Measurement of free radicals OH and HO$_2$ in Los Angeles smog

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Abstract. Atmospheric free radicals hydroxyl and hydroperoxyl (OH and HO$_2$, collectively HOx) are the catalysts that cause secondary or photochemical air pollution. Chemical mechanisms for oxidant and acid formation, on which expensive air pollution control strategies are based, must accurately predict these radical concentrations. We have used the fluorescence assay with gas expansion (FAGE) technique to carry out the first simultaneous, in situ measurements of these two radicals in highly polluted air during the Los Angeles Free Radical Experiment. A complete suite of ancillary measurements was also made, including speciated hydrocarbons, carbon monoxide, aldehydes, nitric oxide, nitrogen dioxide, and ozone along with meteorological parameters. Using this suite of measurements, we tested the ability of a lumped chemical mechanism to accurately predict radical concentrations in polluted air. Comparison of model predictions with measured radical concentrations revealed generally good agreement for OH early and late in the day, including the early evening hours, when OH persisted at low concentrations after dark. During midday, however, modeled [OH] was high by about 50%. Agreement for HO$_2$ was quite good in the early morning hours, but model-calculated HO$_2$ concentrations were significantly too high during midday. When we used our measured HO$_2$ concentrations as model input, agreement between calculated and measured OH concentrations was improved. It seems likely that (1) the model's HOx sources are too large, (2) there are unaccounted HO loss processes in Los Angeles air, and/or (3) the complex parameterization of RO$_2$/HO$_2$ radical chemistry in the reaction mechanism does not adequately describe the behavior of these radicals in the Los Angeles atmosphere.

1. Introduction

Hydroxyl OH and hydroperoxyl HO$_2$ radicals collectively play a catalytic role in tropospheric photochemistry. This catalysis results in the formation of ozone and other deleterious oxidants, acids, and fine particles in polluted areas. A thorough understanding of this role is necessary for efficient, cost-effective pollution control. Current understanding is incorporated into chemical mechanisms [Lurmann et al., 1987; Stockwell et al., 1990; Carter, 1990], which necessarily must be lumped or parameterized owing to the presence of more than 100 reactive hydrocarbons in polluted air. Pathways for HO$_2$ (OH + HO$_2$) radical generation include photolysis of nitrous acid, ozone, and aldehydes and the reactions of ozone with alkenes.

Until recently, the difficulty in measuring HO$_2$ species, present at mixing ratios between $10^{14}$ and $10^{11}$, has precluded direct comparison with predictions of chemical reaction mechanisms. Most measurements of hydroxyl radical have been made in relatively clean air environments [Hard et al., 1992b, 1995; Perner et al., 1987; Eisele and Tanner, 1991; Eisele et al., 1996]. A recent study of tropospheric OH in clean air [Crosley, 1997], which included three independent OH measurement techniques [Harder et al., 1997; Tanner et al., 1997; Mather et al., 1997] and a suite of relevant ancillary measurements necessary for photochemical modeling, concluded that modeled OH values were about 1.5 times higher than measured values [Mount and Williams, 1997]. A recent study of oxidant capacity in moderately polluted air (NO$_x$ < 10 ppb and O$_3$ < 100 ppb) combined a range of supporting measurements with direct OH measurements. In that investigation of air along the North Sea coast, measured OH was 30% higher than model predictions [Forberich and Comes, 1997]. Neither of those two studies measured HO$_2$.

Although urban measurements of OH [Hard et al., 1984, 1986; Hofzumhaus et al., 1996, Dorn et al., 1996] or HO$_2$ [Mihelcic et al., 1990; Hard et al., 1992a] have been made, there were no simultaneous urban measurements of both HO$_2$ radicals and only one of these studies has included the suite of measurements necessary to test model predictions. Recent measurements of RO$_2$ in polluted air [Hu and Stedman, 1995] do not include sufficient supporting measurements for model testing. The goal of the Los Angeles Free Radical Experiment (LAFRE) was to investigate and test the accuracy of photochemical models in predicting radical concentrations in a highly polluted environment.

2. Los Angeles Free Radical Experiment (LAFRE)

The experiment was situated in Claremont, California, 55 km downwind from downtown Los Angeles (see Figure 1) during September 1993. All participating groups were located in an
Protection Agency 120 ppb, 1-hour O3 standard. This is an excellent downwind site, without sizable nearby emissions and with regular running water for laser cooling and several power outages limited the amount of high-quality data. Nevertheless, an excellent data set was obtained over a continuous 3-day period.

The California Air Resources Board (CARB) supported ancillary measurements at the site, yielding an extensive data set that allows direct comparison of measured radical concentrations with photochemical models. These are the first direct observations of OH and HO2 in the Los Angeles basin, and the most extensive supporting data set ever obtained in polluted air.

2.1. OH and HO2 Measurement

Hydroxyl and hydroperoxyl measurements were made with the fluorescence assay with gas expansion (FAGE3) instrument [Chan et al., 1990] adapted to our mobile laboratory. A complete description of the mobile laboratory FAGE3 setup is given elsewhere [Hard et al., 1995], so an abbreviated description of the field instrument is provided here.

Fluorescence assay with gas expansion (FAGE3) [Hard et al., 1984] utilizes low-pressure, laser-induced fluorescence for direct OH measurement. Measurements of HO2 are accomplished by in situ conversion of HO2 to OH by nitric oxide (NO) added to the flowing sample airstream. Our FAGE instrument employs multiple, continuous channels of airflow that are intersected by a single laser beam [Hard et al., 1995] in a cell with no internal windows. Nozzle orifices are 63 cm above the detection zone, 46 cm above the mobile laboratory roof, and 3 m above ground level. During LAFRE one of the channels was utilized for OH measurements, one channel for HO2 measurement, and one channel for an OH source that was used to monitor the laser line for tuning and normalization to laser power. The cell pressure was 3.5 torr.

2.2. Ancillary Measurements

As is generally accepted today, radical HO2 measurements without supporting chemical, spectral, and meteorological data are of little value. On the other hand (as discussed below), the short chemical lifetimes of OH and HO2 in polluted air make their concentrations independent of long-range transport, as long as adequate supporting data are available. The following data were provided by CARB contractors: continuous wind, temperature, NO, NOy, NOx, NOy = (NOy - NOx), peroxyacetyl nitrate (PAN), H2O, CH2O, HONO (most nights), HNO3 (limited data set), and 4-hour averages of CO, CH4, volatile organic compounds (VOC) (more than 100 species), and carbonyls (nine species). Typical hydrocarbon and carbonyl data are illustrated in Table 1. Unfortunately, cost precluded more frequent hydrocarbon and carbonyl measurements than the 4-hour integrated samples.

Nitric oxide, nitrogen dioxide, and ozone were also measured with instruments housed within our air-conditioned mobile laboratory. Nitrogen oxides were determined by ozone chemiluminescence (Thermo Electron (TECO) 14C) and ozone was determined by UV absorption (Dasibi 1003-AH). During morning and afternoon periods (i.e., traffic rush hours), the resultant NO compares well with the 1-hour-averaged luminol-based measurements made by Unisearch Associates, sited about 15 m from the Portland State University mobile lab. These instruments were checked for calibration accuracy as part of the CARB quality assurance procedures. During midday, NO was below the detection limit of the luminol instrument. The TECO instrument was modified with a FeSO4 converter for NO2 determination. This converter is known to have interferences from PAN, so NO2 data were corrected using measured PAN concentrations; all corrections were <10% of the NO2 concentrations. Standard meteorological parameters were measured. AtmAA Inc. collected electropolished canister air samples and dinitrophenylhydrazine cartridges for subsequent determination of speciated hydrocarbon and aldehyde concentrations. Canister and cartridge sampling systems were located within 8 m of the FAGE probes. A PFA Teflon line 0.3 m from the FAGE probes directed ambient air to our NOx and ozone measuring instruments.

2.3. Calibration of OH and HO2

A complete description of the absolute calibration procedure for OH is given by Hard et al. [1995]. A continuously stirred tank reactor (CSTR) constructed of Teflon film is placed over the ambient sampling nozzles. Hydroxyl radical concentrations are maintained within the black-light-illuminated CSTR by the addition of a hydrocarbon (mesitylene, C9H12) and NO to a flow of humidified zero air. The steady state concentration of OH present in the CSTR can be determined by measuring the consumption of mesitylene during its residence time in the CSTR. Since the only significant agent in the CSTR for consuming mesitylene is the hydroxyl radical, a simple steady state treatment gives

\[ [\text{OH}] = \frac{[\text{C}_9\text{H}_{12}]_{\text{in}}}{[\text{C}_9\text{H}_{12}]_{\text{out}} - 1} / k \tau \]

where \([\text{C}_9\text{H}_{12}]_{\text{in}}\) and \([\text{C}_9\text{H}_{12}]_{\text{out}}\) are the inflow and steady state concentrations, respectively, of mesitylene, \(k\) \((6 \pm 1 \times 10^{11} \text{ cm}^3/\text{s})\) [Perry et al., 1977]) is the rate constant for the reaction of mesitylene with OH, and \(\tau\) is the residence time in the CSTR. (Steady state
Table 1. Typical Concentrations of Hydrocarbons, CO, and Aldehydes During the Los Angeles Free Radical Study

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
<th>Species</th>
<th>Concentration</th>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>12.48</td>
<td>cis-1,3-Dimethylcyclohexane</td>
<td>0.20</td>
<td>iso-Pentane</td>
<td>1.44</td>
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<tr>
<td>Propane</td>
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<td>cis-1,4-Dimethylcyclohexane</td>
<td>0.97</td>
<td>Pentane</td>
<td>7.28</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>5.29</td>
<td>1,1-Dimethylcyclohexane</td>
<td>0.34</td>
<td>Cyclopentane</td>
<td>1.71</td>
</tr>
<tr>
<td>Butane</td>
<td>12.93</td>
<td>cis-1,3-Ethylmethylcyclopentane</td>
<td>0.15</td>
<td>2,2-Dimethylbutane</td>
<td>3.97</td>
</tr>
<tr>
<td>iso-Octane</td>
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<td>iso-Propylcyclopentane and</td>
<td>0.08</td>
<td>2-Methylpentane</td>
<td>5.00</td>
</tr>
<tr>
<td>Butene</td>
<td>12.93</td>
<td>Trimethylhexane</td>
<td></td>
<td>2-Methylpentane</td>
<td>4.90</td>
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<tr>
<td>2,3-Dimethylbutane</td>
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<td>1,1,3-Trimethylcyclohexane</td>
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<td>Hexane</td>
<td>4.06</td>
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<td>0.11</td>
<td>Methylpentane</td>
<td>7.87</td>
</tr>
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<td>meta-Propylene</td>
<td></td>
<td>2,2-Dimethylpentane</td>
<td>1.63</td>
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<tr>
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<td>2.06</td>
<td>1,1,2-Trimethylcyclopentane</td>
<td>0.11</td>
<td>2,2-Dimethylpentane</td>
<td>2.28</td>
</tr>
<tr>
<td>3-ethylpentane and</td>
<td>0.38</td>
<td>1,3,5-Trimethylbenzene</td>
<td>0.19</td>
<td>Heptane</td>
<td>1.63</td>
</tr>
<tr>
<td>Dimethylcyclopentane</td>
<td></td>
<td>Ethylbenzene</td>
<td>2.93</td>
<td>2,2,3-Trimethylpentane</td>
<td>3.81</td>
</tr>
<tr>
<td>Octane</td>
<td>1.18</td>
<td>meta-Xylene</td>
<td>3.19</td>
<td>2,5-Dimethylhexane and 0.80</td>
<td>1.18</td>
</tr>
<tr>
<td>2,3,5-Trimethylhexane</td>
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<td>para-Xylene</td>
<td>1.68</td>
<td>Trimethylpentane</td>
<td>1.28</td>
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<tr>
<td>2,4-Dimethylpentane</td>
<td>0.29</td>
<td>1,1,3-Trimethylcyclohexane</td>
<td>0.34</td>
<td>3-Methylpentane</td>
<td>3.87</td>
</tr>
<tr>
<td>4,4-Dimethylpentane</td>
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<td>meta-Propylene</td>
<td>0.61</td>
<td>1-Hexene</td>
<td>1.97</td>
</tr>
<tr>
<td>2-Methyl-4-ethylhexane</td>
<td>0.18</td>
<td>1,1-Dimethylcyclopentane</td>
<td>0.39</td>
<td>cis-3-Hexene</td>
<td>0.07</td>
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<td>2,6-Dimethylhexane</td>
<td>0.21</td>
<td>1,3-Dimethylcyclohexane</td>
<td>0.39</td>
<td>trans-3-Methyl-2-pentene</td>
<td>0.04</td>
</tr>
<tr>
<td>2,3-Dimethylhexane</td>
<td>0.13</td>
<td>Ethanol (Acetaldehyde)</td>
<td>6.58</td>
<td>trans-2-Pentene</td>
<td>0.20</td>
</tr>
<tr>
<td>4-Methylcyclopentane</td>
<td>0.53</td>
<td>Ethanal (Acetaldehyde)</td>
<td>6.58</td>
<td>1,3-Dimethylcyclopentane</td>
<td>0.53</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>0.45</td>
<td>Acetone</td>
<td>1.27</td>
<td>Ethylcyclopentane</td>
<td>0.67</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.35</td>
<td>Butanol</td>
<td>0.66</td>
<td>1,1,2,3-Dimethylcyclopentane</td>
<td>0.31</td>
</tr>
<tr>
<td>2,2-Dimethylcycloheptan</td>
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<td>Crotonal</td>
<td>0.95</td>
<td>C5 Aldehyde</td>
<td>0.57</td>
</tr>
<tr>
<td>2,3-Dimethylcycloheptan</td>
<td>0.25</td>
<td>Methylocyclohexane</td>
<td>0.49</td>
<td>C5 Aldehyde</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*Hydrocarbons and CO, (nmol C) mol⁻¹*

*Aldehydes, nmol mol⁻¹*
The measured conversion of nitric oxide to nitrogen dioxide is used
as a tracer for HO2 using a steady state analysis similar to that described for the OH-mesitylene calibration. A separate Teflon CSTR was constructed solely for HCHO-NO calibrations to eliminate possible RO chemistry from residual mesitylene oxidation products on the walls of the OH calibrator. In this system, unlike the mesitylene tracer system for which OH is the tracer's only significant loss process, the nitric oxide tracer reacts with ozone, OH, and organic peroxy radicals as well as with HO2. Nevertheless, to a good approximation the HO2 concentration in the calibrator is given by an equation similar to that for OH:

\[
[\text{HO}_2] = \frac{([\text{NO}]_0/[\text{NO}]_{\text{out}} - 1)}{(k_1 + \gamma)} \tag{2}
\]

Note that as with the mesitylene-OH calibration system, detailed knowledge of HO2 production in the CSTR is not required to calculate steady state [HO2] using the tracer technique. The FAGE HO2 response factor is determined by relating the measured photon signal due to OH converted from HO2 (by NO in the FAGE probes) to the HO2 concentration calculated from (2).

\[
\text{HO2 response factor} = \frac{\text{net signal}}{[\text{HO2}]_{\text{meas}}} \tag{3}
\]

We have identified three potential systematic errors that are unique to the HO2 + NO CSTR calibration. First, ozone produced in the reactor makes (2) underestimate HO2. Second, net HONO formation from OH + NO leads to export of HONO in the outflow, a net loss of NO, and a corresponding overestimate of HO2 by (2). Third, despite experimental conditions that minimize organic peroxy radicals, HOCH2O2 is an unavoidable HCHO oxidation product that reacts only with NO in this system, leading to an overestimate of HO2 by equation (2). We measured FAGE OH signals and reactor ozone concentrations concurrently during each calibration and used these to calculate the corresponding corrections to FAGE HO2 and calibrated HO2, respectively. For the second and third systematic errors we used a kinetic model of the full reaction system, including inflow and outflow of reactants and products, to calculate corrections for HONO export and HOCH2O2 reaction. These three terms together yielded a typical net correction of less than 10%. Additional calibration uncertainties may be taken as systematic and are due to uncertainties in the residence time in the CSTR (10%) and in the rate constant for HO2 + NO (15% [DeMore et al., 1997] to 25% [Atkinson et al., 1997]). Thus the systematic error in HO2 is 18-27%. Our estimated overall random uncertainty (2 σ) in the HO2 response factor during September 1993 was ±20%.

A calibration is shown in Figure 3. Figure 3a models the concentrations of NO, NO2, O3, and the HO2 signal over the course of a 1.5-hour period, beginning with the initiation of photolysis. In the model, an initiation period of about 30 min is required for model-predicted HO2 to reach agreement with HO2 calculated via (2) using modeled NO values. (Equation (2) is valid only at steady state. A non-steady state treatment is also available, as we have described [Hard et al., 1995] for OH.) Figure 3b presents experimental values for NO, NO2, and O3 at equilibrium in the CSTR and compares [HO2] calculated via equation (2) with the FAGE HO2 signal.

In more recent HO2 CSTR calibrations we have added CO to the calibration mixture and have replaced some of the black-lights with UVB lamps. These steps increase the photolysis rate of CH2O relative to NO and decrease the CH2O concentration necessary to attain HO2 concentrations in the ambient range. The benefits of these changes are less ozone export (relative to NO conversion by HO2), less HONO production from OH + NO, and less HOCH2O2 production. As a result, all three systematic errors are greatly reduced and can be made negligible.

Owing to the time requirements to employ either the OH or HO2

![Figure 2. OH field calibration. Shown are the results of a continuously stirred tank reactor (CSTR) fluorescence assay with gas expansion (FAGE) OH calibration performed in the field. The OH concentrations labeled GC-OH (where GC is gas chromatography) are calculated using equation (1). FAGE OH values are calculated using the OH response factor given in the text. A 15-min averaging time with 1 σ error bars for FAGE data is shown.](image)
CSTR calibrations, a rapidly deployable secondary standard was developed to provide a relative OH reference signal that could be used to frequently assess FAGE OH system response. This secondary standard, the horizontal calibrator (HCAL), consists of a 6-foot-long, aluminum lined, 8-inch-diameter PVC pipe in which a 254-nm UV germicidal lamp illuminates an ambient airflow of 8 L s⁻¹ delivered by an upstream muffin fan (see Figure 4). Elevated levels of CO and O₃ are added at the entrance of the pipe. These concentrations are high enough to dominate the chemical production and loss of OH in the reactor gas stream and reduce the influence of the local ambient trace gas composition.

\[
O₃ + hν \rightarrow O(D) + O_2
\]

\[
O(D) + H_2O \rightarrow 2OH
\]

\[
CO + OH + O_3 \rightarrow HO_2 + CO_2
\]

Figure 3. HO₂ calibration model and data, showing (a) model run for UV-irradiated formaldehyde/NOx system, and (b) field calibration results in the CSTR. NO out and NO₂ out are the concentrations at equilibrium. The concentrations of NO and NO₂ flowing into the reactor are 110 and 22 ppb, respectively.

Figure 4. Schematic of horizontal calibrator (HCAL) used for rapid field calibration checks. Carbon monoxide, ozone, and ambient air were photolyzed to generate a relatively constant (+10%) and high concentration (~8 x 10⁷ molecule cm⁻³) of OH.
The hydroxyl radical profile within the HCAL was modeled using the same polluted air mechanism employed to analyze the ambient radical data. In this case, \([O_3]\) and \([CO]\) were increased to the experimentally added concentrations and the ozone photolysis rate was increased 1000-fold over ambient to match the observed OH concentration within the HCAL. The calculation was run for 4 s corresponding to the HCAL transit time. Figure 5 shows the relatively constant OH values calculated for the HCAL at different times of the day, thus verifying that OH chemistry is dominated, as intended, by its formation through photolysis of ozone and removal by added CO. OH rises rapidly upon entering the HCAL to values that only vary slightly from calibration to calibration. The HCAL is somewhat sensitive to both ambient hydrocarbon and NOx; doubling of either of these concentrations in modeling runs results in ~10% change of the OH generated.

The HCAL was employed at approximately 2-hour intervals during each measurement day (Figure 6). Hydroxyl radical signal was normalized to the ozone concentration measured at the exit of the HCAL tube. During the measurement period discussed here, FAGE signal response to OH varied ± 20% (2 σ) during the day. It is important to note that OH is generated in the HCAL using \(O_3\) and CO added to ambient air. Hence the OH response of the system is monitored in situ with air in which ambient concentrations are varying dramatically over the course of the day. The relative insensitivity of the system response to varying ambient conditions indicates that potential calibration problems, if present, are minor.

Potential interferences for OH and HO\(_2\) in FAGE have been exhaustively discussed elsewhere [Hard et al., 1992a, b, and references therein]. Field tests for \(O_3\) interference on September 24, 1993, using ambient air with an artificially elevated \(O_3\) concentration of 11 ppm, gave an interference of \(5 \times 10^4\) OH cm\(^{-3}\), which corresponds to a conservative upper limit of \(1 \times 10^5\) OH cm\(^{-3}\) under ambient conditions. That upper limit is for 250 ppb, the highest ambient \(O_3\) concentration we encountered in 1993.

For HO\(_2\), the two principal interferences are from organic peroxy radicals (RO\(_2\)) and HNO\(_4\). The overall detection efficiency for typical RO\(_2\) species at our 1993 FAGE pressure, probe length, and reagent NO concentration was approximately 18% of that for HO\(_2\). In daylight, the sum of the ambient concentrations of those RO\(_2\) species that react with NO to give HO\(_2\) cannot exceed the HO\(_2\) concentration. (This is because HO\(_2\) is also a direct product of CO oxidation and formaldehyde photolysis and because the rate coefficients for the ambient NO reactions of RO\(_2\) and HO\(_2\) are comparable.) Therefore 18% is a conservative upper limit to the RO\(_2\) interference in our 1993 HO\(_2\) results. Subtraction of estimated values for the RO\(_2\) interference would increase the discrepancy between the measured and model-predicted HO\(_2\).

**Figure 5.** Model-calculated concentrations of OH generated in the horizontal calibrator at four times during the day using ambient concentrations. The resultant OH concentrations are normalized by the measured ozone concentration.

![Figure 5](image)

**Figure 6.** FAGE signals normalized to measured ozone concentration during HCAL calibration checks during ambient measurement periods. Each point represents a 40-s measurement interval.
The HNO₄ interference is proportional to ambient NO₂, which governs the ambient HNO₄/HO₂ ratio, and to the rate of dissociation of HNO₄ during its brief exposure to low pressure in the FAGE probe. For our 1993 conditions, plus a conservatively high ambient NO₂ of 200 ppb, the calculated HO interference from ambient HNO₄ was less than 0.2% of the signal from ambient HO₂.

3. Results

3.1. Description of Data

Measurements were carried out in late September, which typically coincides with the highest ozone levels in the Los Angeles basin; the U.S. National Ambient Air Quality Standard (pre-1997) was exceeded by more than a factor of 2 during the period September 24-27. Visual observation and radiometer readings indicated clear-sky conditions for these 3 days. Figure 7 shows the daily concentrations of OH and HO₂ with 15- and 6-min averaging times, respectively. These averaging times were chosen to maximize temporal resolution while maintaining reasonable signal-to-noise ratios. The uncertainties in the field measurements are ~1 x 10⁶ and ~1.5 x 10⁷ molecule cm⁻³ for OH and HO₂, respectively, conservatively based on the standard deviation of the mean during the above stated averaging periods. The representative 1σ error bars on Figure 7 have a small diurnal variation due to ambient light, which increases background photon signal in the FAGE instrument. The error bars are determined by the standard error of the mean of the signal and include both instrumental noise and actual fluctuations in ambient radical concentrations during the averaging time. Also shown in Figure 7 are calculated [Madronich, 1987] UV light intensity and measured concentrations of O₃, NO₂, and NO (1-min averaging times).

Figure 7. Measured ambient concentrations of OH, HO₂, ozone, NO and NO₂ during September 24 through 26, 1993. FAGE OH and HO₂ data were averaged over 15- and 6-min intervals, respectively. Ozone, NO, and NO₂ measurements were averaged over 1-min intervals.
3.2. Modeling of OH and HO$_2$

Hydroxyl and hydroperoxyl radical concentrations were modeled using our own numerical integration program PAMOL, which employs the predictor-corrector algorithm of Gear [1971]. The chemical reaction mechanism of Lurmann et al. [1987] was used for all simulations. This mechanism, termed CAL, has been used extensively for examining ozone formation in polluted air [Dodge, 1989]. Inputs to the calculation include measured 1-min average NO, NO$_2$, and O$_3$ concentrations. Measured concentrations of speciated NMHC, carbonyls, and CO were assigned to the appropriate model surrogate species. PAMOL employed phytolysis rates from the model of Madronich [1987]. Since hydrocarbons, aldehydes, and CO were only available with 4-hour averaging times, their concentrations in the model remain constant during the 4-hour collection periods (0-4, 6-10, 12-16, 18-22 hours) extrapolated to the preceding and following hours. Ironically, hydrocarbons and aldehydes, which are among the more stable of the reactive species in the atmosphere, have measurement averaging times many times longer than those obtainable for many radical species and reactive compounds, including our own HO$_2$ measurements, thus limiting the resolution of measurable changes in ambient photochemistry. Future measurement campaigns should shorten this averaging time. PAMOL linearly interpolates between data points for each input parameter at every integration step as determined by the Gear algorithm and calculates the concentrations of all other species, including OH and HO$_2$. In an additional calculation (described below), HO$_2$ was constrained at the measured concentration with only OH floating.

Chemical inhomogeneities, airflow complexities, and surface chemical reactions are present at all ground-based experimental sites. The elevated NMHC and NO$_x$ levels of urban air shorten the photochemical response time of the HO$_x$ system, resulting in less sensitivity to surface effects than in clean air.

Under virtually all LAFRE conditions, radical concentrations are in local chemical (steady state) equilibrium with the dominant, higher-concentration species. This is not surprising; smog photochemistry is very fast, with the calculated OH and HO$_2$ molecular lifetimes approximately 40 ms and 1 s near noon (Figure 8). The instrumental OH and HO$_2$ averaging times are set by experimental limitations. One can use the measured (or simulated extreme) variation in controlling variables, with adjustable averaging times, to determine whether the OH and HO$_2$ predictions are sensitive to the averaging times of the controlling variables. Thus, although the calculation is carried out as a numerical integration with constrained measured species concentrations, it functionally amounts to a continuous steady state calculation.

Figure 9, based on the Claremont ancillary data of September 24, shows the effect on the model-predicted OH concentration of increasing the averaging time for NO, NO$_2$, O$_3$, and UV. The results at 1 min (the NO$_x$ / O$_3$ data storage interval) are tracked almost identically by those at 5-min averaging (not shown). Those at 20 and 65 min show small deviations except when OH is decreasing steeply, in the afternoon. Chemical inhomogeneities and airflow complexities are undoubtedly present, but Figure 9 indicates that they do not obscure the photochemical information that can be drawn from OH measurements in urban air.

Figures 10a and 10b and 11a and 11b compare modeled and measured radical concentrations for OH and HO$_2$ on September 24 and 25. On September 24 (Figure 10a), OH agreement is excellent except at midday (1200-1600 LT), when modeled concentrations are significantly higher than measured. Note that OH radical
Figure 10. For September 24, 1993, model-calculated (a) OH compared with measured OH, (b) HO2 compared with measured HO2, and (c) OH using measured HO2 as part of input data. Solid curves denote model-calculated data, while bars denote measured values.

The situation on September 25 (Figure 11) is similar. Agreement between measured and modeled HO2 concentrations is achieved in the early daylight (0800-1200 LT) and late evening (2000-2200 LT) hours, with modeled concentrations significantly higher than measured at midday. In Figure 11c we again use the measured HO2 concentrations as model inputs and obtain significant improvement in agreement between measured and modeled OH during midday and also in the evening hours.

As stated above, the systematic errors are 18-27% and 18% for HO2 and OH, respectively, in addition to an overall 28% random error for both measurements. After correcting the OH model calculation with our measured HO2 concentrations, there is no evidence for systematic disagreement between measured and modeled OH values within our systematic uncertainty. However, there is significant variance between measured and modeled HO2 concentrations that cannot be explained by systematic errors because the discrepancy varies greatly at different times of the experiment. Furthermore, the estimate of random error for HO2 is based on the standard error of the mean of ambient measurements that includes actual fluctuations of the ambient concentration. The magnitude of these fluctuations as seen in the model predictions for HO2 (see Figures 10b and 11b) is about 20%. Whereas these fluctuations are comparable to the random error for HO2, they are not significant compared to the random error for OH. Thus we conclude that the CAL mechanism incorrectly predicts HO2 concentrations in the Los Angeles atmosphere during the period of the measurements, and the magnitude of this error varies from 0% to ~100%, but we cannot further discern any model errors in OH prediction once measured HO2 values are employed.

3.3. Radical Balance Calculation

Figures 12 and 13 present the CAL mechanism's dominant chemical reactions contributing to formation and loss of OH and HO2, respectively, on September 25. (The situation on September 24 is similar.) These figures indicate that radical recycling dominates HOx chemistry at all times. HO2 + NO → OH + NO2 dominates OH formation and HO2 loss (Figures 12 and 13), while the lumped RO2R + NO → NO2 + HO2 dominates HO2 formation. In the CAL mechanism, hydrocarbons are lumped according to their reactivity into about a half dozen different surrogate species. These different surrogates have differing primary atmospheric reactivity, and they generate radical oxidation products with varying yields. All these RO2 species then funnel through the lumped species RO2R to form HO2. It is both an art and a science to develop a realistic simulation of smog photochemistry since so many hydrocarbons (VOCs) and oxygenates (OVOCs) are involved. Hydroxyl reactions with carbon monoxide, VOCs, and carbonyls are the major OH recycling processes. The only significant radical loss process is the OH + NO2 reaction to form nitric acid. The HO2 self-reaction to form H2O2 was always so insignificant at the high measured NO concentrations that cannot be explained by systematic errors or uncertainties in the experiment. Furthermore, the estimate of random error for HO2 is based on the standard error of the mean of ambient measurements that includes actual fluctuations of the ambient concentration. The magnitude of these fluctuations as seen in the model predictions for HO2 concentrations is about 20%.

According to the CAL mechanism, major radical generation sources (in approximate descending order, Figures 12 and 13) are the photolyses of nitrous acid, ozone, formaldehyde, and di甲醛 and the nonphotolytic ozone/alkene reaction [Pauson and Orlando, 1996], which dominates after 1600 LT. Review of OH and HO2 rates in Figures 12 and 13 indicates that almost all the major OH parents and reaction partners were measured in this study. Nevertheless, significant disagreement persists into the evening hours after dark in small but significant concentrations and that the model reproduces this behavior reasonably well. This situation on September 24 was enhanced after nightfall by downslope air movement off the San Gabriel Mountains across Foothill Boulevard to the north, picking up NO exhaust emissions from passing traffic. (Daytime winds were strongly from the west and did not pass over any nearby heavily traveled roads.) Also on September 24 (Figure 10b), good agreement between measured and modeled HO2 concentrations is achieved in the early daylight (0800-1200 LT) and late evening (1900-2200 LT) hours, with modeled concentrations significantly higher than measured at midday. In Figure 10c we have constrained [HO2] in the calculation to the measured concentrations, rather than letting the model calculate HO2. This is seen to significantly improve agreement between modeled and measured OH concentrations during periods when the modeled HO2 concentration was higher than measured. That is, the measured HO2 concentrations are more consistent with measured OH concentrations than the modeled HO2, indicating modeling errors in predictions of HO2 concentrations.

The situation on September 25 (Figure 11) is similar. Agreement for measured and calculated OH (Figure 11a) is generally good, although calculated midday OH is high, and the model does not reproduce the late evening persistence of OH. The difference in evening OH between September 24 and 25 may be due to the much higher evening NO concentrations on September 24. As on
Figure 11. Same as Figure 10, but for September 25, 1993.

Figure 12. Rates of reactions in the September 25, 1993, modeling experiment that are significant in the formation or destruction of OH in the lumped mechanism. Note the split logarithmic rate scale. Concentrations (top) are measured OH (points), modeled OH (solid curve), and UV irradiance (gray curve).
between measured and modeled radical concentrations was found. As stated above, agreement between measured and calculated OH concentrations is improved if we constrain the model to our measured HO2 concentrations, indicating that measured [OH] is in better agreement with measured [HO2] than with modeled [HO2]. The major uncertainty in the HO2 rates is, of course, the varying yields of the lumped RO2R entity that then produces HO2 in its reaction with ambient NO.

Since lumped RO2 chemistry is necessarily quite complex in CAL or any other polluted air mechanism, we only briefly discuss its major features here [see, e.g., Atkinson [1997]]. RO2 is known to have several fates in the atmosphere. Organic peroxy radicals may (1) contribute to ozone formation by oxidation of NO to NO2, identical to the role of HO; (2) react with NO2 to form peroxynitrates; (3) react with NO to produce an organic nitrate, in competition with case 1; or (4) react with HO2 or another RO2 entity to produce peroxides. The last reaction is analogous to the self-reaction of HO2 to produce hydrogen peroxide. All these processes are of atmospheric significance. The first process, a chain propagation step, contributes to ozone accumulation as mentioned. The second forms PAN and analogous irritants and lacrymators, which can be transported for long distances and ultimately dissociate to regenerate NO2 and the RO2. The formation of organic nitrates from the RO2 + NO reaction is generally a significant reaction channel that requires molecular rearrangement and is thus favored by increasing chain length in the RO2 species. Process 4 was not significant in the Claremont study owing to high NO concentrations at all times. Processes 2-4 are all chain termination reactions. Bowman and Seinfeld [1994] have traced typical reaction pathways for RO2 radicals in polluted air and shown that ozone yields are sensitive to the VOC/NO ratio through this reaction pathway. Although organic nitrates from RO2 + NO reactions have been extensively studied for several model compounds and a parametrized yield equation is available (e.g., Atkinson [1997]), the large range of compounds present in the Los Angeles atmosphere includes many species for which these yields can only be estimated. Thus the yields of organic nitrates represent a major area of uncertainty in the CAL mechanism and in other such mechanisms for ozone formation in polluted air. This uncertainty is especially large in the present Los Angeles study since radical-balance calculations show that the reactions of peroxo radicals with species other than NO are negligible in the CAL mechanism. To the extent that RO2 radicals go through the organic nitrate formation route, they not only do not generate ozone, but they also fail to produce additional HO2 radicals. Thus one explanation for higher modeled HO2 concentrations relative to measured values is that the CAL mechanism underestimates the organic nitrate formation channel. However, we reiterate that the CAL (or any other model's) treatment of RO2/HO2 yields is exceedingly complex. Mass balance is not even attempted in these models, and organic nitrate yields are not even included in the mechanisms.

Aside from the RO2 + NO recycling reaction, the dominant unquantified (by experimental measurement) radical sources in the CAL mechanism are nitrous acid photolysis and photolysis of dicarbonyl compounds, formed chiefly from aromatic hydrocarbon oxidation. Both OH and HO2 come to photochemical and thermochemical equilibrium with their corresponding acids, nitrous and peroxyacetic. The rapid equilibration of HO2 with peroxyacetic acid has no significant effect on steady state HO2 concentrations, and the corresponding rates of formation and loss have been subtracted from the curves representing gross production and loss of HO2 in Figure 13. In contrast, although nitrous acid is in slow, inconsequential equilibrium with OH via HONO + hv → OH + NO and OH + NO + M → HONO + M, the CAL mechanism provides a significant OH source through 2NO2 + H2O → HONO + HNO3. This "reaction," discovered in smog chambers, presumably occurs heterogeneously. Recently, nitrous acid has been shown to form from this reaction on soot particles [Ammann, 1998].
During nighttime, HONO accumulates since it is not photolyzed. At sunrise, this accumulated HONO provides a significant OH source up to about noon (Figure 12). Long-path (differential absorption spectroscopy (DOAS)) absorption measurements of HONO were made during the study by a CARB contractor. Typical predawn concentrations in the 1-3 ppb range were reported, and reported concentrations declined to zero after sunrise. No measurements of HONO were made during the September 24-26 period. In contrast, the CAL mechanism predicts an accumulation of about 5 ppb HONO by dawn on both days.

Although dicarbonyls have been documented as aromatic hydrocarbon oxidation products in numerous laboratory studies, their existence as gas phase constituents of polluted air is on less firm grounds. The carbonyl analysis did not find any detectable concentrations, although the analysis was not designed to look for them and certainly does not disprove their presence. The CAL mechanism uses three lumped dicarbonyl species: glyoxal, methylglyoxal, and all other dialdehydes. Of these, only the latter two are radical sources.

We have tested the significance of the HONO and dicarbonyl sources by successively removing them from the numerical integration as shown in Figure 14 for September 25. The black curves for OH and HO2 present the "standard" calculation with both sources as predicted by the CAL mechanism. The gray curves have both HONO and dicarbonyl chemistry removed. Significant reduction in calculated OH and HO2 occurs, with the largest change for OH in the morning hours. This is associated with removal of the HONO photolytic source: a model run (not shown) with the dicarbonyl source set to zero is little different from the standard model run for OH up to about 1100 LT. In contrast, after about 1100 LT the removal of the dicarbonyl source accounts for nearly all the differences between the black and gray curves for both OH and HO2.

What do measured radical concentrations say of these modeling scenarios? The picture is clearer with HO2 since its relative noise is less owing to its higher concentration. Up to about 1500 LT, measured HO2 agrees best with model runs that have both sources removed. The dicarbonyl-included scenario fits measured HO2 around 1600 LT well, but predicts [HO2] much lower than measurements the rest of the afternoon and evening, at a time when possible ozone/alkene radical sources would be increasing in relative importance. The situation is less clear with the noisier OH data, and it is difficult to judge which scenario fits measured [OH] best.

4. Conclusions

Although many atmospheric reactions are well understood, particularly inorganic reactions and the oxidation of lower molecular weight alkanes and alkenes, much of the chemistry for photochemical smog is highly parameterized in air quality models. This is because of large uncertainties in reaction mechanisms for higher molecular weight VOC, especially aromatic and biogenic (terpene) hydrocarbons and also because of the large number of reactions occurring. Although unavoidable, parameterization can obscure true uncertainties in detailed photochemistry. Smog chamber measurements place important constraints on model construction, but uncertainties remain with respect to yields of unmeasured products and to parameterization of HO2/RO2 yields and reactivities. For instance, while the OH concentration in a smog chamber can be calculated from hydrocarbon decay and reaction parameters adjusted to give the correct hydrocarbon profiles, HO2 and RO2 concentrations cannot be separately deduced, since both contribute to ozone accumulation. The major goal in many smog chamber modeling exercises is correct prediction of ozone concentrations, but the number of degrees of freedom in such models allows considerable uncertainty to remain in the details of the chemical processes. Furthermore, wall-influenced processes in smog chambers are of uncertain applicability to the ambient atmosphere.

Radical measurements in polluted air provide a unique test of parameterized photochemical mechanisms since measured OH and HO2 concentrations reach rapid photochemical equilibrium with the surrounding chemical environment and therefore can be compared with predictions of chemical models, eliminating the potentially confounding effects of emissions and transport, while probing smog photochemistry in its native environment. Our radical measurements in Los Angeles indicate that while the CAL model appears to generally reproduce measured OH concentrations (a significant accomplishment), it does not adequately predict the HO2 concentrations. This discrepancy is likely due to (1) incomplete representation of HO2 and RO2 chemistry in the model; (2) overprediction of HONO formation source strength, most important in the morning, and (3) underprediction of the afternoon/evening significance of the dicarbonyl-photolysis and/or ozone-alkene radical sources. Of course, there may be additional unquantified radical formation or loss processes at work as well.

This study, the first major radical balance experiment in highly polluted air, has provided much useful information and serves as a model for more in-depth field experiments in the future. Some of the shortcomings of this study that should be addressed in future work include the following: (1) averaging times for VOC and carbonyls significantly shorter than the 4-hour averages employed here; (2) a simpler, more robust, and more quantitative, continuous check on OH and HO2 response during ambient measurements; (3) extension of model calculations to other polluted air mechanisms; (4) simultaneous measurements of aerosol size distribution to address possible heterogeneous processes related to radical production and loss. These considerations will be addressed in future FAGE campaigns.

![Figure 14: Modeling experiment using the September 25 data set for (a) OH and (b) HO2. Black curves represent the standard model, which includes carryover of HONO and dicarbonyls from the previous day. For the gray curves, the rates of HONO photolysis and dicarbonyl reactions were set to zero. Points are measured values.](image-url)
Acknowledgments. We wish to thank the California Air Resources Board (CARB) and their staff, especially Bart Croes, Ash Lastgari, and John Holmes, for their support of this project. We would also like to thank the CARB contractors, Kochi Fung of AtmAA., Inc. (hydrocarbon and carbonyl analysis) and G. Mackay of Unisearch Inc. (HONO, nitrogen oxides, and ozone). Finally, we wish to thank the reviewers for their careful review and helpful comments and suggestions. The research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency, Office of Research and Development, through grants R819305 and R823319 to Portland State University.

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(Received June 3, 1998; revised December 17, 1998; accepted December 23, 1998.)