TECHNICAL PROGRESS REPORT (8/94)
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 Judith Weinstein-Lloyd
 SUNY/Old Westbury

Research conducted under this program has furthered the development of a method for real-time analysis of hydrogen peroxide, methyl hydroperoxide (MHP) and hydroxymethyl hydroperoxide (HMHP), the most abundant peroxides in the atmosphere. Analysis is based on the reaction between H_2O_2 and $Fe(II)$ (Fenton's reagent) to form hydroxyl radical, which is scavenged by benzoic acid (BA) to produce o-, m- and p-hydroxy benzoic acids (OHBA); the latter are detected by their fluorescence, which is enhanced by complexation with $Al(III)$ ion.

Fenton reagent is expected to be specific for H_2O_2 because organic peroxides react more slowly with $Fe(II)$ and do not yield the hydroxyl radical in reactions analogous to (1).

We have deployed the Fenton method in a number of major field studies; the results have been used to test models of atmospheric photochemistry (Kleinman et al., 1994; Sillman et al., 1993) and diurnal profiles we observed have shed light on the mechanism of formation of H_2O_2 and organic peroxides (Lee et al., 1994). The technique has also been adapted for analysis of peroxides in precipitation in an undergraduate analytical chemistry/ instrumental analysis course (Weinstein-Lloyd and Lee, 1994).

Methods Development

A new instrument was constructed, similar to that developed for peroxide analysis by Lazrus et al. (1985), but incorporating three channels and an improved scrubber coil designed to collect gaseous peroxides without sampling line losses. A schematic diagram of one channel is shown in Figure 1. Speciation is accomplished by using different fluorescence reagents as summarized in the Table below and exploiting the tendency of HMHP to hydrolyze to H_2O_2 at high pH. If H_2O_2 , HMHP and MHP are the only ambient peroxides, channel 1 will

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measure total peroxides, channel 2 H_2O_2 alone, and channel 3 the sum of HMHP and H_2O_2 . As discussed below, we have observed interference

CHANNEL	FLUORESCENCE REAGENT	ENHANCING REAGENT	SCRUBBING SOLUTION pH
1	pOHPAA	NaOH	9
2	Fenton/OHBA	Al(III)	5.3
3	Fenton/OHBA	Al(III)	9

from organic peroxides in the Fenton channels, which can be corrected to obtain reliable values of H_2O_2 , MHP and HMHP. We determined optimum analytical conditions by studying the effects of concentration of Fe(II), BA, Al(III), pH and temperature on fluorescence intensity. We also determined the excitation and emission wavelengths and reaction times yielding maximum fluorescence intensity. Details of these results and others described in this section can be found in the two methods publications (Lee, et

al.,1990; Lee et al,1994).

Interference Studies

Earlier coil-based peroxide techniques exploited the rapid sequestering of SO_2 by HCHO to prevent potential loss of H_2O_2 through reaction with co-collected SO_2 . We conducted a laboratory study to assess the extent of H_2O_2 loss by reaction with added SO_2 as a function of scrub pH. Alkaline solutions showed the least interference, presumably because of the rapidity of SO_2 - HCHO complexation. We found that a pH of 5.4 was sufficient to prevent hydrolysis of HMHP while still protecting against SO_2 up to 250 ppbv; this pH is used for the channel 2 scrub.

HPLC Studies

We have pursued the development of a method to detect peroxides using HPLC separation followed by post-column derivatization with pOHPAA reagent and fluorescence detection. We determined the effect of factors such as reagent concentration, pH and flow rate on peak resolution and sensitivity and performed preliminary field measurements of ambient peroxides using an air scrubbing coil for sampling (Haff et al.,1994). Previous HPLC peroxide detection methods have relied on cryogenic sampling methods, which are prone to interference from co-collected species. We intend to further refine this technique for routine deployment in the field.

The relative response of Fenton and pOHPAA reagents to organic peroxides was assessed by analyzing mixtures of H_2O_2 , HMHP and MHP after separating the peroxides by HPLC. Equilibrium mixtures of H_2O_2 and HMHP were prepared by reacting H_2O_2 with HCHO (Marklund,1971). Mixtures of MHP and H_2O_2 were synthesized by ^{60}Co radiolysis of methane and oxygen-containing solutions. Two peaks were observed upon post-column reaction with both pOHPAA and Fenton reagent; the peak area ratio of H_2O_2 to MHP was four times larger with Fenton than with pOHPAA; that of H_2O_2 to HMHP was 2.5 times larger. These ratios remained constant for peroxide mixtures of variable composition, and were used to extract concentrations of the individual peroxides from the three channels. Figure 2 shows the results of such an experiment with the Fenton and pOHPAA chromatograms overlaid.

Figure 2

Interestingly, these experiments indicate a substantially larger radiolytic yield of CH_3OOH than had been previously reported (Schuchmann and von Sonntag, 1983) which we attribute to prompt product analysis after radiolysis. This work has demonstrated that cobalt-60 radiolysis can be used for the reproducible (and safe) synthesis of organic peroxides in aqueous solution.

We devoted substantial effort to understanding why the Fenton channels respond to organic peroxides. We obtained fluorescence spectra of isomeric methoxybenzoic acids (MBA's), the expected products of reaction (2) when CH_3OOH undergoes reaction with Fe(II) . The MBA's do not complex with Al(III) and p-MBA does not fluoresce. As shown in Figure 3, the o-isomer contributes a significant (8%) signal to the fluorescence from Al-OHBA at $\lambda=305\text{nm}$. Further conclusions await our studies of the isomer product distribution from the Fenton reaction.

Peroxide Monitoring

The 3-channel peroxide monitoring instrument has been deployed in a number of major field studies. The goals of these programs are described in the Appendix; the results have been described at several symposia and full descriptions are in various stages of preparation for publication.

Figure 4 illustrates the mean diurnal profile of hydrogen peroxide observed during 28 days in June, 1992 in Metter, Georgia; the light bars enclose one standard deviation. Average MHP and HMHP concentrations were below 0.5 ppbv and exhibited no obvious diurnal trends. However, concentrations of HMHP comparable to H_2O_2 were observed on several occasions on humid, hazy days coinciding with high ozone concentrations.

Measurements taken during a two-week period at Atlanta, Georgia showed a mean maximum hydrogen peroxide concentration of 3.8 ppbv, with significant HMHP and MHP concentrations on several days. During a high ozone episode on 8/3/92 (Figure 5), H_2O_2 peaked near 3 ppbv in the late afternoon. HMHP concentration, a significant fraction of the total for most of the day, was 1 ppbv when monitoring commenced, and did not follow solar intensity. MHP was not detectable most of

the day, but rose dramatically in the afternoon. These patterns support the idea that there is a non-photolytic source for organic peroxides.

Peroxide concentrations were determined as part of the 1993 NARE campaign in Halifax, Nova Scotia with the two-channel Kok instrument, modified to include Fenton chemistry, aboard the Battelle G-1

aircraft. The median peroxide concentration was 2.5 ppbv and was principally H_2O_2 . Concentrations varied from the detection limit to over 12 ppbv. Figure 6 illustrates hydrogen peroxide measurements taken during a vertical profile over the North Atlantic on 8/28/93. A sharply defined layer of high concentration was observed near the surface, with concentration gradually declining from 3 to 1 ppbv above this layer. Concentrations of ozone and water vapor, both required for production of OH and hence H_2O_2 , are shown for comparison. High H_2O_2 concentrations in the lower layer are clearly associated with high ozone. This layer also exhibited high concentrations of NO_y , indicating that it contained well-aged air. The observed decline in H_2O_2 above the layer, where ozone is fairly constant, is associated with declining water concentration (J. Weinstein-Lloyd, et al., 1994).

We have been monitoring peroxide concentrations in the air at Long Island, New York for over a year to obtain information about seasonal variations. The measurements show very little organic peroxide and considerably more day-to-day than seasonal variability, as shown in Figures 7, 8, and 9 (Halper et al., 1994).

○ A.M. ● P.M.

Photochemical Models

Our peroxide measurements have been used to test photochemical model simulations of ozone production. Kleinman et al. (1994) used a free-radical budget equation to compare the rate of O_3 production to observed concentration changes in Metter, GA. Measured peroxide concentrations were compared with results of the Urban Airshed and University of Michigan models (Sillman et al., 1993b). Both models significantly overestimate peroxide concentration, suggesting that the experimental methods fail to collect or detect all peroxides, or that deposition velocities underestimate peroxide loss.

APPENDIX PEROXIDE FIELD MEASUREMENTS SUPPORTED BY THIS GRANT

LOCATION	DATE	PROGRAM	MEASUREMENT GOALS
Long Island, New York	November 1992 to present		Methods testing and determination of seasonal trends in H ₂ O ₂ and organic peroxides. We are also conducting limited additional measurements (meteorological parameters, ozone, SO ₂).
Metter, Georgia	July-August 1991	Southern Oxidant Study (SOS)	Measurement of peroxides as part of a major ground-based field study to investigate ozone non-attainment in a rural areas. The three-channel system was deployed in the Brookhaven National Laboratory's mobile laboratory at George L. Smith State Park. Collaborators measured other important chemical species and meteorological parameters from the laboratory platform.
Metter, Georgia	June-July 1992	SOS	"
Atlanta, Georgia	July-August 1992	SOS	Peroxide measurements as part of a field study to investigate ozone nonattainment in an isolated large city dominated by mobile source emissions and relatively simple meteorology. The three-channel peroxide system was deployed in a trailer on the campus of Georgia Institute of Technology. Collaborators measured other chemical species on the ground at this as well as 4 neighboring sites, and from towers, a balloon, and a helicopter.
Halifax and Yarmouth Nova Scotia	August 1993	North Atlantic Regional Experiment (NARE)	Peroxide measurements as part of an international study to investigate the persistence and chemical transformation of pollutants affecting the formation of tropospheric ozone as they are emitted from the continental coast and travel out over the North Atlantic. Measurements were made using our three-channel system on the ground, and on two airplanes using the commercially available two-channel Kok systems which we modified to incorporate Fenton chemistry.

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PRESENTATIONS

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