | Points                   | Mean  |
| NO                      | 480                   | 8.5   | 372                      | 90.1  |
| $\text{CH}_3\text{OOH}$ | 381                   | 481.9 | 276                      | 104.4 |
| $\text{H}_2\text{O}_2$  | 381                   | 431.0 | 274                      | 128.2 |
| Acetone                 | 30                    | 303.2 | 89                       | 353.4 |
| $\text{CH}_3\text{I}$   | 231                   | 0.19  | 138                      | 0.09  |
| PAN                     | 94                    | 7.0   | 157                      | 34.1  |
| CO (ppbv)               | 419                   | 84.3  | 281                      | 71.7  |
| $\text{O}_3$ (ppbv)     | 472                   | 20.1  | 333                      | 30.9  |

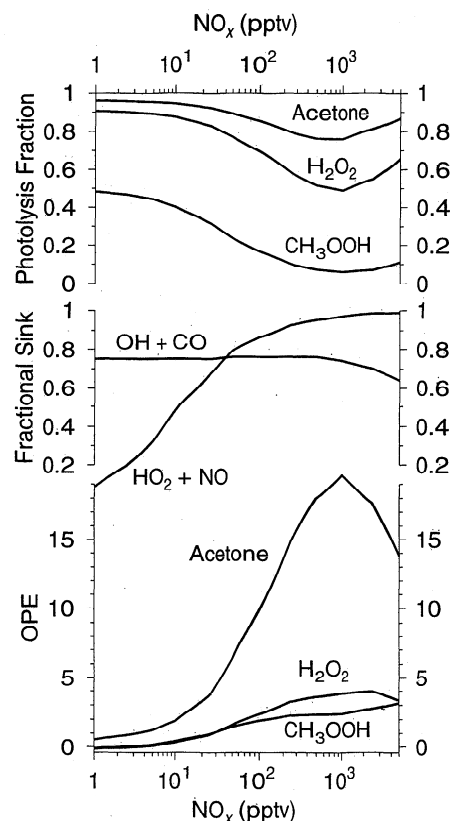
introduced into a chemical environment where the pre-existing  $\text{NO}_x$  concentration is very low, it will produce many more ozone molecules than when the  $\text{NO}_x$  concentration is very high.

We extend the concept of OPE to the peroxides and acetone as follows. First we run a baseline simulation with the same model conditions as given above. The mixing ratios of acetone,  $\text{CH}_3\text{OOH}$ , and  $\text{H}_2\text{O}_2$  were initially fixed at 500 pptv, 600 pptv, and 600 pptv respectively, but allowed to vary during the model run. The altitude was 12 km and the  $\text{H}_2\text{O}$  mixing ratio 29 ppmv. We then ran three perturbation simulations, in each of which one of the three  $\text{HO}_x$  precursors was increased by 10 pptv. The OPE was defined as the number of additional ozone molecules produced in the perturbed simulation over the baseline, divided by how much of the additional 10 pptv of  $\text{HO}_x$  precursor was used up after 10 days.

$$\text{OPE}(\text{H}_2\text{O}_2) = \frac{[\text{O}_3]_{\text{perturb}} - [\text{O}_3]_{\text{baseline}}}{10 + [\text{H}_2\text{O}_2]_{\text{baseline}} - [\text{H}_2\text{O}_2]_{\text{perturb}}}$$

Square brackets refer to mixing ratios in pptv at the end of the 10 day run. Analogous expressions can be written for  $\text{CH}_3\text{OOH}$  and acetone. In practice, the OPE's converge to constant values after 1–2 days, so that the definition is not very sensitive to the length of the simulations. The  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  perturbations are damped out after several days. Acetone has a longer lifetime, and about half of the initial 10 pptv perturbation is used up after 10 days. The lifetime of ozone in the upper troposphere is quite long. The ozone increases associated with the perturbations in the  $\text{HO}_x$  precursor concentrations therefore persists much longer than the perturbations themselves.

The OPE's of the three  $\text{HO}_x$  precursors were calculated using the method described above for a range of fixed  $\text{NO}_x$  mixing ratios. The results are shown in the bottom panel of Figure 3. All three OPE's increase with  $\text{NO}_x$  for  $\text{NO}_x$  less than 1000 pptv. The main rea-



**Figure 3.** (top) The fractional loss of each species over the first five days of the simulations that can be attributed to photolysis, plotted versus  $\text{NO}_x$ . The balance of the loss is due to OH attack. (middle) The fractional sink of OH and  $\text{HO}_2$  that can be attributed to reaction with CO and NO respectively. (bottom) Ozone production efficiencies of  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ , and acetone versus  $\text{NO}_x$ .

son for this is that increasing the NO concentration increases  $\text{HO}_x$  recycling. The number of ozone molecules produced per  $\text{HO}_x$  molecule created is roughly proportional to the number of times a  $\text{HO}_x$  molecule completes the cycle given by Reactions (1) and (2) before being converted to some other molecule. Increasing the NO concentration increases  $\text{HO}_x$  recycling, and ozone production, by increasing the likelihood that  $\text{HO}_2$  will react with NO. The fraction of  $\text{HO}_2$  reacting with NO is plotted versus  $\text{NO}_x$  in the middle panel of Figure 3. This fraction was calculated by taking the rate of Reaction (1) and dividing it by the sum of the rates of all reactions involving  $\text{HO}_2$ . It is less than 10 percent for  $\text{NO}_x$  less than 1 pptv, but increases to above 95 percent for  $\text{NO}_x$  larger 1000 pptv. This increase is largely responsible for the increasing OPE's of the three  $\text{HO}_x$  precursors in this  $\text{NO}_x$  interval.

Figure 3 also shows that the OPE's of acetone and  $\text{H}_2\text{O}_2$  decrease with  $\text{NO}_x$  for  $\text{NO}_x$  larger than 1000 pptv. This is due to the increasing importance of the  $\text{OH} + \text{NO}_2$  nitric acid formation reaction. As a  $\text{HO}_x$  sink, this reaction decreases both  $\text{HO}_x$  recycling and ozone production. The decrease in the relative impor-

tance of the CO oxidation as an OH sink for  $\text{NO}_x$  larger than 1000 pptv is also shown in Figure 3.

In addition to  $\text{HO}_x$  production via photolysis, acetone and the peroxides can function as  $\text{HO}_x$  sinks by being subject to OH attack. The top panel of Figure 3 plots the fractional destruction of the three  $\text{HO}_x$  precursors that occurs via photolysis. For  $\text{NO}_x$  less than 1000 pptv, OH concentrations increase with  $\text{NO}_x$ . This increases the likelihood of OH attack on the three  $\text{HO}_x$  precursors, decreases the number of  $\text{HO}_x$  precursors available for photolysis, and inhibits the growth of the OPE's. The OPE of acetone increases more rapidly with  $\text{NO}_x$  than the other two because it is least susceptible to OH attack.

### 3. Discussion and Conclusions

The central importance of ozone to tropospheric chemistry derives from the fact that ozone photolysis is the strongest direct source of OH. Ozone is also an important greenhouse gas. We have demonstrated that  $\text{HO}_x$  precursors can produce ozone in the upper tropical troposphere, and that the size of this production depends very strongly on the ambient NO concentration. Because of this strong dependence, it will be important to take into account observed correlations between NO and the various  $\text{HO}_x$  precursors when estimating their impact on the ozone budget of the tropical troposphere. The anticorrelation between the peroxides and NO seen in PEM West B will diminish their impact on ozone, while the impact of acetone will be increased because it is positively correlated with NO.

There are however a number of questions that remain unresolved. It is unclear to what extent the correlations discussed in this paper apply to other tropical regions and seasons. For example, biomass burning can increase near surface concentrations of both peroxides and NO. It is also likely that the anticorrelations between the peroxides and NO seen in the upper troposphere during PEM West B were partly driven by *in situ* chemistry, and not solely by transport from the boundary layer. OH concentrations usually increase with NO, so that peroxide concentrations in air parcels recently detrained from convective clouds will tend to decrease more rapidly when the NO concentration is higher. And finally, the OPE estimates given here are probably upper limits. We have also done OPE calculations in which the  $\text{NO}_x$  concentration was allowed to float (as opposed to the fixed  $\text{NO}_x$  simulations discussed here). In this case, the injection of additional  $\text{HO}_x$  precursors decreases the  $\text{NO}_x$  lifetime. This is because higher OH concentrations increase the rate of conversion of  $\text{NO}_x$  to  $\text{HNO}_3$ . Injecting additional acetone also tends to decrease  $\text{NO}_x$  by increasing PAN formation [Arnold *et al.*, 1997]. Although the  $\text{NO}_x$  decreases associated with additional amounts of  $\text{HO}_x$  precursors are small, they decrease the ozone production efficiencies of acetone and the two peroxides by about 50 percent.

**Acknowledgments.** This research was partially supported by the NASA Global Tropospheric Experiment (GTE) and the Subsonic Assessment Program. We thank all investigators from GTE/PEM-West (B) for making their data available.

### References

- Arnold, F., et al., Acetone in the upper troposphere and lower stratosphere: Impact on trace gases and aerosols, *Geophys. Res. Lett.*, 24, 3017-3020, 1997.
- Chatfield, R. B., J. A. Vastano, H. B. Singh, and G. Sachse, A general model of how fire emissions and chemistry produce African/oceanic plumes ( $\text{O}_3$ , CO, PAN, smoke) in TRACE A, *J. Geophys. Res.*, 101, 24,279-24,306, 1996.
- Chatfield, R. B., and P. J. Crutzen, Sulfur Dioxide in remote oceanic air: Cloud transport of reactive precursors, *J. Geophys. Res.* 89, 7111-7132, 1984.
- Folkins, I., P. O. Wennberg, T. F. Hanisco, J. G. Anderson, and R. J. Salawitch, OH,  $\text{HO}_2$ , and NO in two biomass burning plumes: Sources of  $\text{HO}_x$  and implications for ozone production, *Geophys. Res. Lett.*, 24, 3185 - 3188, 1997.
- Hoell, J. M., et al., The Pacific Exploratory Mission - West Phase B: February - March 1994, *J. Geophys. Res.*, 102,, 28,223 - 28,239, 1997.
- Jaeglé, L. et al., Observed OH and  $\text{HO}_2$  in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, 24, 3181-3184, 1997.
- Jacob, D. J., et al., Origin of ozone and  $\text{NO}_x$  in the tropical troposphere: a photochemical analysis of aircraft observations over the South Atlantic basin, *J. Geophys. Res.*, 101, 24,235-24,250, 1996.
- Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and implications for regional and global ozone distributions, *J. Geophys. Res.*, 92, 4191-4207, 1987.
- McKeen, S. A., et al., The photochemistry of acetone in the upper troposphere: A source of odd-hydrogen radicals, *Geophys. Res. Lett.*, 24, 3177 - 3180, 1997.
- Prather, M. J., and D. J. Jacob, A persistent imbalance in  $\text{HO}_x$  and  $\text{NO}_x$  photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett.*, 24, 3189 - 3192, 1997.
- Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob, High concentration and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature* 378, 50-54, 1995.
- Wennberg, P. O., et al., Hydrogen radicals, nitrogen radicals, and the production of ozone in the upper troposphere, *Science*, 279, 49 - 53, 1998.

I. Folkins, Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J1. (e-mail: folkins@atm.dal.ca)

R. Chatfield, H. Singh, Y. Chen, Earth Science Division, NASA Ames Research Center, MS 245-5, Moffett Field, CA 94035. (email: chatfield@clio.arc.nasa.gov)

B. Heikes, GSO/CACAS, University of Rhode Island, South Ferry Rd., Narragansett, RI 02882-1197. (email: zagar@notos.gso.uri.edu)

(Received September 22, 1997; revised January 26, 1997; accepted March 16, 1998.)