P1.4 HYDROPEROXYL RADICAL DETECTION BY MCLA CHEMILUMINESCENCE

J. B. Weinstein-Lloyd[1]*, J. Zheng[2], S. R. Springston[3]
[1]SUNY / Old Westbury, Old Westbury, NY 11568
[2]SUNY / Stony Brook, Stony Brook, NY 11794
[3]Brookhaven National Laboratory, Upton, NY 11973

1. INTRODUCTION

Hydroperoxyl radical (HO_2) is produced from the reaction of hydroxyl radicals (OH) with carbon monoxide (CO) and organic compounds in the atmosphere, and by photolysis of formaldehyde (HCHO). HO_2 plays a key role in the NO_x catalytic cycle that produces tropospheric O_3. HO_2 is a precursor of hydrogen peroxide (H_2O_2) and methyl hydroperoxide (CH_3OOH), both of which can oxidize SO_2 in raindrops or aerosols. Detection of HO_2 radicals is a challenge due to their low abundance and short lifetime. Current measurement techniques include the chemical amplifier method (Cantrell et al., 1996), matrix isolation ESR spectroscopy (Mihelcic et al, 1990), conversion to OH, followed by detection by laser induced fluorescence (Brune et al, 1998); and the peroxy radical chemical ionization mass spectroscopy technique (Tanner et al., 1997). These methods have been deployed in recent field programs with varying degrees of success and remain under development.

We have developed a flow injection method for HO_2 analysis based on the chemiluminescence produced when an aqueous solution of HO_2 and its conjugate base O_2^- react with MCLA (Figure 1), a synthetic analog of the luciferin from the crustacean *Cypridina* (Nishida et al., 1989). MCLA is a specific probe for HO_2 (aq), and does not exhibit interference from OH, hydrogen peroxide or singlet molecular oxygen (Nakano et al., 1986). We calibrate with stable aqueous O_2^- standards produced in submicromolar concentration using ^{60}Co gamma radiolysis.

The method is simple, low-cost and has minimal size and power requirements, making it attractive for field measurements of gaseous HO_2. HO_2 is highly water soluble (Henry's Law constant = 9×10^3 M/atm), and subsequent equilibration with its conjugate base O_2^- should increase the solubility. We have incorporated a glass coil scrubber as a collecting device, using pH 9 borax buffer as scrubbing solution, and deployed the instrument for gas-phase detection at Brookhaven National Laboratory. The daily profile obtained demonstrates that the technique can be used to measure atmospheric HO_2 radicals following collection into aqueous solution.

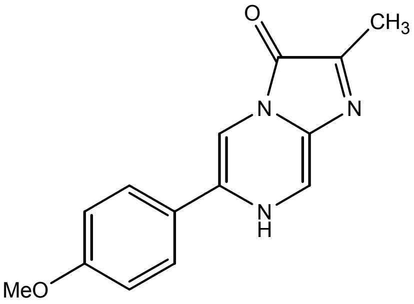

Figure1. MCLA.

2. EXPERIMENTAL

2.1 *Aqueous HO_2 Standards*

We use ^{60}Co gamma radiolysis to produce standards. The advantage of this method over earlier methods using the xanthine / xanthine oxidase system is that the $HO_2(aq)$ production rate can be determined quantitatively by dosimetry. Standards are prepared from an air saturated 1.5 mM sodium formate solution adjusted to pH 11 with NaOH, containing 5μM EDTA. Formate acts as a scavenger for primary free radicals (H, OH and e^-_{aq}) from radiolysis of H_2O, converting them into an equilibrium mixture of HO_2 and O_2^- (Bielski et al., 1985). The ^{60}Co gamma source intensity, measured by ferrous sulfate dosimetry, was 2.77 rads/min, producing 0.290 μM O_2^- (aq) radicals per minute. This solution is then immediately diluted by 100 into unirradiated formate solution, giving a 3 nM O_2^- standard. The radicals decay through self-reaction (R1 to R3), with rate constants $k_1 = 8.3 \times 10^5$, $k_2 = 9.7 \times 10^7$ and $k_3 < 0.3$ L mol^{-1} s^{-1} (Bielski et al., 1985).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad \text{R1}$$

$$HO_2 + O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad \text{R2}$$

$$O_2^- + O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \qquad \text{R3}$$

The overall self-reaction rate is a function of pH and can be determined spectrophotometrically by observing the absorbance spectrum of O_2^- at 240 nm. At pH 11, we observed a self-reaction rate on the order of 100 $M^{-1}s^{-1}$, in agreement with published rate constants. Thus, the radiolytically-produced 3 nM standards are essentially stable, with a half-life longer than 30 days.

---

* *Corresponding author address:* Judith B. Weinstein-Lloyd, State University of New York, Chemistry / Physics Dept., P.O. Box 210, Old Westbury, NY 11568; e-mail: Lloydj@oldwestbury.edu.

2.2 *Instrumentation*

Details of the apparatus, described in a recent publication in *Analytical Chemistry* (Zheng et al., 2003), are summarized here. Two high precision syringe pumps are used to deliver a reagent stream and a carrier stream at 1.0 mL/min each to a McPherson chemiluminescence detector. The reagent stream is 9 μM MCLA in 1:100 (v/v) ethanol/H_2O, adjusted to pH 2.3 with HCl. O_2^-(aq) samples are injected into the carrier stream using a six-port injection valve. The carrier stream consists of unirradiated sodium formate solution. The chemiluminescence detector has a 0.5 mL spiral reaction cell that permits reagents to mix directly in front of the photomultiplier tube.

2.3 *Modification for gas-phase HO_2 measurement*

Modification of the instrument for gas-phase measurement consisted of adding a glass coil scrubber to collect HO_2(g) into a pH 9 borax scrubbing solution. This device has proven to be very efficient for collecting H_2O_2 (which has a smaller Henry's law constant than HO_2 at pH 9) and does not exhibit line losses. A schematic diagram of the HO_2 analyzer is shown in Figure 2. The analyzer operates automatically, making one injection every 2 minutes. We obtain the background signal using a water trap with an in-line Teflon filter to remove any small droplets.

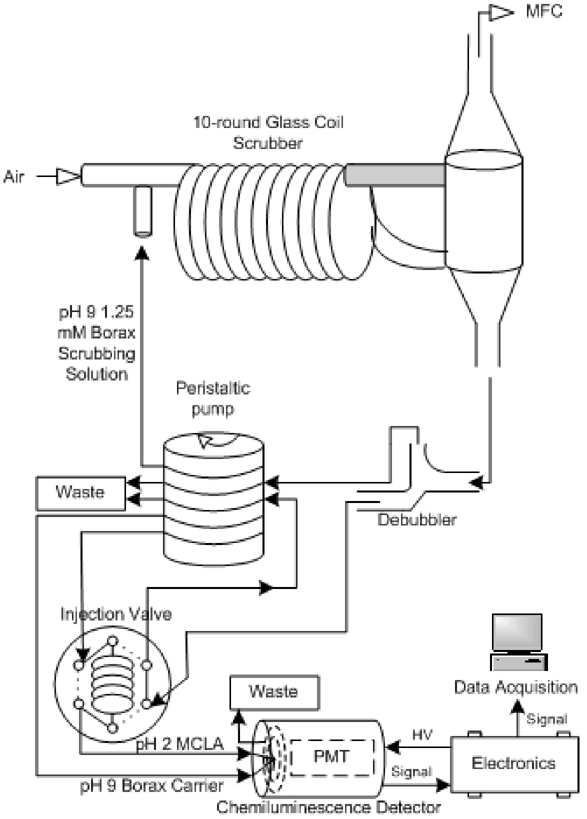

Figure 2. Schematic diagram of HO_2 detector with glass coil scrubber

3. RESULTS AND DISCUSSION

3.1 *Optimization*

There are three competing reactions in the detector cell. These are the reaction between MCLA and HO_2(aq) to give the desired chemiluminescence signal, the self-reaction of HO_2(aq), and oxidization of MCLA by O_2. In acidic solution, MCLA is stable toward air oxidation, but HO_2 (aq) rapidly self-reacts (R1 and R2). In basic solution, O_2^- exhibits a slower self-reaction rate (R3), but oxidation of MCLA by O_2 consumes all the MCLA in a few minutes. By adjusting the pH of the MCLA reagent stream, we found a maximum signal size for final pH around 3.

We anticipated that signal intensity would increase with increasing [MCLA], and we did observe a positive dependence of signal on concentration between 0 and 9 μM. However, there was a decrease for MCLA concentrations between 9 and 15 μM, most likely due to an inner filter effect.

We also investigated the effects of flow rate and injection volume. Light emission began immediately after mixing, and was complete within a few seconds. Slower flow resulted in a larger peak area, becoming constant at flow rates higher than 1 mL/min. It seems reasonable to assume that larger injections would result in higher peak area, and indeed our experiments supported this assumption. However, increasing the injection volume too much resulted in a smaller signal due to dilution of the reagent. The optimum injection volume was 200 μL

3.2 *Interference Studies*

Under our experimental conditions, we expect that 10 pptv HO_2(g) will produce an aqueous-phase HO_2 concentration of 0.5 nM. Several soluble atmospheric oxidants have the potential to interfere with the HO_2 measurement. OH and $^1O_2$ both are strong oxidants, but their abundances in the atmosphere are much less than HO_2. Hydrogen peroxide may be present at concentrations several orders of magnitude higher than HO_2. Addition of 1 μM H_2O_2(aq), the concentration expected from scrubbing 10 ppbv H_2O_2(g), generated a small interference, on the order of 0.1 nM HO_2 (aq). We examined NO_x interference using a gas-phase standard, and observed no response up to 40 ppbv NO and 89 ppbv NO_2.

The only significant interference we observed was from O_3, which may be present at concentrations above 100 ppbv. We used an O_3 generator to produce gaseous standards up to 90 ppbv, and scrubbed into high pH solution as described earlier. We observed a constant signal equivalent to 2 pptv HO_2 for 25 to 90 ppbv O_3. Ozone is known to decompose in basic solution; the proposed mechanism is shown below (R4 to R6), where R4 is the rate-limiting step, with $k_4 = 70 \pm 7$ mol^{-1} s^{-1} (Staehelin and Hoigné, 1982):

$O_3 + OH^- \rightarrow O_2^- + HO_2$ R4

$O_2^- + O_3 \rightarrow O_3^- + O_2$ R5

$O_3^- + H_2O \rightarrow OH + OH^- + O_2$ R6

Thus, O_3 is expected to produce peroxy radicals via R4, but destroy them through R5. The artifact signal we observe may reflect a fixed net radical production via these two reactions. We correct for the small constant background signal produced from ambient O_3 below 90 ppbv by subtraction.

3.3 Calibration

The $HO_2(aq)$ standards were prepared through radiolysis, as described above, in concentrations between 3 and 24 nM. The calibration curve is shown in figure 3. The pH of the mixing stream inside the spiral cell is near 3. At this pH, the half-life of $HO_2(aq)$ with respect to reaction with MCLA is 1 s, while the self-reaction has a half-life of 30 s. Thus, there is no significant loss of $HO_2(aq)$ due to self-reaction during the calibration. The calibration is linear in both peak size and peak area up to 1 µM $HO_2(aq)$, and has a detection limit of 0.1 nM, based on three times the baseline noise.

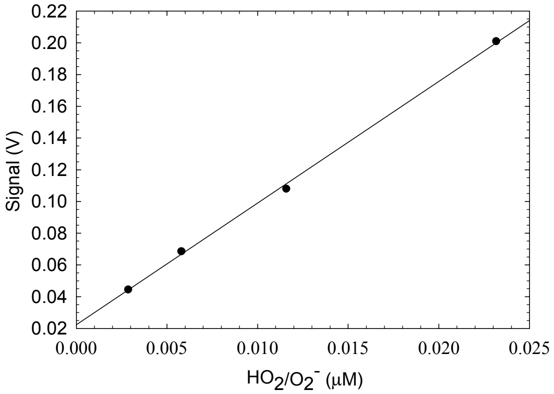

Figure 3. Calibration Curve with pH 11 HO_2/O^-_2 Standards

4. FIELD MEASUREMENT

Ambient $HO_2(g)$ measurement on July 17, 2003 at the Brookhaven National Laboratory field site is shown in Figure 4. The HO_2 analyzer was set up inside an air-conditioned shed with the glass coil mounted on the roof. There are no tall buildings or trees within 100 ft of the shed, and no major pollution sources near the site except local traffic, which may contribute some NO_x emissions. Weather conditions were clear most of the day with only occasional small scattered cloud, and winds were NW at ~6 mph most of the day. HO_2 started to build up after sunrise but the rate slowed between 7:30 and 9:00, which we believe was due to loss from NO produced by rush hour traffic. Local traffic also may explain the temporary decreases observed at 12:30 and 15:30. The profile reached a maximum of ~7.5 pptv at 14:00 EST, about 2 hours after the maximum solar intensity. These concentrations are reasonable for clean rural conditions. Figure 5 shows the O_3 photolysis rate and local temperature during the measurement. It is plausible that HO_2 concentration would peak after solar noon, because of contributions from O_3 and biogenic hydrocarbons, which would have accumulated later in the afternoon. Local temperature increased until 14:00 and did not begin to decrease until 18:00, and emissions of hydrocarbons and formaldehyde, which are precursors to HO_2, we expect to increase with temperature.

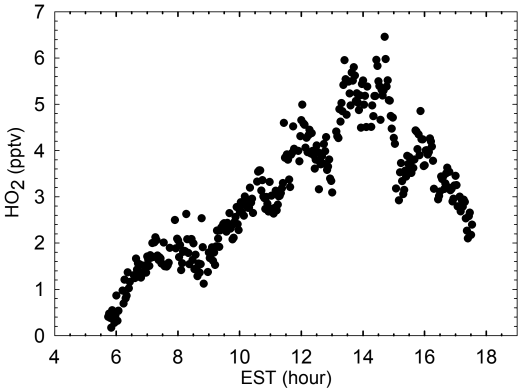

Figure 4. Daytime profile of HO_2 measured at BNL on July 17, 2003.

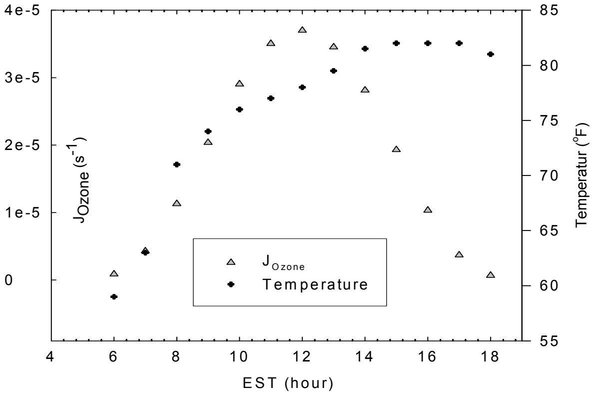

Figure 5. O_3 photolysis frequency (from QUICK TUV CALCULATOR at www.acd.ucar.edu./TUV) and temperature for field measurement.

In summary, the new instrument produced reasonable results in this first field measurement. Further validation will require deployment in a study where all pertinent meteorological parameters and trace gas abundances are measured, and comparison with radical concentrations derived from photochemical model calculations.

5. REFERENCES

Bielski, B.H.J.,Cabelli, D.E., Arudi, R.L., 1985: Reactivity of HO_2/O_2^- Radicals in Aqueous Solution. *J. Phys. Chem. Ref. Data*, **14**, 1041-1100.

Brune, W.H., Faloona, I.C., Tan, D., Weinheimer, A.J., Campos, T., Ridley, B.A., Vay, S.A., Collins, J.E., Sachse, G.W., Jaegle, L., Jacob, D.J., 1998: Airborne in situ OH and HO_2 observations in the cloud-free troposphere and lower stratosphere during SUCCESS. *Geophys. Res. Lett.*, **25**, 1701-1704.

Cantrell, C.A., Shetter, R.E., Calvert, J. G., 1996: Dual-Inlet Chemical Amplifier for Atmospheric Peroxy Radical Measurements. *Anal. Chem.*, **68**, 4194-4199.

Staehelin, J., Hoigné, J., 1982: Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide, *Environ. Sci. Technol.*, **16**, 676-681.

Mihelcic D., Volz-Thomas, A., Patz, H.W., Kley, D., Mihelcic, M., 1990: Numerical Analysis of ESR-Spectra from Atmospheric Samples. *J. Atmos. Chem.*, **11**, 271-291.

Nakano M., Sugioka, K., Ushijima, Y., Goto, T., 1986: Chemiluminescence probe with *Cypridina* luciferin analog, 2-methyl-6-phenyl-3,7-dihydroimidazo[1,2-*a*]pyrazin-3-one, for estimating the ability of human granulocytes to generate O_2^-. *Anal. Biochem.*, **159**, 363-369.

Nishida A., Kimura, H., Nakano, M., Goto, T.A., 1989: A Sensitive and Specific Chemiluminescence Method for Estimating the Ability of Human Granulocytes and Monocytes to Generate O_2^-. *Clin. Chim. Acta.*, **179**, 177-182.

Tanner D.J., Jefferson, A. Eisele, F.L., 1997: Selected ion chemical ionization mass spectrometric measurement of OH. *J. Geophys. Res.*, **102**, 6415-6425.

Zheng J., Springston, S.R., Weinstein-Lloyd, J., 2003: Quantitative Analysis of Hydroperoxyl Radical Using Flow Injection Analysis with Chemiluminescence Detection. *Anal. Chem.*, **75**, 4696-4700.