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Diurnal HO₂ Cycles at Clean Air and Urban Sites in the Troposphere

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We have determined HO₂ concentrations at two Oregon sites for continuous periods of 36 to 48 hours, using fluorescence assay with gas expansion. At the sea level coastal site (45°N 124°W), NNW winds prevailed during daytime, and a point measurement of very low total nonmethane hydrocarbon concentration indicated the presence of remote tropospheric air of oceanic origin. At the urban site, HO₂ was determined during moderately low ozone pollution levels. At both sites, maximum daily [HO₂] was in the range of $1\text{--}2 \times 10^8 \text{ cm}^{-3}$ under clear-sky conditions, with an estimated overall uncertainty of 40%. HO₂ was detected by continuous low-pressure sampling with flowing chemical conversion to HO, which was detected by laser-excited fluorescence. The instrumental response to HO₂ was calibrated by the self-decay of HO₂ at atmospheric pressure. Interference in the measured daytime HO₂ concentrations by RO₂ was estimated at less than 20%.

INTRODUCTION

Hydroperoxyl radical, HO₂, is created by the tropospheric photooxidation of hydrocarbons, carbon monoxide, and hydrogen, whose sources are both biospheric and human-made. This oxidation is initiated by chemical reactions of the latter species with the closely related free radical, HO. Partially oxidized hydrocarbons, such as formaldehyde, are photodissociated by sunlight to yield HO₂. These reactions can lead to tropospheric ozone production, for which HO₂ is an essential intermediate.

Anderson *et al.* [1981] and Stimpfle *et al.* [1990] determined HO₂ in the upper stratosphere by converting it to HO via NO addition, detecting the product HO by the fluorescence excited with an HO resonance lamp. Traub *et al.* [1990] detected stratospheric HO₂ between 23 and 49 km by balloon-borne far-infrared emission spectroscopy, and Mihelcic *et al.* [1990] determined HO₂ by electron-spin resonance (ESR) in cryogenic matrix samples collected in the troposphere. Hard *et al.* [1984] measured HO₂ near ground level in urban air by low-pressure conversion to HO, using laser-excited fluorescence (LEF) with chemical modulation.

In measurements of related species, Mihelcic *et al.* [1978, 1985, 1990] measured RO₂ (R = organic radical) by ESR in both stratospheric and tropospheric matrix samples. Cantrell and Stedman [1982] measured HO₂ + $\sum_i a_i [\text{RO}_2]_i$ by chemical amplification of NO conversion; here a_i represents the ability (relative to HO₂) of the i th RO₂ species (and its subsequent products) to oxidize NO to NO₂ under the chosen NO and CO reagent conditions. Parrish *et al.* [1986] measured the imbalance in the atmospheric NO-NO₂-O₃ photochemical steady state under a wide variety of conditions. Parrish *et al.* assigned excesses in the NO₂-to-NO ratio to species represented by HO₂ and RO₂, which produce ozone, and to unidentified free radicals which are neutral with respect to net O₃ production.

In the present work HO₂ is determined by fluorescence assay with gas expansion (FAGE) [Hard *et al.*, 1984, 1986, 1992; Chan *et al.*, 1990], a method which employs low-pressure laser-excited fluorescence to observe the hydroxyl radical HO, using chemical modulation to distinguish the desired signal from the background. In the HO₂ determination mode, NO is added to the low-pressure flowing sample, converting HO₂ to HO:

The efficiency of the HO₂-to-HO conversion is discussed below.

Ambient HO₂ was measured at two Oregon sites, one coastal and the other inland urban. The coastal site sampled sea level North Pacific air which was free from local pollution sources under suitable wind conditions. The urban site (downtown Portland) was subject largely to automotive pollutant sources.

KINETIC PRINCIPLES OF FAGE HO₂ DETERMINATION

The efficiency of HO₂ detection as HO following (R1) is limited by another reaction also driven by the NO reagent:

Thus the yield of HO from the above mechanism is pressure dependent via M, and low-pressure conditions are most effective for HO₂ determination.

In the present method a constant NO flow is added to both air sampling channels of FAGE. The signal from the HO product is turned on and off (modulated) in each sample channel by addition of isobutane (*i*-C₄H₁₀, here called *i*-BuH) to the flow, alternating between the two channels, via

Earlier [Hard *et al.*, 1984] we used NO alone as the modulating reagent, similarly to the approach of Anderson *et al.* [1981] and Stimpfle *et al.* [1990]. The reason for the change to chemical modulation by isobutane is to avoid possible interferences, discussed in a later section. The isobutane also modulates ambient HO via (R3), with somewhat higher overall efficiency, but the resulting small HO signal is comparable with the measurement uncertainty of the much more abundant HO₂.

At the LEF detection zone, the conversion efficiency of HO₂ to HO is

$$E_c = [\text{HO}]/[\text{HO}_2]_0 \quad (1)$$

$$= \{ \exp(-k_1[\text{NO}]t_r) - \exp(-k_2[\text{NO}][\text{M}]t_r - k_3[\text{i-BuH}]t_r) \} \times k_1[\text{NO}] / (k_2[\text{NO}][\text{M}] + k_3[\text{i-BuH}] - k_1[\text{NO}])$$

where $[\text{HO}_2]_0$ is the initial HO₂ concentration after expansion to low pressure and t_r is the transit time from the nozzle to the detection zone. Equation (1) is obtained by successive integration of the differential equations for $[\text{HO}_2]$ and $[\text{HO}]$ with respect to time from the nozzle exit ($t=0$) to t_r [Hard *et al.*, 1984]. Under real flow conditions, t_r is not constant with radial position in the sample flow at the detection zone, and highest flow rate occurs along the tube axis. Given sufficient information on the flow field, an area-weighted value of E_c could be calculated for the common intersection of the sample flow, laser beam, and detector mask image. Instead, we have obtained an effective value of $t_r = 16$ ms ($\pm 25\%$) from the measured modulation of external HO by isobutane in the absence of NO [Hard *et al.*, 1992]; the error limits are due largely to uncertainty in the HO+isobutane reaction rate coefficient. For the latter value we have used $k_3 = 2.5 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ [Greiner, 1970; Darnall *et al.*, 1978] (molec = molecules). The observed value of t_r is somewhat closer to the expected transit time for the core of laminar flow, 12.5 ms, than to the hypothetical plug-flow residence time, 25 ms. Here we should stress that t_r and E_c need not be known accurately, since the overall response of the FAGE instrument to HO₂ is obtained independently by external calibration; however, t_r and E_c are useful for instrument description and the estimation of upper limits to the possible interferences.

Equation (1) assumes pseudo-first-order reaction of HO₂ in (R1), and of HO in (R2) and (R3). The reagent mole fractions used in these experiments (see below) exceed those of HO₂ and HO by at least a factor of 10⁶, so this condition is clearly fulfilled.

The behavior of equation (1) is plotted in Figure 1 as a function of reaction time t_r at the NO concentration used in our experiments, without isobutane (E_{c0} , top curve) and modulated with isobutane (E_{ci} , bottom curve). The net HO₂ signal is proportional to the difference between the two curves at the transit time t_r . The vertical lines indicate the laminar, observed, and plug-flow transit times just discussed. Without isobutane, reaction (R2) limits the maximum achievable conversion efficiency of HO₂ to HO:

$$(E_{c0})_{\max} = \left(\frac{k_2[\text{M}]}{k_1} \right)^{\frac{k_2[\text{M}]}{k_1 - k_2[\text{M}]}} \quad (2)$$

This maximum value of E_{c0} occurs at a value of $[\text{NO}]$ given by

$$[\text{NO}((E_{c0})_{\max})] = (1/t_r) \ln(k_1/k_2[\text{M}]) / (k_1 - k_2[\text{M}]) \quad (3)$$

Equations (2) and (3) are obtained by differentiating equation (1) with respect to t_r and setting the derivative of E_{c0} equal to zero [Hard *et al.*, 1984].

With currently recommended values of k_1 and k_2 [Atkinson *et al.*, 1989], the value of $(E_{c0})_{\max}$ is 94% at 4 torr. In the present experiments, we used an NO concentration $[\text{NO}]_{\text{std}} < [\text{NO}((E_{c0})_{\max})]$ to minimize interferences discussed in a later section.

Fig. 1. Conversion efficiency of HO₂ to HO versus transit time in FAGE probe. Top curve: with standard $[\text{NO}]$ used in HO₂ determination, this curve represents the theoretical gross HO₂ signal. Bottom curve: same, with standard isobutane concentration, this curve represents the theoretical background signal. The net signal due to HO₂ is the difference (at any transit time) between these two curves. Vertical lines: L, residence time of core of laminar flow; P, plug-flow residence time; M, observed residence time [Hard *et al.*, 1992].

For the HO produced by (R1), the modulation efficiency at the transit time t_r due to isobutane injection, is

$$E_{\text{mod}} = 1 - E_{ci} / E_{c0} \quad (4)$$

Neglecting wall losses of HO₂ and HO, the overall chemical efficiency E_{chem} with which a net HO₂ "signal" is produced is

$$E_{\text{chem}} = E_{c0} E_{\text{mod}} = E_{c0} - E_{ci} \quad (5)$$

E_{chem} and E_{mod} are plotted against $[\text{NO}]$ in Figure 2. We emphasize again that equations (1) through (5) are used only to describe instrumental behavior and to aid in the selection of reagent concentrations and are not needed for calibration of the instrument's response to ambient HO₂. A

Fig. 2. HO₂ to HO conversion efficiencies versus NO. Dotted curve is E_{mod} , the efficiency of modulating the HO₂ to HO signal with isobutane; solid curve is E_{chem} , the chemical efficiency with which a net HO₂ signal is produced as HO (see text or Table 1 for definitions of efficiencies). Vertical solid line is $[\text{NO}]_{\text{std}}$, the NO concentration used in these measurements. Vertical dashed line: $[\text{NO}]$ giving maximum conversion efficiency $(E_{c0})_{\max}$. (Read $2.5\text{E}+13$ as 2.5×10^{13} .)

summary of the efficiency terms just defined is given in Table 1.

EXPERIMENT

The HO₂ instrument is a modification of the FAGE instrument described earlier [Hard *et al.*, 1984, 1986] designed to measure both HO and HO₂. Hard *et al.* [1992] provide a detailed description of the FAGE2 instrument used in these experiments. For the "clean air" experiments, the instrument was installed in a converted motor home used as a field research vehicle. These experiments were performed in August 1987 at our Pacific coastal site (45°N 124°W). The HO₂ sampling point was located 7 m horizontally and 5 m vertically from mean high tide. The site, in Lincoln City, Oregon, was a compromise between the desire for a remote site and the need for three-phase electrical power. Under suitable weather conditions, which were present during part of our measurement period, offshore winds brought remote North Pacific air to the coastal site, as evidenced by hydrocarbon analysis discussed below.

The urban HO₂ data were obtained in August 1986 at a rooftop site at Portland State University in downtown Portland, Oregon. This site was used earlier for the ambient HO measurements of June and November 1985 with FAGE2 [Hard *et al.*, 1986], and for the ambient HO and HO₂ measurements of August and October 1983 with FAGE1 [Hard *et al.*, 1984].

The 30-Hz Nd:YAG-pumped Rh6G dye laser (Quantel YG580 + TDL50) was frequency-doubled and tuned to the Q_{1,1}' + R_{2,3} line group of the A²Π (ν'=1) ← X²Σ (ν''=0) band of HO at 282 nm. The instrumental conditions were the same as those described for HO determination [Hard *et al.*, 1992], except for the methods of chemical modulation and calibration.

In HO measurements with FAGE, the isobutane modulating reagent is admitted in a carrier gas (air) to the 8 L/min sample flow about 5 mm downstream from the entrance of each nozzle through three small inlets at 120° intervals, flush with the interior wall and connected via a low-volume manifold. In HO₂ determination, the 200 mL/min N₂ carrier gas transported the reagent NO continuously to both sample probes. The NO reagent flow (Scientific Gas Products, 5% in N₂) was filtered by NaOH pellets, Ascarite, and FeSO₄, to remove N oxides and oxyacids. The constant NO flow was regulated by a Tylan mass flow controller; the resulting NO concentration in the flow tubes was [NO]_{std} = 3.7 × 10¹² cm⁻³. A controlled flow of isobutane (Matheson instrument grade, 99.5%), was delivered alternately to the two probes, in order to modulate the HO (produced from HO₂ by reaction (R1)) by chemical removal [Hard *et al.*, 1984, 1986, 1992]. As in [HO] determination, the pressure in the sample tubes and detection zone was 4 torr.

The ambient UV irradiance (290-400 nm) was monitored by a Si photoconductor filtered by a Corning 9863 filter, facing the zenith. Ozone was monitored by its UV absorption (Dasibi 1003-AH). H₂O was measured with a dewpoint hygrometer (General Eastern 1100DP). The NO monitor (Thermo-Electron model 12) had not yet been modified for clean-tropospheric NO determination purposes at the time of this experiment; thus its output revealed only those periods when the data were influenced by local combustion sources. Wind direction and speed were provided by a vane and an anemometer connected to a small weather station (Heathkit ID-4001) and were converted to S→N and W→E vector components for averaging by the computer. Hydrocarbon samples were taken on the van's roof, using evacuated stainless steel canisters kindly offered by James Greenberg of the National Center for Atmospheric Research

TABLE 1. Glossary of HO₂ Measurement Quantities

Term	Definition	Equation
E_c	conversion efficiency of HO ₂ to HO as a function of FAGE pressure (expressed as number density [M]), added [NO], probe transit time t_r , and added modulating reagent concentration [<i>i</i> -BuH]	(1)
E_{c0}	conversion efficiency without isobutane [*] : efficiency for producing the gross HO ₂ signal	(1)
E_{ci}	reduced conversion efficiency with isobutane [*] , used for background measurement	(1)
[M]	flow tube number density, equivalent to 4 torr under standard flow tube operating conditions	(1)
$(E_{c0})_{max}$	maximum achievable HO ₂ conversion efficiency (not optimal, since RO ₂ interference is proportionately less at lower conversion efficiencies; see Figure 6)	(2)
[NO($E_{c0})_{max}$]	nitric oxide concentration required to give maximum HO ₂ conversion efficiency	(3)
E_{mod}	efficiency of modulation (by isobutane) of HO produced from HO ₂	(4)
E_{chem}	overall chemical efficiency with which a net HO ₂ signal is produced as HO	(5)
r	measured response factor for HO ₂ , photons per unit time per unit ambient HO ₂ concentration	(6)
s_1	slope of inverse signal versus time curve in HO ₂ self-calibration (e.g., Figure 5a)	
[NO] _{std}	standard flow-tube nitric oxide concentration used in these experiments for reduction of HO ₂ to HO: 3.7 × 10 ¹² cm ⁻³ .	

^{*}The net HO₂ signal efficiency as HO is the difference $E_{c0} - E_{ci}$.

(NCAR), who also provided hydrocarbon and CO analyses of these samples.

For the HO₂ + HO₂ self-calibration procedure, the initial HO₂ concentration was provided by UV irradiation of CH₂O vapor in dry air in a continuously stirred tank reactor (CSTR), made of fluoro-ethylene polymer (FEP) teflon film. Air in the reactor was sampled continuously by the two FAGE nozzles. The air flow into the CSTR was provided by a pure-air generator (AADCO 20 L/min); a small fraction of the flow (120 mL/min) was bubbled through CH₂O in water in contact with the solid polymeric form (MCB, containing 12% CH₃OH as stabilizer) maintained at 0°C by an ice bath. The pure-air generator yielded air with an upper-limit dewpoint of less than -18°C. The vapor pressure of the liquid H₂O in the CH₂O source at 0°C was 4.6 torr, but the flow through this bubbler was a negligible fraction of the total. After mixing of these unequal air streams, the partial pressure of H₂O in the CSTR was less than 1 torr, due largely to any residual water vapor passing through the pure-air generator. During irradiation, the temperature of the reactor was 1° to 2°C warmer than the surrounding air. After steady state HO₂ signals were observed, the UV lamps and the stirring fan were turned off, and the resulting HO₂ signal decay was recorded over a period of 3 min. To secure a useful second-order region of the decay curve the following precautions were found necessary. Teflon bags previously used for hydrocarbon-loss calibration of HO response [Hard *et al.*, 1986; Chan *et al.*, 1990] were found unsatisfactory for HO₂ calibration. (The likely cause for the this problem was wall-stored mesitylene-NO_x photooxidation products (e.g., sources of RO₂ radicals), desorbing and reacting with HO₂, competing with the desired second-order self-reaction of HO₂. When the calibration was performed outdoors, exclusion of daylight was necessary; otherwise new HO₂ production interfered with the desired decay. An alternative HO₂ source, photolysis of Cl₂ in an H₂ + air mixture, gave much higher [HO₂], but the early portion of the decay curve was non-second order, suggesting release of HO₂ from a reservoir species such as H₂O₄ [Sander *et al.*, 1982; Fitzgerald *et al.*, 1985] accumulated during the steady state preparation of HO₂. In contrast, at the much lower initial HO₂ concentrations prepared with the CH₂O photolysis system, the early and middle portions of the decay agreed, indicating negligible contribution from thermal dissociation of reservoirs. A further disadvantage of the Cl₂-H₂ system, absent in CH₂O photolysis, was corrosion of the metallic outer parts of the nozzle by the HCl product.

RESULTS AND DISCUSSION

Ambient Data

Ambient HO₂ data, obtained at our coastal Oregon site during August 24-26, 1987, are shown in Figure 3. A strong diurnal variation of HO₂ under sea level conditions is evident. The 6-min averaging time is one-tenth of that used in our report of the HO diurnal cycle at this site [Hard *et al.*, 1992], made possible by the nearly 100-fold greater radical concentration observed here.

Winds exhibited a typical diurnal pattern for this site, moderate NW to NNW during the day, and falling to low speeds during the night (bottom panel of Figure 3). Offshore fog was present during this period, enveloping the

Fig. 3. Coastal HO₂ data, August 24-26, 1987, Lincoln City, Oregon, plotted with 0.1 hour averaging time. Abscissa in hours, Pacific daylight time. The vertical error bar represents ± 2 times the average of the tenth-hourly standard errors of the mean [HO₂] data. Continuous ultraviolet light intensity (UV) in arbitrary units, see text.

site at night, and persisting until 0830 LT (local time, Pacific Daylight Time) on the 25th and throughout the 26th. On the 26th, visual observation, confirmed by the UV data in Figure 3, indicated that the daytime fog was bright, and therefore the fog layer was shallow.

Ozone showed a weak diurnal variation, indicating low impact of local emissions. Nocturnal wind reversal often brings much lower nighttime ozone to this site. During daytime periods, ozone remained between 20 and 25 ppb.

As mentioned above, the NO measurements were only sensitive enough to detect intrusion of land-based sources. Peaks in NO coincided with E winds and reductions in O₃, which occurred sporadically between 2200 LT and 1000 LT on both nights. H₂O (not shown in Figure 3) was in the 8 to 11 torr range.

One hydrocarbon grab sample was taken during the period covered by Figure 3, at 1525 LT on August 25, and its analysis (provided by James Greenberg, NCAR) is given in Table 2. This sample shows total nonmethane hydrocarbon (TNMHC) concentrations (6.3 ppbvC) that are very low compared to continental and even some remote maritime levels (see, for instance Greenberg and Zimmerman [1984]). Listed for comparison are data from the samples nearest in time (afternoons of August 22 and 27). In the latter samples, TNMHC were 2-4 times higher and C₃-C₅ hydrocarbons may have been increased by emissions from a restaurant kitchen whose vents were 30 m N of our sampling point.

In Figure 3, there is a morning lag of at least 2 hours between the rise of ambient UV levels and that of daytime HO₂. The HO₂ rise corresponds to an increase in the speed of the west component of the wind. Such behavior might be explained by the occurrence of nocturnal temperature inversions. HO₂ is believed to increase with altitude in the lower troposphere [Logan *et al.*, 1981]. Horizontal wind speed, as well as vertical mixing rates, are weaker during the night; morning breakup of an inversion occurs after sufficient heating by the Sun. This leads 1) to the removal of fog droplets (removing a known HO₂ sink [Chameides and Davis, 1982; Schwartz, 1984; Jacob, 1986; Mozurkewich *et al.*, 1987; Lelieveld and Crutzen, 1990]) and 2) to a possible

TABLE 2. Hydrocarbon Analysis Summary

	August 22, 1987	August 25, 1987	August 27, 1987
methane	1772	1705	1696
CO	156	113	202
ethane	0.73	0.58	0.61
ethene	0.17	0.36	0.43
ethyne	0.98	0.04	nd
propane	0.50	0.07	0.40
propene	0.03	0.11	0.30
propyne	nd	nd	nd
isobutane	0.27	nd	0.19
<i>n</i> -butane	0.98	nd	0.50
butenes	nd	nd	nd
isopentane	0.93	0.03	0.27
<i>n</i> -pentane	0.39	nd	0.15
pentenes (total)	0.09	nd	0.29
isoprene	0.06	nd	0.06
other alkanes	0.50	0.03	0.15
other alkenes	0.17	0.10	0.35
aromatics (total)	0.45	0.34	0.46
benzene	0.15	0.03	0.09
toluene	0.15	0.21	0.14
terpenes	0.03	0.03	nd
TNMHC, ppbVC	25.8	6.3	14.8

Hydrocarbon analyses by James Greenberg, National Center for Atmospheric Research. Units are parts per billion by volume of compound in air, except for TNMHC, whose units are parts per billion by volume of carbon (atoms) in air (molecules). The abbreviation nd means not detected.

increase in vertical mixing, introducing HO₂ from the region above the inversion.

Figure 4 shows ambient HO₂ data observed in urban air during the period August 26-27, 1986, at our rooftop site in downtown Portland Oregon. The first afternoon of this period (from 1500 LT) shows the latter half of a diurnal cycle in HO₂ whose peak concentration is similar to that of the clean air measurements of Figure 3. The second day in Figure 4 was partially cloudy, as indicated by the spikes in the relative UV light intensity. Measured HO₂ concentrations are lower on the second day, consistent with higher NO levels during this period. Significant nighttime HO₂ signals occur during a period of 4 hours when [O₃] > [NO] on the first night. In contrast, HO₂ signals are quite low during the second night, which had elevated NO concentrations at all times.

Calibration

The decay of HO₂ in the dark due to the parallel reactions

is used to calibrate the HO₂ response of FAGE. The net rate coefficient $k_{4a} + k_{4b}$ at 1 atm and 298 K is given as $2.9 \times 10^{-12} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ in the review by Atkinson *et al.* [1989], and this rate coefficient is accelerated by 7.4% per 1 torr of H₂O vapor, which is the upper limit to its partial pressure in the calibration chamber. Since (R4a) and (R4b) are second order with respect to HO₂, a plot of the inverse of the decaying fluorescence signals (after background subtraction, and in arbitrary units) versus time should give a linear least squares fit, yielding a slope s_1 , as in Figure 5a.

Fig. 4. Rooftop HO₂ data, August 26-27, 1986, downtown Portland, Oregon, plotted with 0.1 hour averaging time. Abscissa and UV units same as in Figure 3.

The response r (in photons per unit time per unit HO₂ concentration) is given by

$$r = 2(k_{4a} + k_{4b})/s_1. \quad (6)$$

The same decay is plotted on a linear scale in Figure 5b, where equation (6) has been used to convert the signal to HO₂ concentration. Deviation of the final portion of the decaying signals from the least squares line in Figure 5a is ascribed to first-order reactions of HO₂ with CH₂O and/or with trace contaminants. Several decay experiments were performed in succession, and their results were averaged to obtain a value of $r = 0.22 (\pm 30\%) \text{ photons s}^{-1} (1 \times 10^6 \text{ radicals cm}^{-3})^{-1}$. Moreover, calibration of the FAGE

Fig. 5. Calibration by HO₂ + HO₂ self-decay. (a) Squares are inverse signal data; solid line is least squares linear fit. (b) Squares are HO₂ signal on linear scale, ordinate derived from slope of Figure 5a and equation (6); solid curve is second-order decay curve corresponding to straight line in Figure 5a. (Read 3.0E-04 as 3.0×10^{-4} .)

response to HO during the same period gave $r = 1.0$ ($\pm 25\%$) in the same units. Thus the observed response to HO₂ was 0.22 times the response to HO, implicitly incorporating wall loss of either radical species. At $[\text{NO}]_{\text{std}}$ and at the measured residence time, the product of the calculated chemical conversion and modulation efficiencies of HO₂ is 0.28 ($\pm 25\%$) (Figure 2), while that of HO is 0.95 ($\pm 3\%$) [Hard et al., 1992]. Thus the ratio of the predicted chemical signal efficiencies of the two species is $0.28/0.95 = 0.295$, which is about 33% greater than the ratio of the observed responses. It would not be surprising if HO₂ had a lower chemical signal efficiency, due to a higher removal rate of HO (following HO₂ conversion to HO) at the flow tube walls in the presence of the relatively large (and constant) flow of NO employed for reduction of HO₂ to HO (i.e., by $\text{HO} + \text{NO} \rightarrow \text{HONO}$). In contrast, any heterogeneous reaction of HO₂ would be expected as reduction to HO by NO at the flow tube walls.

Interferences

1. Other peroxy radicals (RO₂), where R is an organic radical, are a potential source of interference in the determination of HO₂, via

followed by HO production via (R1) and (R2) and chemical modulation via (R3). If RO₂ = alkylperoxy, then (R6) is somewhat faster than (R5a) at the 4 torr detection pressure, but not fast enough to be treated as instantaneous, as assumed in our previous treatment [Hard et al., 1984]. Moreover, at the NO concentration $[\text{NO}]_{\text{std}}$ used here for HO₂ conversion, the reactions

compete with (R6), reducing subsequent HO₂ production, resulting in lower calculated RO₂ interference. Implicit integration of the differential equations for RO₂, RO, and their HO₂ and HO products, with $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, and $i\text{-C}_3\text{H}_7$, allows calculation of the respective RO₂ net chemical signal efficiencies in chemical modulation by isobutane, relative to E_{chem} of ambient HO₂. The latter ratios are plotted in Figure 6 as functions of reagent [NO]. These calculations conservatively used the plug-flow transit time of $t_r = 25$ ms to calculate upper limits to the RO₂ interference; the actual transit time (Figure 1) is about 40% shorter [Hard et al., 1992]. The $\text{C}_2\text{H}_5\text{O}_2$ and $(n,i)\text{-C}_3\text{H}_7\text{O}_2$ radicals give approximately the same efficiency curve, which is somewhat higher than that of CH_3O_2 . Acylperoxy radicals (RCO₂) produce much less interference than RO₂ at $[\text{NO}]_{\text{std}}$ since they must undergo two additional kinetic steps to yield HO:

followed by the sequence of reactions (R5), (R6), and (R1). The resulting interference versus [NO] for the case of acetylperoxy radical ($\text{R} = \text{CH}_3$) is shown in the bottom curve of Figure 6. At $[\text{NO}]_{\text{std}}$, we obtain relative signal efficiencies $(E_{\text{chem}})_{\text{RO}_2} / (E_{\text{chem}})_{\text{HO}_2}$ for CH_3O_2 , the C_2 and C_3

Fig. 6. Overall chemical signal efficiencies of RO₂ species relative to HO₂, as a function of [NO]. Solid curve is $\text{R} = \text{CH}_3$, dotted curves are $\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, diamonds show $\text{CH}_3\text{C(=O)OO}$ as an example of acylperoxy radical behavior. Vertical solid line is $[\text{NO}]_{\text{std}}$. Vertical dashed line is [NO] giving maximum HO₂ conversion efficiency $(E_{\text{c0}})_{\text{max}}$. (Read 2.5×10^{13} as 2.5×10^{13} .)

alkylperoxy radicals, and CH₃CO₃ of 0.03, 0.08, and 0.004, respectively.

To predict interference from RO₂, representative [RO₂]/[HO₂] ratios in ambient air are necessary. Our previous discussion [Hard *et al.*, 1984] attempted to set an upper limit of less than 1 to this ratio by comparing $\sum_i k_{5ai}[RO_2]_i$ with $k_1[HO_2]$ at steady state, since the sources of HO₂ include not only the reaction chain (R5a) + (R6) but also aldehyde photolysis and the reactions of HO with CO, H₂O₂, and H₂. That upper limit is supported further by competition for the RO₂ and RO intermediates by reactions (R5b), (R7a), and (R7b). However, the postulated limit fails when ambient air is not in photochemical steady state, at night in particular, or when reaction with NO is not the predominant fate of HO₂. The limit appears to be valid in the daytime for remote air (assuming insignificant nonmethane hydrocarbons) at 45°N at all tropospheric altitudes at the equinox [Logan *et al.*, 1981]. At ground level the latter authors predict midday-maximum and nighttime CH₃O₂/HO₂ ratios of 0.25 and ~10, respectively. For tropical ground-level equinoctial conditions, radical-radical recombination paths which remove RO₂ and HO₂ are predominant and lead to higher CH₃O₂/HO₂ ratios [Logan *et al.*, 1981].

Recently, Madronich and Calvert [1990] have examined the possible influence of peroxy radical self-reactions (RO₂+RO₂) on the chemistry of the marine (40°N, equinox) and Amazon (equator, July 1) planetary boundary layer (PBL). Their modeling effort studied the effect of permutation reactions on the concentrations of HO₂ and a variety of RO₂ species. Such reactions tend to raise HO₂ and lower RO₂. Radical concentrations were tabulated for noon of a 5-day simulation with and without continuous emission sources, and with and without the permutation reactions included in the model. For the most realistic case, which includes both permutations and emission sources, the model yielded HO₂, alkylperoxy, and acylperoxy radical concentra-

tions of 3.2×10^8 , 7.6×10^8 , and 1.0×10^8 molecules cm⁻³, respectively, for the marine PBL. For the Amazon PBL simulation the respective concentrations were 1.1×10^9 , 4.6×10^9 , and 7.9×10^9 . Assuming that (E_{chem})_{C₂H₅SO₂} and (E_{chem})_{CH₃CO₃} are representative of the alkylperoxy and acylperoxy radicals, respectively, the resulting interferences by these radicals at noon are 20% and 0.1% of [HO₂] in the 40°N marine PBL and 33% and 1% of [HO₂] for the Amazon PBL. These calculations are summarized in Table 3.

Donahue and Prinn [1990] modeled NMHC chemistry for the tropical (15°S) remote marine boundary layer (MBL). For their "base case," their Figures 6 and 7 provide the approximate daytime maximum and nocturnal radical concentrations listed in the bottom half of Table 3. A major uncertainty in these radical results arose from the fluxes of heavy alkenes, for which there were insufficient experimental concentration data. To estimate interferences, we lump the primary, secondary, and tertiary alkylperoxy radical concentrations and assume their effective value of E_{chem} is that of C₂H₅O₂. Then the estimated daytime maximum interferences by CH₃O₂, nonmethane RO₂, and RCO₃ are 5%, 14%, and 0.2%, respectively, and 12%, 54%, and 0.08% at night. Thus the total RO₂ interferences we estimate for Donahue and Prinn's tropical marine conditions are 20% of [HO₂] at the daytime peak and 66% at night. If similar behavior were to hold for the midlatitude MBL at 45°N, then the small residual signals observed at night in Figure 3 would be due primarily to RO₂.

2. Reversible thermal dissociation of HNO₄ (HO₂NO₂), which yields HO₂ when the sample pressure is reduced, is a potential source of HO₂ interference. High steady state values of the ambient [HNO₄]/[HO₂] ratio correspond with low temperatures and high [NO₂]. For example, under the extreme conditions of 273 K and 1 ppm NO₂ at ground level, we calculate [HNO₄]/[HO₂] = 1.2×10^4 in the air

TABLE 3. RO₂ Interferences Calculated From Model Predictions of Ambient [HO₂] and [RO₂]

Species	Relative Efficiency ^a	40°N MBL, Noon ^b	Interference ^c	Amazon, Noon ^d	Interference
HO ₂	1.0	3.2E8 ^e		1.1E9	
alkylperoxy	0.08	7.6E8	0.19	4.6E9	0.33
acylperoxy	0.0044	1.0E8	0.001	7.9E9	0.01
total			0.19		0.34
Species	Relative Efficiency	15°S MBL, Noon ^f	Interference	15°S MBL, Night ^f	Interference
HO ₂	1.0	4.E8		5.E7	
CH ₃ O ₂	0.03	7.E8	0.05	2.E8	0.12
RCH ₂ O ₂	0.08	3.E8		3.E8	
R ₂ CHO ₂	0.08	3.5E8	0.14 ^g	3.5E7	0.54 ^g
R ₃ CO ₂	0.08	3.E7		2.5E6	
RCO ₃	0.0044	2.2E8	0.002	9.E6	0.0008
total			0.19		0.66

^a Overall chemical efficiency of conversion and modulation in FAGE2, normalized to that of HO₂. For alkylperoxy radicals the efficiencies are assumed equal to that of ethylperoxy.

^b Madronich and Calvert [1990], 40°N marine boundary layer, equinox.

^c Interference relative to concurrent HO₂ signal.

^d Madronich and Calvert [1990], Amazon boundary layer, July 1.

^e Read 3.2E8 = 3.2×10^8 radicals cm⁻³.

^f Donahue and Prinn [1990], 15°S marine boundary layer.

^g Sum of calculated interferences due to RCH₂O₂, R₂CHO₂, and R₃CO₂.

before sampling. The latter result is obtained from the pressure- and temperature-dependent rate coefficients for HNO₄ production and thermal dissociation recommended by Atkinson *et al.* [1989]; we neglect other removal reactions of HNO₄. After expansion through the sampling nozzle and transit through the low-pressure flow tube for $t_r = 25$ ms, which is an upper limit to the transit time for air reaching the detection zone, part of the HNO₄ dissociates, part of the resulting HO₂ reacts with NO to form HO, and part of the HO reacts with NO or isobutane. Implicit integration of the differential equations for HNO₄, HO₂, and HO gives an estimate of the consequent interference. The yield of new HO₂ from the dissociation of HNO₄ during transit is 1.4% of the value of ambient [HO₂] immediately after expansion through the sampling nozzle. At the standard NO and isobutane reagent concentrations, the net modulated interference from this added HO₂ is 9×10^{-3} times the net signal from ambient HO₂. Thus an upper limit to the HNO₄ interference, under the above extreme steady state ambient conditions, is 1% of the signal from ambient [HO₂], and is thus negligible. For comparison, if we were to perform the HO₂ measurement in a 1 atm flow tube with the same 25 ms residence time, using NO and isobutane reagent concentrations reduced in inverse proportion to the pressure, the HNO₄ interference would grow to 40% of the signal from ambient HO₂.

Moreover, even under perturbed ambient conditions, the reaction $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_4 + \text{M}$ is the only known source of atmospheric HNO₄. If HO₂ is removed by a perturbation (such as either mixing of NO from local sources or attenuation of daylight), then a corresponding decline in HNO₄ (by thermal dissociation) ensues with a characteristic time of 5 min at 273 K, or shorter times at higher temperatures. Thus the absolute value of the HNO₄ interference cannot be greater than that which existed before the perturbation, and cannot approach the value of perturbed [HO₂] unless the latter drops by a factor of at least 100 in a time much shorter than 5 min. Except for the latter restriction, we conclude that HNO₄ interference in the detection of HO₂ by FAGE is not significant in either polluted or remote tropospheric air at ground level, for either steady state or perturbed external conditions.

3. Laser photolysis of ambient O₃ (in the presence of H-containing species), H₂O₂, organic hydroperoxides, HNO₃, or HONO, can produce HO, leading to an HO-resonant background. As demonstrated elsewhere [Hard *et al.*, 1992], HO-resonant backgrounds arising from laser photolysis are modulated via the isobutane reagent's effects on fluorescence efficiency, resulting in a very small positive interference contribution. In the case of O₃, a larger negative interference results from the reaction of isobutane with O(¹D). The absolute value of this dominant negative offset under the present conditions is less than -1% of peak daytime HO₂. Laser-photolytic interferences of this type other than O₃ have been treated by Smith and Crosley [1990] and are completely negligible for HO₂ measurements.

4. Other laser photolysis paths, such as $\text{CH}_2\text{O} + h\nu$, produce H atoms, which react with O₂ to produce HO₂ at a rate too slow to be significant ($\tau = 555$ ms at 4 torr). Moreover, during its brief residence time in the FAGE2 laser excitation zone, conversion of the HO₂ product to HO via reaction (R1) proceeds to only 1.4% of the conversion of ambient HO₂. The latter consideration likewise applies to any photolysis path that produces HO₂ directly.

5. Laser photolysis of ozone or NO₂ at 282 nm produces O atoms, which react with alkenes to give partial yields of the vinoxy radical CH₂CHO, which reacts with O₂ to yield HO [Atkinson and Lloyd, 1984]:

Reaction (R10), driven by sunlight photolysis, may contribute slightly to ambient HO; however, the time constant for (R10) at 4 torr is 380 μs , too slow to contribute significant HO during the brief period of laser excitation, relative to the net HO signal from HO₂.

6. Laser photolysis of the HONO produced in reaction (R2) recreates HO. In the absence of isobutane, this HO production increases $(E_{c,0})_{\text{max}}$ by a multiplicative factor greater than 1 but much less than 2. Since (R3) competes with (R2) for the HO product of (R1), modulation with isobutane leads to a similar, but smaller, multiplicative increase in $E_{c,0}$. This minor multiplicative enhancement of the HO₂ response is independent of ambient conditions, and is not an interference since it is implicitly accounted for in the calibration procedure. No zero offset arises from this mechanism.

7. Production of HONO or HNO₃ by wall reactions between the reagent NO and adsorbed or gas-phase constituents leads to an observed photolytic source of false HO that is more significant than the other photolytic sources (3 through 6 above). We observed this effect by injecting high reagent NO concentrations into the HO₂ probe, resulting in a strong spectroscopic signal. This signal proved to be HO-resonant, proportional to reagent NO flow, and roughly proportional to the square of the laser power. The squared dependence indicates that this interference source is photolytic, i.e., one laser photon photodissociates a precursor to produce HO which is then detected by a second photon in the same laser pulse. This signal persisted even when the NO reagent was filtered successively by NaOH pellets, ascarite, and FeSO₄, and when the sample air was supplied by a pure air generator. One conceivable reaction sequence initiated by the reagent NO is

where (R11), negligible in the gas phase at 4 torr, may occur on the wall. Reaction (R12) has been documented to occur in smog chambers [Carter *et al.*, 1982]. This photolytic HO source is the reason why we use $[\text{NO}]_{\text{std}} < [\text{NO}((E_{c,0})_{\text{max}})]$, and why we modulate with isobutane with constant NO injection. Since NO flows in both sample probes, this HO source is present as a background which is largely subtracted out when the channel with the isobutane is subtracted from the signal channel. Since it raises the total background, it may degrade the instrument's sensitivity. The only net interference comes from quenching of this photolytic HO signal by the isobutane modulating reagent in the background channel. This reduces the background slightly in the channel with the isobutane, producing a net false positive signal that is known from other measurements to be two decades below the gross photolytic background, and is below the detection limit under standard instrumental conditions. However, if either chemical modulation with NO or spectral modulation were used instead of isobutane modulation, the interference would be approximately $+3 \times 10^6 \text{ cm}^{-3}$, based on measurements with FAGE2. This is lower than the ambient

daytime peak HO₂ concentration of $1.6 \times 10^7 \text{ cm}^{-3}$ we observed on 2 days in 1983 with FAGE1 [Hard et al., 1984] using NO modulation and is comparable with the uncertainty in [HO₂] in the latter measurements.

Reduction of Interferences

It is desirable to further reduce contributions to the HO₂ signal from RO₂ species (estimated at 20% here), as well as any other significant interferences, in future measurements. Regarding the RO₂ interference source, Figure 6 shows that by lowering E_{chem} for HO₂, RO₂ interference could be further reduced by a reduction in the reagent [NO]. This approach would require an increase in signal averaging times but would be acceptable in many applications. If maximum HO₂ response (and therefore optimum time resolution) is required, then we can exploit the [M]-dependence of the RO₂ interference by varying the cell pressure, adjusting [NO] and [isobutane] as necessary to retain the desired E_{chem} . A reduction in the FAGE internal pressure from 4 to 2 torr, via a twofold reduction in nozzle area (keeping the same transit time t , and adjusting reagent concentrations to maintain the same HO₂ conversion and modulation), yields a 62% decrease in the upper-limit daytime RO₂ interference from 20% to less than 8%.

Interference sources 2 and 6 above are negligible. Sources 3, 4, 5, and 7, which are proportional to the first power of the laser flux, are greatly reduced by the use of the FAGE3 instrument [Chan et al., 1990], in which a copper-laser-pumped dye laser delivers lower pulsed flux and higher pulse repetition rate than the YAG/dye laser used above.

COMPARISON WITH MODEL PREDICTIONS AND OTHER MEASUREMENTS

Logan et al. [1981] predicted HO₂ concentrations of $3.3 \times 10^8 \text{ cm}^{-3}$ (45°N latitude, 0 km altitude, equinox) at the midday maximum and $1 \text{ to } 10 \times 10^6 \text{ cm}^{-3}$ at night. For the marine boundary layer at 40°N Madronich and Calvert [1990] predicted HO₂ concentrations of $3.2 \times 10^8 \text{ cm}^{-3}$ at noon. For the tropical remote MBL at 15°S, Donahue and Prinn [1990] predicted [HO₂] of $4 \times 10^8 \text{ cm}^{-3}$ at the daytime maximum and $5 \times 10^7 \text{ cm}^{-3}$ at night.

Mihelcic et al. [1990] observed an HO₂ level of 38 pptv ($8.3 \times 10^8 \text{ cm}^{-3}$) at midday at a mountain site (Schauinsland, 1150 m altitude, 48°N) in the Black Forest, via numerical deconvolution of peroxy-radical ESR spectra in cryocondensed samples. Approximately 1 hour earlier the same day, Mihelcic et al. found 13 pptv HO₂, 86 pptv alkyl-RO₂, and 16 pptv CH₃CO₃.

Cantrell and Stedman [1982] employed a peroxy-radical chemical amplifier (PERCA) to measure a weighted sum of HO₂ and RO₂. The amplifier was based upon reaction (R1), driven by an added excess of NO reagent, and

for which excess CO was also added. This cyclic reaction chain regenerates HO₂ and accumulates NO₂. The NO and CO concentrations were adjusted to achieve sufficient chain length to allow detection of the NO₂ product. RO₂ contributed to NO₂ via generation of HO₂ via (R5a) and (R6), followed by the above chain. Experiments at the rooftop of the National Center for Atmospheric Research in Boulder, Colorado, yielded daytime peroxy radical signals ranging from below $1 \times 10^9 \text{ cm}^{-3}$ to $2 \times 10^{10} \text{ cm}^{-3}$.

Parrish et al. [1986] measured the sum of oxidants O_x other than ozone which contribute to the oxidation of atmospheric NO to NO₂. In the absence of such oxidants, the photochemical steady state expression is

$$j_{\text{NO}_2}[\text{NO}_2]/(k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3]) = 1$$

Parrish et al. measured O_x as the discrepancy

$$[\text{O}_x] = j_{\text{NO}_2}[\text{NO}_2]/(k_{\text{NO}+\text{O}_3}[\text{NO}]) - [\text{O}_3]$$

which can be caused either by significant contributions from (R1) and (R5a) + (R6) or other chemical processes, or by non-steady state kinetics due to local sources of NO_x (which were presumed absent). At Niwot Ridge, Colorado, they observed average summer midday O_x of 60 ppb in units of equivalent ozone concentration, which would be equal to $3.5 \times 10^9 \text{ cm}^{-3}$ (142 pptv) if the excess oxidant were assumed to consist entirely of HO₂.

Taken as HO₂, the oxidant concentrations detected indirectly in surface air by Cantrell and Stedman and by Parrish et al. were more than one decade higher than the directly detected HO₂ concentrations reported by Mihelcic et al. [1990], Hard et al. [1984], and in the present work. This difference is worthy of further study.

SUMMARY: MEASUREMENT ACCURACY, PRECISION, AND UNCERTAINTY

Based upon multiple calibration determinations, we assign a random calibration uncertainty of $\pm 30\%$ (see above). Improvement in this uncertainty could be obtained by finding calibration conditions which would extend the linearity of the curves in Figure 5 by reducing the first-order HO₂ removal process. An additional systematic error of 30% is associated with the uncertainty in the rate constants $k_{\text{ho}} + k_{\text{ub}}$. Uncertainties in the chemical conversion and modulation efficiencies are attributable to uncertainties in the governing rate constants (equations (1)-(5)), as well as to a possible contribution to heterogeneous processes in HO₂ reduction to HO or in subsequent HO loss. Since these conversion efficiencies are calculated only for the purpose of instrument design, and since their effects are incorporated into the calibration procedure, they do not introduce any additional uncertainty per se. Another source of error in the HO₂ measurement arises from the photon counting statistics of the acquired signal. The statistics for FAGE2 HO measurements have been discussed in detail by Hard et al. [1992]. The only difference in their application to HO₂ lies in the larger relative HO₂ concentration, which allows shorter averaging times than with HO. For the present paper an averaging time of 0.1 hour has been chosen, and the resultant signal uncertainty is $< 10\%$. Shorter averaging times would clearly give acceptable signal-to-noise ratio as well. The resultant of the random calibration uncertainty, the rate coefficient uncertainty, and the ambient HO₂ signal uncertainty, $(0.30^2 + 0.30^2 + 0.10^2)^{1/2}$, is an estimated overall uncertainty of 44%. An additional source of systematic uncertainty lies in the potential contribution of RO₂ species to the HO₂ signal. These interferences have been estimated here from kinetic theory, with appropriate RO₂ concentrations from atmospheric models. The estimates (Table 3) indicate the HO₂ concentrations we measured in daytime at 45° N may be 20% high due to RO₂ contributions, and larger RO₂ interferences (relative to [HO₂]) are expected at night. Adjustment of measurement conditions to optimize for HO₂ selectivity was discussed

above, and future measurements will minimize the relative response from RO₂.

CONCLUSION

We have observed the diurnal cycle of atmospheric HO₂ at coastal and urban sites near the Earth's surface. We have achieved self-calibration of the instrument by the self-decay of HO₂. We have considered several possible interferences. The observed small nighttime signals at both sites may contain, besides ambient HO₂, significant contributions from interferences by RO₂. The lowest nighttime HO₂ signals observed, before midnight August 26 and after 0600 August 27, 1987 (Figure 4), are indicative of the low level of positive photolytic signal associated with the NO reagent (interference 7 above). With a change to lower laser pulse energy and higher repetition rate, the only known remaining interference is due to RO₂, which model calculations suggest may contribute 20% of the observed daytime HO₂ signal and more than half of the signal at night. The RO₂ interference can be reduced to less than 3% of concurrent daytime maximum HO₂ (and 10% of nighttime HO₂) by changes in the operating parameters of FAGE.

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