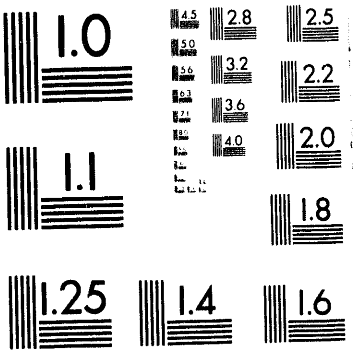
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FORMATION OF GAS-PHASE PEROXIDES IN A RURAL ATMOSPHERE: AN INTERPRETATION OF THE RECENT SOS/SERON FIELD RESULTS

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ABSTRACT

Hydrogen peroxide (H_2O_2) and certain organic peroxides such as methyl-hydroperoxide (MHP, CH_3OOH) and hydroxymethyl-hydroperoxide (HMHP, $OHCH_2OOH$) are gas-phase oxidants present in the atmosphere at ppbv concentration levels. These oxidants play an important role in atmospheric chemistry. In addition, precipitation containing H_2O_2 is toxic to trees, and it has also been suggested that organic peroxides formed presumably by ozone reactions with biogenic alkenes are responsible for leaf disorders. Recently, we have developed a nonenzymatic method for aqueous-phase H_2O_2 measurement, using Fenton reagent and fluorescent hydroxy-benzoic acid. The new method, in conjunction with the well-known method of p-hydroxyphenylacetic acid (POHPAA) and horseradish peroxidase for total peroxides, and together with an improved gas scrubber to mitigate sampling line problems, has been successfully deployed in recent SOS/SERON field measurements in rural Georgia. For the first time, continuously measured and speciated gas-phase peroxide data have become available, making it possible to examine some aspects of the ozone chemistry leading to the formation of these oxidants. It is observed that daily H_2O_2 maximum frequently occurs at a different time than does HMHP, and that H_2O_2 concentration, but not HMHP, tends to correlate with solar fluxes measured at the same location. These findings seem to indicate that the formation mechanisms for H_2O_2 and organic peroxides are basically different. It is likely that H_2O_2 is formed from radical-radical recombination, while HMHP is formed by ozone-alkene reactions. Since the gas-phase ozone-alkene reactions are usually too slow to account for the diurnal concentration variations observed for HMHP, heterogeneous processes involving ozone and alkenes are also a possibility.

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1. INTRODUCTION

Hydrogen peroxide (H_2O_2) and certain organic peroxides such as methyl hydroperoxide (MHP, CH_3COOH) and hydroxymethyl hydroperoxide (HMHP, $OHCH_2OOH$) are gas-phase oxidants present in the atmosphere at ppbv concentration levels (Olszyna *et al.*, 1988; Hellpointner and Gäb, 1989; Hewitt and Kok, 1991). These oxidants play an important role in atmospheric chemistry, including the oxidation of S(IV) to S(VI) in aqueous droplets (Penkett *et al.*, 1979; Daum *et al.*, 1984; Gervat *et al.*, 1988; Zhou and Lee, 1992). In addition, precipitation containing H_2O_2 is toxic to trees (Masuch *et al.*, 1986; Kettrup *et al.*, 1991), and it has also been shown that organic peroxides are present inside leaves of plants that have been exposed to O_3 (Hewitt *et al.*, 1990). Recently, we have developed a nonenzymatic method for aqueous-phase H_2O_2 measurement, using Fenton reagent and fluorescent hydroxybenzoic acid (Lee *et al.*, 1990). The new method, in conjunction with the well-known p-hydroxyphenylacetic acid (POHPAA) - horseradish peroxidase technique for total peroxides (Lazrus *et al.*, 1986) and an improved gas scrubber to mitigate sampling line problems, has been successfully deployed in recent SOS/SERON field measurements in rural Georgia (Lee *et al.*, 1993a; 1993b). For the first time, continuously measured and speciated gas-phase peroxide data have become available, making it possible to examine some aspects of the ozone chemistry leading to the formation of peroxides.

Traditionally, hydrogen peroxide and organic peroxides in the atmosphere were thought to be formed from radical recombination:

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (1)$$

where R is an alkyl group, an acyl group, or a hydrogen atom. The free radicals were produced from photochemical reactions initiated by the photolysis of ozone and NO_2. However, recent laboratory experiments have shown that gas-phase ozone reactions with alkenes in the presence of water vapor may lead to the formation of both aerosols and peroxides (Gäb *et al.*, 1985; Becker *et al.*, 1990; Simonaitis *et al.*, 1991; Hewitt and Kok, 1991), with lower reactant concentrations and lighter alkenes expected to produce a greater amount of peroxides. The gas-phase reaction is believed to proceed by addition of ozone to the unsaturated C=C bond forming a molozonide, which subsequently decomposes into a carbonyl molecule and a 'hot' Criegee biradical, RR'COO* (Martinez *et al.*, 1981). At atmospheric pressure, the excited Criegee biradical is collisionally stabilized and undergoes bimolecular reaction with other gases. In the case of ozone reactions with terminal alkenes such as 1-butene and isoprene, the stabilized biradical, H_2COO, is expected to react with water vapor in hot and humid environments to form HMHP according to the following reactions:

$$RCH{=}CH_2 + O_3 \rightarrow H_2COO + RCHO \qquad (2)$$

$$H_2COO + H_2O \rightarrow HOCH_2OOH \qquad (3)$$

Thus, field measurements of H_2O_2 and HMHP carried out in rural Georgia on hot and humid summer days appear to be ideally suited for testing the atmospheric oxidant formation mechanisms postulated on the basis of laboratory observations. It is rationalized that, since H_2O_2 is formed mostly from recombination of HO_2 radicals resulting from photochemical activities, its daytime concentration variations should correlate with solar flux changes measured at the same time and location. On the other hand, HMHP concentrations should be related to the concentration of ozone, alkenes, and absolute humidity.

2. EXPERIMENTAL

The work reported here is a part of the Southern Oxidant Study (SOS), which was initiated in response to the problem of photochemical oxidant formation in the southeastern US (UCAR, 1991). The site, which is located in George L. Smith Park near Metter, Georgia, belongs to a multi-tier measurement network called Southeastern Regional Oxidant Network (SERON). During 4 weeks of the summer of 1991, this SERON site was operated by Brookhaven National Laboratory. A detailed description of the sampling site, instrumentation, and meteorological conditions has been given by Kleinman *et al.* (1993), addressing the formation of ozone in the southeastern US. In particular, the sampling method for H_2O_2 and HMHP, together with some of the SOS/SERON data, has been described elsewhere (Lee *et al.*, 1993a).

3. RESULTS AND DISCUSSION

Daytime gas-phase peroxide measurements were made over a two-week period starting July 25, 1991. Because of some technical difficulties experienced with the first-time deployment of the newly developed sampling method, data were actually obtained for ten days covering July 26-31, August 5, 6, and 8-10. During this period, ambient H_2O_2 concentrations varied between 1 and 4 ppbv, whereas HMHP varied between 0.5 and 5 ppbv. The high HMHP concentration levels usually occurred on hot, humid, and hazy days. It was observed that daily H_2O_2 maximum frequently occurred 1 to 2 hours earlier than HMHP.

Figure 1 shows the peroxide concentration profiles obtained on July 29. It was an average summer day with noontime temperature around 32°C and 60% RH. The ozone level was almost flat at 43 ppbv. The H_2O_2 concentration was found to correlate reasonably well with the solar flux as shown in Figure 2. Note that the points in Figure 1 are 1-minute average values, whereas in Figure 2 they are 10-minute averages. Although the general shapes of the two profiles, solar flux vs. time and H_2O_2 vs. time, look very much alike, the use of longer average values makes the correlation somewhat better, because it damps out the high frequency oscillations observed in the solar flux.

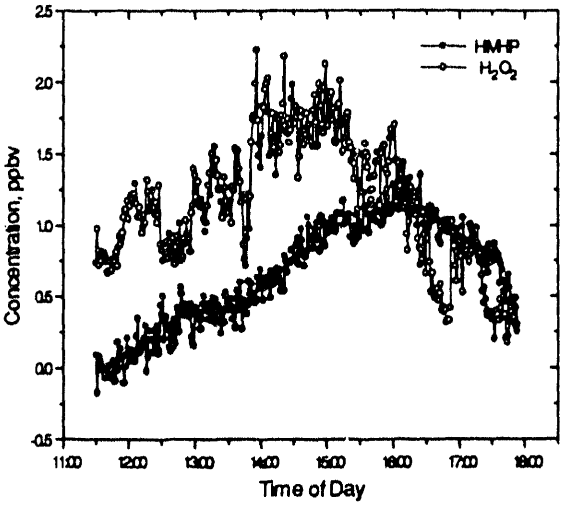

Figure 1 Peroxide concentration profiles, July 29, 1991.

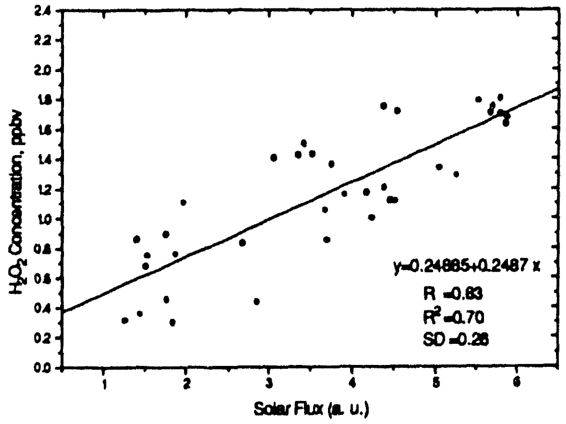

Figure 2 Correlation of H_2O_2 with solar flux, July 29, 1991.

The following day, July 30, was a rather eventful day with periods of showers. The average daytime temperature was about a relatively cool 27°C. Figure 3 shows the periodic changes in solar flux as showers passed by. Since showers provided a very effective removal process for gas-phase H_2O_2, which is highly soluble in water, the H_2O_2 concentration profile appeared to follow the solar flux remarkably well, as photochemical activity resumed after each period of showers.

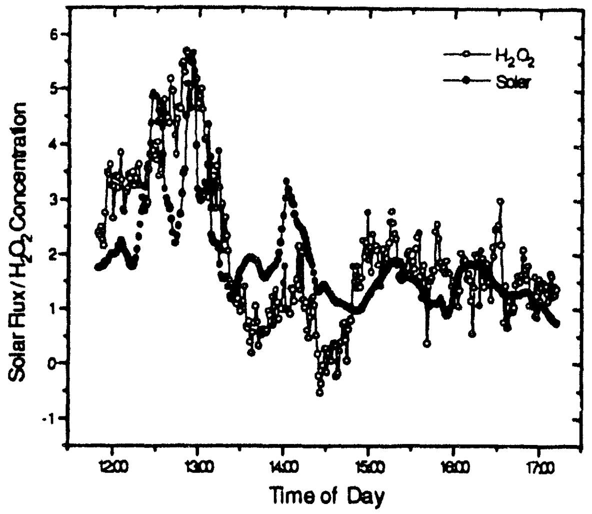

Figure 3 H_2O_2 and solar flux profiles, July 30,1991.

If the formation of HMHP in the atmosphere occurs mainly via alkene ozonolysis according to (2) and (3), it follows that daily HMHP levels would be determined by ozone and alkene concentrations. Unfortunately however, there was no extensive effort on site to measure alkene concentrations except for a few canister samples taken occasionally during the entire program. Kleinman et al. (1993) reported an average isoprene concentration of 6 ppbv based on 9 to 12 canister samples. It is known that emissions of isoprene and monoterpene from vegetation are controlled by changes in light and temperature (Guenther et al., 1993). A sharp increase in isoprene emission is observed at leaf temperatures less than 30°C. Emissions continue to slowly increase with higher temperatures until a maximum emission is reached at about 40°C, after which emissions rapidly decline. This temperature dependence can be described by an enzyme activation mechanism that includes denaturation at high temperatures. Because of the temperature dependence of isoprene, we would expect daily HMHP concentration to depend on seasonal daytime temperature. The 10-day data reported in this study indeed indicate such a trend as shown in Figure 4, where the maximum daily HMHP concentrations are plotted vs. mean daytime temperature taken between 1100 and 1800 hrs, during which time the peroxide measurements were routinely made. Of course, in addition to reactant concentrations, the ozone-alkene reaction rate also depends on temperature, again contributing to the observed HMHP concentration increase with increasing temperature.

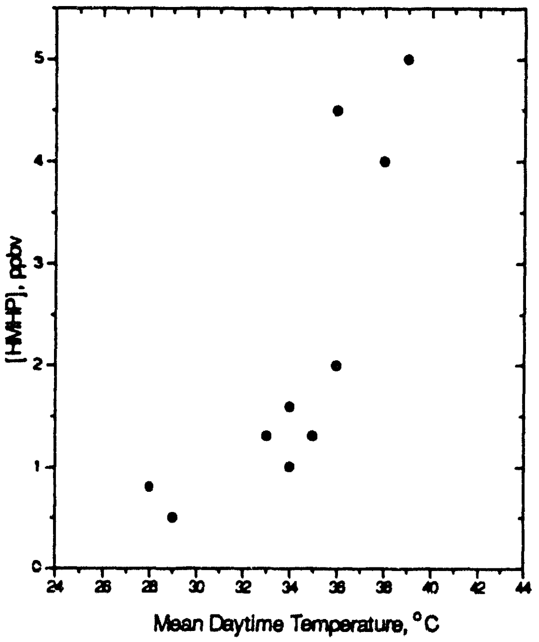

Figure 4 Dependence of ambient HMHP on temperature

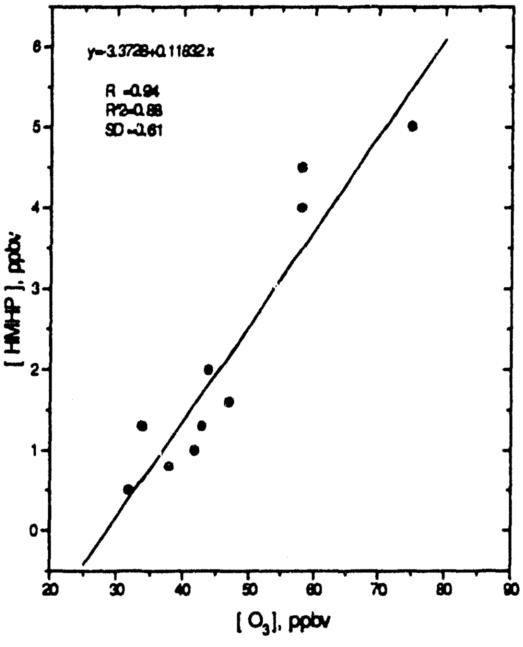

Figure 5 Correlation of HMHP with ambient ozone.

Likewise, the alkene ozonolysis mechanism should predict a positive correlation between HMHP and ozone concentrations. Kleinman et al. (1993) have tabulated the maximum daily ozone concentrations for the entire experimental period. These ozone data, together with the HMHP data reported in this study, were used to test this hypothesis and the results are shown in Figure 5. As discussed above, the atmospheric HMHP concentration is controlled by several factors, of which the ambient ozone concentration is predominant. The good correlation shown in Figure 5 is a strong indication that atmospheric HMHP is formed by molecular reactions involving ozone, not by radical-radical recombinations as in the case of H_2O_2 and some other organic peroxides such as methyl hydroperoxide (MHP, CH_3OOH). No strong correlation was found between H_2O_2 and ozone concentrations in our 1991 data.

4. CONCLUSION

As part of the SOS/SERON study carried out in Metter, Ga in the summer of 1991, continuous daytime H_2O_2 and HMHP concentrations were obtained using the nonenzymatic fluorescence method newly developed at Brookhaven National Laboratory. These data, in conjunction with the measurements of solar flux, ozone concentration, and ambient temperature, have offered a unique opportunity to examine in detail the formation of oxidants in the rural southeastern US. It is concluded that, while H_2O_2 is mostly formed from recombination of radicals resulting from photochemical activity, HMHP is a product of molecular reactions involving ozone and alkenes emitted from local biogenic sources.

5. ACKNOWLEDGMENT

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6. REFERENCES

Becker, K. H., K. T. Brockman, and J. Bechara (1990) Production of hydrogen peroxide in forest air by reaction of ozone with terpenes, *Nature*, **246**, 256-258

Daum, P. H., S. E. Schwartz, T. J. Kelly, and L. Newman (1984) Measurements of the chemical composition of stratiform clouds. *Atmos. Environ.*, **18**, 2671-2684

Gäb, S., E. Hellpointner, W. V. Turner, and F. Korte (1985) Hydroxymethyl hydroperoxide and bis(hydroxymethyl) peroxide from gas phase ozonolysis of naturally occurring alkenes. *Nature*, **316**, 535-386

Gervat, G. P., P. A. Clark, A. R. W. Marsh, I. Teasdale, A. S. Chandler, T. W. Choulaton, M. J. Gay, M. K. Hill, T. A. Hill (1988) Field evidence for the oxidation of SO_2 by H_2O_2 in cap cloud. *Nature*, **333**, 241-243

Guenther, A. B., P. R. Zimmerman, and P. C. Harley (1993) Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analysis. *J. Geophys. Res.*, **98**, 12609-12617

Hellpointner, E., and S. Gäb (1989) Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation. *Nature*, **337**, 631-634

Hewitt, C. N., and G. L Kok (1991) Formation and occurrence of organic hydroperoxides in the troposphere: Laboratory and field observations. *J. Atmos. Chem.*, **12**, 181-194

Hewitt, C. N., G. L Kok, and R. Fall (1990) Hydroperoxides inplants exposed to ozone mediate air pollution damage to alkene emitters. *Nature*, **344**, 56-57

Kettrup, A., H. G. Kincinski, and G. Masuch (1991) Investigating the effect of hydrogen peroxide on Norwayspruce trees. *Anal. Chem.*, **63**, 1047A-1056A

Kleinman, L., Y. -N. Lee, S. R. Sprinston, L. Nunnermacker, X. Zhou, R. Brown, K. Hallock, P. Klotz, J. H. Lee, L. Newman (1993) Ozone formation at aural site in the southeastern US. *J. Geophys. Res.*, submitted

Lazrus, A. L., G. L. Kok, J. A. Lind, S. N. Gitlin, B. G. Heikes, and R. E. Shetter (1986) Automated fluorometric method for hydrogen peroxide in air. *Anal. Chem.*, **58**, 594-597

Lee, J. H., I. N. Tang, and J. B. Weinstein-Lloyd (1990) Nonenzymatic method for the determination of hydrogen peroxide in atmospheric samples, *Anal. Chem.*, **62**, 2381-2384

Lee, J. H., D. F. Leahy, I. N. Tang, and L. Newman (1993a) Measurement and speciation of gas phase peroxides in the atmosphere. *J. Geophys. Res.*, **98**, 2911-2915

Lee, J. H., Tang, I. N., J. B. Weinstein-Lloyd, and E. B. Halper (1993b) An improved nonenzymatic method for the determination of gas-phase peroxides. *Environ. Sci. Tech.* submitted

Martinez, R. I., J. T. Herron, R. E. Huie (1981) The mechanism if ozone-alkene reactions in the gas phase. A mass spectrometric study of the reactions of eight linear and branched-chain alkenes. *J. Am. Chem. Soc.*, **103**, 3807-3820

Masuch, G., A. Kettrup, R. J. Mallant, and J. Slanina (1986) Effects of H_2O_2 containing acidic fog on young tree. *Int. J. Environ. Anal. Chem.*, **27**, 183-213

Olszyna, K. J., J. F. Meagher, and E. M. Bailey (1988) Gas-phase, cloud and rain-water measurement of hydrogen peroxide at a high elevation site. *Atmos. Environ.*, **22**, 1699-1706

Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton (1979) The importance of atmospheric O_3 and H_2O_2 in oxidizing SO_2 in cloud and rainwater. *Atmos. Environ.*, **13**, 123-137

Simonaitis, R., K. J. Olszyna, J. F. Meagher (1991) Production of hydrogen peroxide and organic peroxides in the gas phase reactions of ozone with natural alkenes. *Geophs. Res. Lett.*, **18**, 9-12

University Corporation for Atmospheric Research, SERON: The Southeastern Regional Oxidant Network, August, 1990

Zhou, X., and Y. -N. Lee (1992) Aqueous solubility and reaction kinetics of hydrxymethyl hydroperoxide. *J. Phys. Chem.*, **96**, 265-272

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