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H_2O_2 Levels in Rainwater Collected in South Florida and the Bahama Islands

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Measurements of H_2O_2 in rainwater collected in Miami, Florida, and the Bahama Islands area indicate the presence of H_2O_2 concentration levels ranging from $(1-7) \times 10^{-5}$ M. No systematic trends in H_2O_2 concentration were observed during an individual storm, in marked contrast to the behavior of other anions (e.g., $[NO_3^-]$, $[SO_4^=]$, and $[Cl^-]$). The data suggest that a substantial fraction of the H_2O_2 found in precipitation is generated by aqueous-phase reactions within the cloudwater rather than via rainout and washout of gaseous H_2O_2.
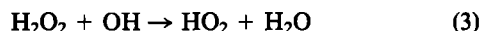
INTRODUCTION

Gaseous H_2O_2 is recognized to be a key component in the photochemistry of the earth's lower atmosphere, and, as a result, there is much interest in understanding the chemical and physical processes that determine its abundance. It is presently believed that atmospheric H_2O_2 is generated exclusively by gas-phase photochemical reactions. In the remote trophosphere, the primary gas-phase photochemical H_2O_2 source is via reaction (1)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (1)$$
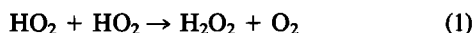
while H_2O_2 may be removed by photolysis

$$H_2O_2 + h\nu \rightarrow 2OH \qquad (2)$$

reaction with OH

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \qquad (3)$$

or by heterogeneous loss processes such as rainout and washout [cf *Levy*, 1973].

On the basis of this mechanism, current photochemical model calculations predict lower and mid-tropospheric H_2O_2 levels of the order of 1 ppbv (cf *Chameides and Tan*, 1981; *Logan et al.*, 1981]. In the urban or polluted atmosphere, significantly higher H_2O_2 concentrations are believed to occur as a result of the oxidation of reactive hydrocarbons [cf *Bufalini et al.*, 1972]. To test the accuracy of these predictions, attempts have been made to measure the gas-phase levels of H_2O_2 by using wet-chemical techniques [cf *Kok et al.*, 1978]. Unfortunately, because H_2O_2 is itself generated in solution by a series of complex reactions when air is bubbled through water, it appears that this technique must be considered unreliable [*Zika and Saltzman*, 1982]. As a result, model-predicted H_2O_2 concentrations still remain unconfirmed by direct atmospheric observations.

Because the reaction of HSO_3^- with H_2O_2 dissolved in cloudwater may be a major pathway by which atmospheric SO_2 is converted to $SO_4^=$ [*Penkett et al.*, 1979; *Moller*, 1980], there is currently great interest in characterizing H_2O_2

concentrations levels in cloudwater and rainwater. In this regard, it is commonly believed that the H_2O_2 in cloudwater arises from the incorporation into the droplets of gaseous H_2O_2 present in the air within and surrounding the cloud. In fact, the measurements of *Kok* [1980], who found $[H_2O_2]$ levels ranging from about 1×10^{-6} M to 3×10^{-5} M in rainwater collected in southern California are not inconsistent with this premise. For instance note that the complete removal of 1 ppbv of H_2O_2 in a cloud containing 1 g of liquid H_2O m^{-3} would result in a $[H_2O_2]$ level in the cloudwater of $\sim 10^{-5}$ M. However, in view of the very limited number of rainwater H_2O_2 measurements and the absence of reliable gas-phase H_2O_2 measurements, we view this agreement between measured and observed $[H_2O_2]$ as qualitative rather than quantitative. Many more measurements of H_2O_2 in rainwater under a variety of conditions are needed to quantitatively test our understanding of the processes that control atmospheric H_2O_2 levels in both the gas and the aqueous phases. Toward this end we report here on recent field measurements of the concentrations of H_2O_2 in rainwater gathered in southern Florida and around the Bahama Islands; to the best of our knowledge these measurements are the first to be carried out in maritime air. Interestingly, these measurements appear to suggest that the chemistry of H_2O_2 in cloudwater is considerably more complex than had been previously assumed.

EXPERIMENTAL

Rainwater samples were collected and analyzed for H_2O_2 concentration by using the fluorescence technique described by *Perschke and Broda* [1961] and *Zika and Zelmer* [1982]. The method involves the addition of a known amount of scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrene) to a pH 7.0 buffered sample. Subsequent addition of a horseradish peroxidase (HRP) phenol mixture catalyzes the oxidation of the scopoletin by H_2O_2, thereby reducing the fluorescence of the sample. The H_2O_2 content of the sample is thus determined from the difference in fluorescence of the sample measured before and after addition of HRP. Calibration curves were obtained by analyzing a series of solutions of known peroxide concentrations prepared by dilution of a 0.01 M H_2O_2 stock solution. By varying the amount of scopoletin, hydrogen peroxide concentrations of 2×10^{-9} M

TABLE 1. Concentration of H_2O_2 In Rainwater

Time	$H_2O_2 \times 10^5$, Moles l^{-1}	Average Rainfall Rate for Collection Interval (ml cm^{-2} min^{-1})	Total Accumulated Rainfall, cm	Wind Velocity, mph
Miami, Florida				
Feb. 2, Noon–4:20 continuous	2.25	0.0014	0.036	SW 15–20
sampling	2.75	0.015	0.072	
	2.05	0.015	0.11	
	2.10	0.015	0.14	
	1.40	0.015	0.18	
4:32	1.80	0.015	0.22	
Feb. 12, 7:00–7:10 P.M.	4:05	· · ·	· · ·	NE 10–20
7:10–7:20 P.M.	3.95	· · ·	· · ·	
Feb. 18, 8:30 P.M.	1.75	· · ·	· · ·	SE 15
March 13, 4:20–4:30 P.M.	4.00	· · ·	· · ·	WNW 10
4:30–4:35 P.M.	2.65	· · ·	0.20	
April 17, 2:00 P.M.	3.45	· · ·	0.06	ESE 15–20
May 7, 4:20 P.M. continuous	7.50	· · ·	· · ·	
sampling	4.75	· · ·	· · ·	
	4.85	· · ·	· · ·	
	3.15	· · ·	· · ·	
	3.43	· · ·	· · ·	
5:00 P.M.	4.9	· · ·	· · ·	
6.55 P.M.	0.9	· · ·	· · ·	
	2.6	· · ·	· · ·	
	1.15	· · ·	1.90	
Bahamas, 25°20'N 77°55'42" W				
May 13, 11:10 A.M.	2.10	0.013	0.10	

to $1 \times 10^{-6} M$ can be accurately determined with a precision of ±2%. Laboratory tests have confirmed that this technique can be used to discriminate between H_2O_2 and other oxidants, such as organic peroxides [*Zika and Zelmer*, 1982]. No interfering oxidants were detected in this work.

The rainwater samples from the Miami area were gathered by using a wet-dry precipitation collector modified by the addition of a linear polyethylene funnel (radius = 13.5 cm) and tube so that the rainwater was delivered directly into a laboratory buret for analysis. A similar system was employed in the region of the Bahama Islands with H_2O_2 determinations carried out in a shipboard laboratory. Measurements of samples obtained by injecting a known quantity of H_2O_2 and distilled water into our precipitation collector confirmed that our collection procedures did not introduce spurious H_2O_2 decay or formation characteristics.

During one rainstorm (i.e., July 22) the concentration of cations and anions in the rainwater was measured in addition to H_2O_2. This measurement was accomplished by using standard ion chromatography and atomic absorption procedures.

RESULTS AND DISCUSSION

Measured concentrations of H_2O_2, $[H_2O_2]$, in rainwater samples collected in Miami, Florida, and the Bahama Islands area, are indicated in Table 1 and Figure 1. We find the range in $[H_2O_2]$ varies from about $1.4 \times 10^{-5} M$ to $7.5 \times 10^{-5} M$. Since $[H_2O_2]$ determined at the urban sampling sites was consistent with that obtained from the Bahamas, it appears that the city samples were not predominantly influenced by pollutants and the associated products of photochemical smog. In addition, our measurements do not give any obvious indication of a correlation between $[H_2O_2]$ and wind direction.

The $[H_2O_2]$ levels reported here tend to be generally somewhat higher than those obtained by *Kok* [1980] for rainwater collected in California. Conceivably, this difference could reflect higher levels of SO_2 in California relative to those of Florida and Bahama Islands, since HSO_3^- (the dissolved form of SO_2) by reacting with H_2O_2 in solution can cause lower $[H_2O_2]$ levels. It is also possible that greater concentrations of H_2O_2 precursors were present in the air we sampled relative to that of *Kok* [1980].

During three rainstorms, the rainwater analysis was carried out continuously to obtain the concentration of dissolved H_2O_2 as a function of time during the course of each storm. As indicated in Table 1 and Figure 1, for the storms of February 2 and July 22, 1981, which occurred during the midday hours, H_2O_2 levels remained fairly constant as a function of time. By contrast, however, H_2O_2 was found to decline significantly as a function of time during the storm of May 7, 1981, which occurred in the early evening. Given the limited data, it is not yet possible to discern if this difference in the H_2O_2 temporal trends is related to the time of day that the storm occurred or to another parameter.

An interesting facet of our data is the striking difference between the variation in the measured $[H_2O_2]$ as a function of time during the course of the storm on July 22 compared with those of $[NO_3^-]$, $[SO_4^=]$, and $[Cl^-]$ (see Figure 1). In the case of $[NO_3^-]$ and excess $[SO_4^=]$, the concentration levels decreased monotonically be a factor of 2–4 over the rainstorm's lifetime. (Note that excess $[SO_4^=]$ is defined as total dissolved $[SO_4^=]$ minus the component due to the marine aerosol, where $[SO_4^=]$ due to the marine aerosol is scaled from the observed $[Na^+]$ level.) On the other hand, $[Cl^-]$ exhibited a more complicated pattern, an initial decrease, then a sharp increase, coinciding with a second pulse in rainfall intensity, and then a precipitous decline. In contrast to these species, $[H_2O_2]$ levels illustrated in Figure 1 gave no indication of a downward trend with time and in fact tended to remain fairly constant over the entire course of the storm.
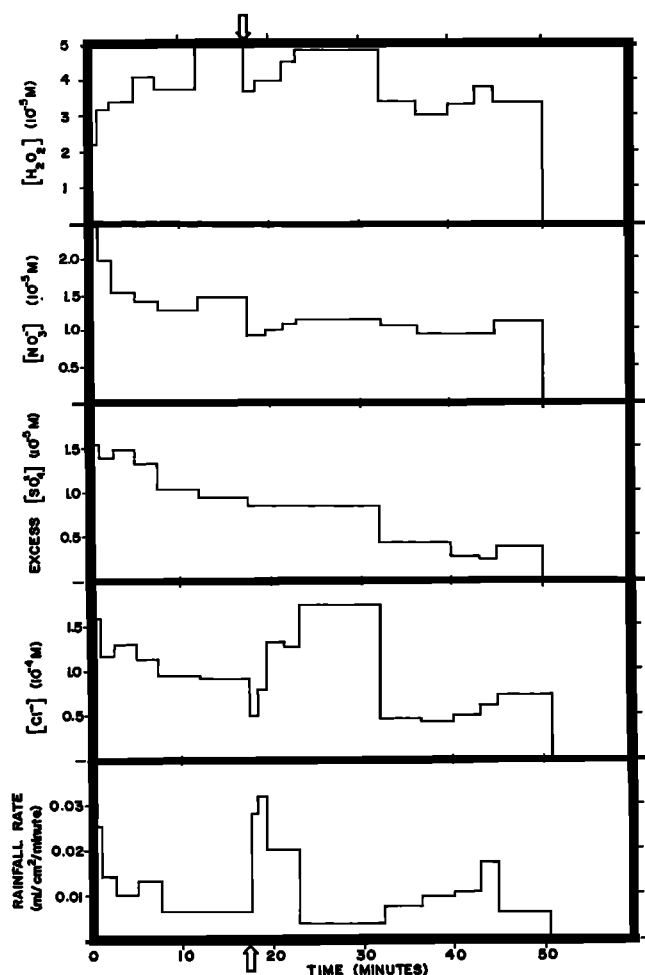
Fig. 1. Observed levels of [H₂O₂], [NO₃⁻], excess [SO₄⁼], [Cl⁻], and rainfall rate during the storm of July 22, 1981, in Miami, Florida, as a function of time. The onset of the storm at $t = 0$ corresponds to 12:50 P.M. EDT and the vertical arrow at approximately $t = 16$ min indicates the brief presence of sunshine during the storm. (Note that excess [SO₄⁼] is derived from the difference between total observed [SO₄⁼] and 0.06 times observed [Na⁺], see text.)

The difference in the variation of [Cl⁻] compared with those of [NO₃⁻] and excess [SO₄⁼] indicates that different mechanisms were responsible for incorporating these species into our rainwater samples. While Cl⁻ most likely originated from marine aerosols scavenged from the atmosphere by cloud and rain droplets, it is probable that the NO₃⁻ and excess SO₄⁼ present in the rainwater we analyzed was derived in large part from the scavenging of gaseous species. Given the high solubility of H₂O₂, we would expect that if the H₂O₂ in our rain samples had been derived from the dissolution of gaseous H₂O₂, then [H₂O₂] would have exhibited a trend similar to that observed for [NO₃⁻] and excess [SO₄⁼]. However, the difference between the time patterns of [H₂O₂] and these latter two species in Figure 1 appears to suggest that the H₂O₂ dissolved in the rain of July 22 was derived from a mechanism different from the mechanism which caused the presence of NO₃⁻ and excess SO₄⁼. One interpretation of our data is that while NO₃⁻ and excess SO₄⁼ was derived from the dissolution of gaseous species, a significant fraction of the H₂O₂ in our samples had been generated in the cloudwater as a result of aqueous-phase

chemical reactions such as those recently proposed by *Chameides and Davis* [1982]. The results of *Zika and Saltzman* [1982] and *Heikes et al.* [1982] documenting the aqueous-phase generation of H₂O₂ when air is bubbled through water is not inconsistent with the above conclusion.

Because of the very limited amount of data presented here, our hypothesis concerning the chemical generation of aqueous-phase H₂O₂ must be considered, at this time, to be highly speculative. Nevertheless, our data does appear to suggest that the processes which control the levels of H₂O₂ in precipitation may be considerably more complex than had been previously assumed. We believe therefore that further laboratory studies of the aqueous-phase chemistry of H₂O₂ as well as direct measurements of H₂O₂ levels in cloudwater and in the gas phase are needed to more accurately establish the budget of H₂O₂ in precipitation.

REFERENCES

Bufalini, J. J., B. W. Gay, Jr., and K. L. Brubaker, Hydrogen peroxide formation from formaldehyde photooxidation and its presence in urban atmospheres, *Environ. Sci. Tech., 6,* 816–821, 1972.

Chameides, W. L., The photochemical role of tropospheric nitrogen oxides, *Geophys. Res. Lett., 5,* 11–20, 1978.

Chameides, W. L., and A. Tan, The two-dimensional diagnostic model for tropospheric OH: An uncertainty analysis, *J. Geophys. Res., 86,* 5209–5223, 1981.

Chameides, W. L., and D. D. Davis, The free radical chemistry of cloud droplets and its impact upon the composition of rain, *J. Geophys. Res.,* this issue.

Heikes, B. G., A. L. Lazrus, G. L. Kok, S. M. Kunen, B. W. Gandrud, S. N. Gitlin, and D. D. Sperry, Evidence for aqueous phase hydrogen peroxide synthesis in the troposphere, *J. Geophys. Res., 87,* 3045, 1982.

Hoffmann, M. R., and J. O. Edwards, Kinetics of the oxidation of sulfite by hydrogen peroxide in acidic solutions, *J. Phys. Chem., 79,* 2096–2098, 1975.

Kok, G. L., K. R. Darnell, A. M. Winer, J. N. Pitts, and B. W. Gay, Ambient air measurements of hydrogen peroxide in the California south coast air basin, *Environ. Sci. Tech., 9,* 1077–1080, 1978.

Kok, G. L., Measurements of hydrogen peroxide in rainwater, *Atmos. Environ., 14,* 653–656, 1980.

Levy, H., Photochemistry of minor constitutents in the troposphere, *Planet. Space Sci., 21,* 575–591, 1973.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res., 86,* 7210–7254, 1981.

Moller, D., Kinetic model of atmospheric SO₂ oxidation based on published data, *Atmos. Environ., 14,* 1067–1076, 1980.

Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton, The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rainwater, *Atmos. Environ., 13,* 123–137, 1979.

Perschke, H., and E. Broda, Determination of very small amounts of hydrogen peroxide, *Nature, 190,* 257–258, 1961.

Zika, R., and E. Saltzman, Production of H₂O₂ in the aqueous phase via aeration of water samples wth ambient air, *Geophys. Res. Lett., 9,* 231–234, 1982.

Zika, R. G., and P. Zelmer, An evaluation of the HRP-Scopoletin method for the measurement of hydrogen peroxide in natural waters, submitted to *Anal. Chem.,* 1982.