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Ian Folkins

R. Chatfield

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Authors

Ian Folkins, R. Chatfield, H. Singh, Y. Chen, and Brian G. Heikes

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

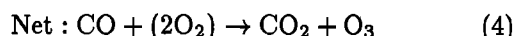
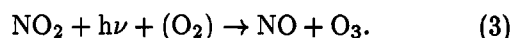
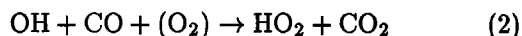
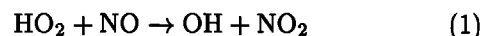
Abstract. HO_x concentrations in the upper tropical troposphere can be enhanced by the presence of acetone and the convective injection of peroxides. These enhancements in HO_x might be expected to increase ozone production by increasing the rate of the HO₂ + NO reaction. We show however that the convective enhancements of hydrogen peroxide (H₂O₂) and methyl hydroperoxide (CH₃OOH) 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 H₂O₂ or CH₃OOH. 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 (CH₃COCH₃) concentrations in the upper tropical troposphere were large enough to make acetone photolysis a significant source of HO_x (= OH + HO₂). Direct measurements of OH and HO₂ appear to confirm the importance of acetone photolysis as a HO_x source [*Wennberg et al.*, 1998, *McKeen et al.*, 1997]. There are however some cases in which observed OH and HO₂ concentrations are larger than can be explained by invoking acetone photolysis in addition to the standard

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 (H₂O₂) and methyl hydroperoxide (CH₃OOH) 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. 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 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 NO_x (= NO + NO₂). This suggests that the amounts of ozone produced by HO_x precursors such as acetone and the peroxides will depend on the ambient NO_x concentration. In Figure 1, CH₃OOH is plotted against 1/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° of the equator), and daylight (solar zenith angle less than 80°) 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). CH₃OOH is anticorrelated with

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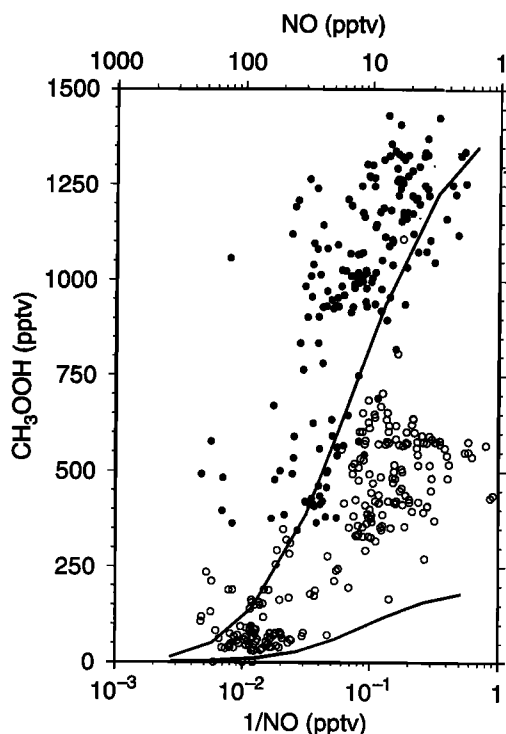


Figure 1. CH_3OOH vs $1/\text{NO}$ (pptv) from PEM West B between 20°S and 20°N , with solid (9–12 km) and open (0–2 km). The upper (1 km) and lower (10 km) curves represent the dependence of CH_3OOH on NO from a photochemical box model. Model NO refers to a day average (between sunrise and sunset) of the last day of a 10 day run.

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 CH_3OOH 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 CH_3OOH to reach steady state. The initial mixing ratios of O_3 , acetone, PAN, CO, CH_4 , HNO_3 , DMS, C_2H_6 , and C_3H_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 O_3 , NO_x , and NO_y were held fixed during the 10 day simulations. The temperature was 290 K, the relative humidity 50 percent, the latitude 15°N , the surface albedo 0.1, and the date March 31. Although the upper 1 km model curve tends to underestimate CH_3OOH somewhat, (due probably to insufficient hydrocarbons), it roughly captures the decrease of the 0–2 km CH_3OOH measurements toward higher 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 CH_3OOH concentrations (open circles). This is in agreement with previous work demonstrating that peroxide concentrations in the up-

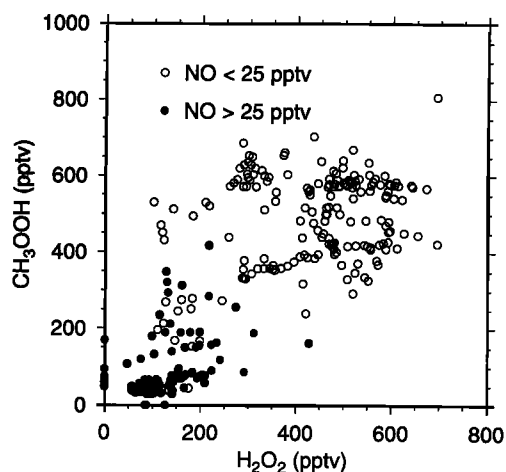


Figure 2. A scatterplot of CH_3OOH versus H_2O_2 . Data is taken from the PEM West B campaign, 9–12 km, between 20°S and 20°N , and solar zenith angles less than 80° .

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

Figure 2 is a scatterplot of CH_3OOH versus H_2O_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 NO mixing ratios were greater than 25 pptv, while open circles denote points with an NO mixing ratio of less than 25 pptv. Almost all high NO points have H_2O_2 and CH_3OOH less than 200 pptv, while almost all low 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 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 NO (≤ 25 pptv with a mean of 8.5 pptv) “marine” and high NO (≥ 25 pptv with a mean of 90.1 pptv) “continental” categories. Methyl iodide (CH_3I), considered a tracer of marine boundary layer air, is twice as high in low NO “marine” than high NO “continental” air. Both H_2O_2 and CH_3OOH are four times higher in the low NO category. Acetone has a mildly positive correlation with 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 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 NO_x . Its remarkable feature is its dependence on the ambient NO_x concentration. When a NO_x molecule is

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

	$\text{NO} \leq 25$ pptv		$\text{NO} > 25$ pptv	
	Points	Mean	Points	Mean
NO	480	8.5	372	90.1
CH_3OOH	381	481.9	276	104.4
H_2O_2	381	431.0	274	128.2
Acetone	30	303.2	89	353.4
CH_3I	231	0.19	138	0.09
PAN	94	7.0	157	34.1
CO (ppbv)	419	84.3	281	71.7
O_3 (ppbv)	472	20.1	333	30.9

introduced into a chemical environment where the pre-existing NO_x concentration is very low, it will produce many more ozone molecules than when the 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, CH_3OOH , and H_2O_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 H_2O mixing ratio 29 ppmv. We then ran three perturbation simulations, in each of which one of the three 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 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 CH_3OOH 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 H_2O_2 and CH_3OOH 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 HO_x precursor concentrations therefore persists much longer than the perturbations themselves.

The OPE's of the three HO_x precursors were calculated using the method described above for a range of fixed NO_x mixing ratios. The results are shown in the bottom panel of Figure 3. All three OPE's increase with NO_x for NO_x less than 1000 pptv. The main rea-

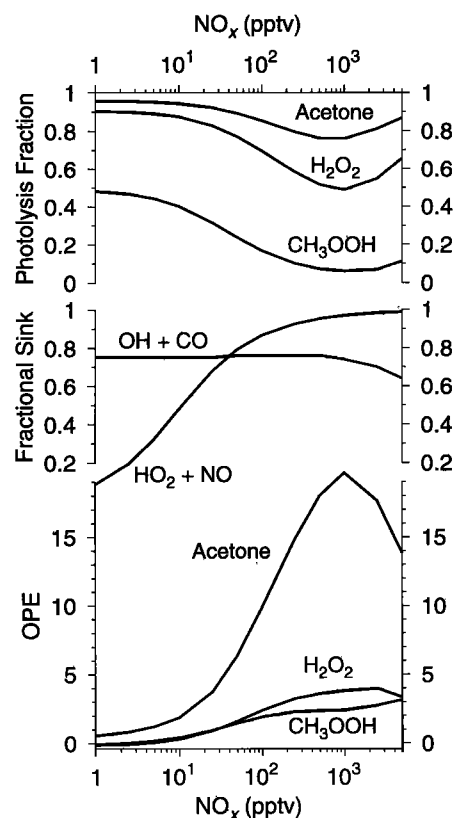


Figure 3. (top) The fractional loss of each species over the first five days of the simulations that can be attributed to photolysis, plotted versus NO_x . The balance of the loss is due to OH attack. (middle) The fractional sink of OH and HO_2 that can be attributed to reaction with CO and NO respectively. (bottom) Ozone production efficiencies of H_2O_2 , CH_3OOH , and acetone versus NO_x .

son for this is that increasing the NO concentration increases HO_x recycling. The number of ozone molecules produced per HO_x molecule created is roughly proportional to the number of times a HO_x molecule completes the cycle given by Reactions (1) and (2) before being converted to some other molecule. Increasing the NO concentration increases HO_x recycling, and ozone production, by increasing the likelihood that HO_2 will react with NO. The fraction of HO_2 reacting with NO is plotted versus 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 HO_2 . It is less than 10 percent for NO_x less than 1 pptv, but increases to above 95 percent for NO_x larger than 1000 pptv. This increase is largely responsible for the increasing OPE's of the three HO_x precursors in this NO_x interval.

Figure 3 also shows that the OPE's of acetone and H_2O_2 decrease with NO_x for NO_x larger than 1000 pptv. This is due to the increasing importance of the OH + NO_2 nitric acid formation reaction. As a HO_x sink, this reaction decreases both HO_x recycling and ozone production. The decrease in the relative impor-

tance of the CO oxidation as an OH sink for NO_x larger than 1000 pptv is also shown in Figure 3.

In addition to HO_x production via photolysis, acetone and the peroxides can function as HO_x sinks by being subject to OH attack. The top panel of Figure 3 plots the fractional destruction of the three HO_x precursors that occurs via photolysis. For NO_x less than 1000 pptv, OH concentrations increase with NO_x . This increases the likelihood of OH attack on the three HO_x precursors, decreases the number of HO_x precursors available for photolysis, and inhibits the growth of the OPE's. The OPE of acetone increases more rapidly with 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 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 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 NO_x concentration was allowed to float (as opposed to the fixed NO_x simulations discussed here). In this case, the injection of additional HO_x precursors decreases the NO_x lifetime. This is because higher OH concentrations increase the rate of conversion of NO_x to HNO_3 . Injecting additional acetone also tends to decrease NO_x by increasing PAN formation [Arnold *et al.*, 1997]. Although the NO_x decreases associated with additional amounts of HO_x precursors are small, they decrease the ozone production efficiencies of acetone and the two peroxides by about 50 percent.

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I. Folkens, Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J1. (e-mail: folkens@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/CACS, University of Rhode Island, South Ferry Rd., Narragansett, RI 02882-1197. (email: zagar@notos.gso.uri.edu)

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