Derivation of Hydroperoxyl Radical Levels at an Urban Site via Measurement of Pernitric Acid by Iodide Chemical Ionization Mass Spectrometry

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Supporting Information

ABSTRACT: Hydroperoxyl radical (HO2) is a key species to atmospheric chemistry. At warm temperatures, the HO2 and NO2 come to a rapid steady state with pernitric acid (HO2NO2). This paper presents the derivation of HO2 from observations of HO2NO2 and NO2 in metropolitan Atlanta, US, in winter 2014 and summer 2015. HO2 was observed to have a diurnal cycle with morning concentrations suppressed by high NO from the traffic. At night, derived HO2 levels were nonzero and exhibited correlations with O3 and NO3, consistent with previous studies that ozonolysis and oxidation by NO3 are sources of nighttime HO2. Measured and model calculated HO2 were in reasonable agreement: Without the constraint of measured HO2NO2, the model reproduced HO2 with a model-to-observed ratio (M/O) of 1.27 (r = 0.54) for winter, 2014, and 0.70 (r = 0.80) for summer, 2015. Adding measured HO2NO2 as a constraint, the model predicted HO2 with M/O = 1.13 (r = 0.77) for winter 2014 and 0.90 (r = 0.97) for summer 2015. These results demonstrate the feasibility of deriving HO2 from HO2NO2 measurements in warm regions where HO2NO2 has a short lifetime.

INTRODUCTION

Hydroperoxyl radical (HO2) plays a key role in the atmosphere and is the dominant form of HOx (OH + HO2). Sources of HO2 include the oxidation of CO and volatile organic compounds (VOC) by hydroxyl radicals (OH), the photolysis of carbonyl compounds, the ozonolysis of alkenes, and the oxidation of VOC by the nitrate radical (NO3).1−6 The last two are important sources of HO2 at night. HO2 is involved in many important atmospheric processes such as the degradation of pollutants, ozone production, and secondary organic aerosol (SOA) formation.7−9 Observations of HO2 are important for understanding and constraining atmospheric chemistry.

Pernitric acid (HO2NO2) is closely coupled to HO2 levels in many regions of the atmosphere. HO2NO2 has a relatively simple chemistry in the atmosphere (Reactions 1−4).10−14

\[
\begin{align*}
\text{HO}_2 + \text{NO}_2 + \text{M} &\rightleftharpoons \text{HO}_2\text{NO}_2 + \text{M} \\
\text{HO}_2\text{NO}_2 + \text{h} \nu &\rightarrow \text{HO}_2 + \text{NO}_2 \\
&\rightarrow \text{OH} + \text{NO}_3 \\
\text{HO}_2\text{NO}_2 + \text{OH} &\rightarrow \text{NO}_2 + \text{O}_2 + \text{H}_2\text{O} \\
\text{HO}_2\text{NO}_2 &\rightarrow \text{deposition/scavenging}
\end{align*}
\]

The thermal decomposition rate constant \( k_{-1} \) is a strong function of temperature, e.g., \( \sim 5 \times 10^{-6} \text{ s}^{-1} \) at \(-30^\circ \text{C} \) and \( \sim 1 \times 10^{-1} \text{ s}^{-1} \) at \( 30^\circ \text{C} \).15 The important role of HO2NO2 in HOx and NOx (NO + NO2) chemistry in cold regions has been widely discussed.14,16−23 In warm regions, as its thermal decomposition is fast and dominates the loss, HO2NO2 chemistry is reduced to a rapidly established steady state with HO2 and NO2 (Reaction 1). Given proper averaging time that allows the equilibrium to be approached, HO2 can be derived from HO2NO2 and NO2 observations.24

\[
[\text{HO}_2] = \frac{k_{-1}[\text{HO}_2\text{NO}_2]}{k_{[\text{NO}_2]} + K[\text{NO}_2]} = \frac{[\text{HO}_2\text{NO}_2]}{K[\text{NO}_2]}
\]

where \( K = k_{-1}/k_{[\text{NO}_2]} \) is the equilibrium constant and \( K \) is a function of temperature alone.\textsuperscript{15}

In this work, we employ chemical ionization mass spectrometry (CIMS) to measure HO2NO2 in metropolitan Atlanta and determine HO2 from observations of HO2NO2 and NO2. Hydrated iodide (I\textsuperscript{−}\cdot(H2O))\textsubscript{n} is used as the reagent ion(s) for CIMS detection of HO2NO2.\textsuperscript{25−27} The I\textsuperscript{−}\cdot(H2O)\textsubscript{n} CIMS
technique is versatile and suitable for detecting of a host of species, such as Cl2, Br2, ClO, BrO, HOCl, HOBr, N2O5, HNO3, HONO, ClNO3, CINO2, HCOOH, HNCO, and CH3C(O)-OOG.25−29 Consequently, HO2NO2 observations and determination of HO2 can be simultaneously performed with measurements of other species using the same instrument. The goal of this work is to evaluate the feasibility of deriving HO2 from HO2NO2 observations in a warm polluted environment.30−32 We had previously observed that high NO2 (500 ppbv) can reduce the HO2 signal,33 and high HO2 can simultaneously be detected with measurements of other species using the same instrument. The goal was to evaluate the feasibility of deriving HO2 from HO2NO2 observations utilizing I (H2O)4.31 Due to instrument availability, we employed different instrumentation and methodology have been discussed by Huey.41 Due to instrument availability, we employed different instrumentation and methodology have been discussed by Huey.41 Due to instrument availability, we employed different instrumentation and methodology have been discussed by Huey.41 We also assessed the inlet loss of HO2NO2 under the same conditions (i.e., flow rate and temperature) as the ambient measurement. HO2NO2 was synthesized (Supporting Information), diluted, and flown through (1) the inlet used for sampling, (2) a new, clean inlet of the same diameter and length as the sampling inlet, and (3) a very short (~30 cm), clean inlet of the same diameter. HO2NO2 signals were found to be the same for all cases, and thus, we concluded that the wall loss of HO2NO2 was minimal.

The detection of HO2NO2 using I (H2O)4 CIMS was similar to that described by Veres et al.25 Briefly, HO2NO2 is ionized by I (H2O)4 and detected on two channels: HO2NO2I− and NO3−.

\[
\text{I}^{-}\text{(H}_2\text{O})_4^- + \text{HO}_2\text{NO}_2^- \rightarrow \text{HO}_2\text{NO}_2\text{I}^- (m/z 206) + \text{nH}_2\text{O} \quad (6)
\]

\[
\text{I}^- + \text{HO}_2\text{NO}_2^- \rightarrow \text{NO}_3^- (m/z 62) + \text{HOI} \quad (7a)
\]

\[
\text{I}^{-}\text{(H}_2\text{O})_4^- + \text{HO}_2\text{NO}_2^- \rightarrow \text{NO}_3^- (m/z 62) + \text{HOI} + \text{nH}_2\text{O} \quad (7b)
\]

We retrieved HO2NO2 concentrations based on the HO2NO2I− channel. We found that the NO3− channel is the major channel with a branching ratio >90%. However, it is known to be nonspecific for HO2NO2. It can be formed via reactions of I−(H2O)4− and several other species (N2O5, NO3, BrONO2, CINO2, ClONO2, CINO3).33,41−43 An assessment of the NO3− channel is given in the Supporting Information.

As we used a quadrupole mass spectrometer of unit mass resolution, the detection at the HO2NO2I− channel can be interfered with by I−(H2Br)− of the same m/z in a bromine-rich environment.30

\[
\text{HOBr} + \text{I}^-\text{(H}_2\text{O})_4^- \rightarrow \text{I}^-\text{Br}^- (m/z 206, 208) + ...
\]

Since the sensitivities to isotopes are proportional to their abundances, this interference can be corrected by tracking the isotope I−(H2Br)− at m/z 208. Nitril chloride (CINO2) is detected as CINO2I− at m/z 208 (53CINO2I−) and 210 (57CINO2I−).33 If CINO2 is present, the 53CINO2I− signal at m/z 208 needs to be subtracted to obtain the 1−(H2Br)− signal, and thus, the 57CINO2I− signal at m/z 210 needs to be tracked. In winter, signals at m/z 208 and 210 were found to only originate from CINO2, based on their correlation and the isotope ratios, which ruled out the I−(H2Br)− interference. In summer, no CINO2I− nor I−Br− was found at m/z 208 or 210.

We had previously observed that high NO2 (500 ppbv) can interfere with HO2NO2 detection using I− with a high resolution time-of-flight CIMS.44 For this reason, NO2 (up to 86 ppbv) was added to the inlet to test for possible interferences to the

<table>
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<tr>
<th>Table 1. Summary of the Measurements in Two Seasons</th>
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<tr>
<td>species</td>
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<td>winter (2014)</td>
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<td>summer (2015)</td>
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“Meteorological parameters include T, p, humidity, wind speed, wind gust, wind direction, total solar radiation, solar UV radiation, cloud base, and precipitation rate.”

**EXPERIMENTAL METHODS**

**Observations.** Observations were made in both winter (November 20, 2014 to January 2, 2015) and summer (June 10 to July 7, 2015), on top of the Georgia Tech Ford ES&T building in metropolitan Atlanta (33°46′N, 84°24′W), 10 m above the ground, and 0.6 km to the west of the Interstate-75/85 highway. Concurrent measurements of HO2NO2, NO2, NOx, CO, O3, and N2O5 (winter only) and meteorological parameters were performed (Table 1). All instruments for gas phase species were housed in a laboratory on the top floor with inlets extending through the roof to sample ambient air. Basic meteorological parameters were measured by a weather station mounted on the roof of the building. Data were reported in local time, UTC−5 h in winter, and UTC−4 h in summer.

**CIMS Measurements of HO2NO2.** The general CIMS instrumentation and methodological have been discussed by Huey.41 Due to instrument availability, we employed different CIMS instruments for each season. Both CIMS instruments had configurations similar to that described by Liao et al.28 The main differences were inlet configurations and flows. The inlets were Teflon FEP tubing (O.D. = 1.22 cm and I. D. = 0.95 cm), 9 and 5 m long, respectively, in winter and summer observations. The inlet flows were 46 slpm (standard liter per minute, standard = 0 °C and 1013 kPa) and 41 slpm, respectively, of which roughly 1.5 slpm was sampled into CIMS and the rest was exhausted. These large flows resulted in relatively short residence times in the inlets, roughly 0.8 and 0.5 s, respectively. We also assessed the inlet loss of HO2NO2 under the same conditions (i.e., flow rate and temperature) as the ambient measurement. HO2NO2 was synthesized (Supporting Information), diluted, and flown through (1) the inlet used for sampling,
ambient measurement. However, no significant interferences due to NO2 were found on either the HO2NO2-1 or the NO5 channels.

A two-step indirect calibration was applied, as a portable HO2NO2 calibration source has not been developed. A known amount of Br2 from a permeation tube (KIN-TEK) was periodically added into the inlet to track the sensitivity variation.28,29

\[
\text{Br}_2 + \cdot I (\text{H}_2\text{O})_n \rightarrow \text{Br}_2 \cdot I (m/z 285, 287, 289) + n\text{H}_2\text{O}
\]  

(9)

Br2 is a convenient proxy as the CIMS instrument has similar sensitivities to HO2NO2 and Br2 on the cluster channels. The Br2 emission rate was determined every 2 or 3 days by a spectrophotometric method.45,46 The relative sensitivity of HO2NO2 and Br2 on the cluster channels was quantified by measuring the resulting NO2 of HO2NO2 thermal decomposition with a cavity attenuated phase-shift spectroscopy (CAPS, Aerodyne) (Supporting Information). The sensitivities to HO2NO2 (HO2NO2-1 channel) were ~25 and ~15 Hz/ppbv, respectively, in both seasons. Commonly, we have estimated the limit of detection (LOD) based upon the standard deviation of the variations of background signals.29,48 In this work, we defined the LOD as twice the standard deviation (2σ) of the background variation. The LODs of HO2NO2 for both seasons were 0.2 and 0.6 pptv, respectively, based on a 1 min integration time. The uncertainties for HO2NO2 measurement were 22% in winter and 16% in summer, mostly from calibration.

**Determination of HO2.** HO2NO2 observations were combined with measurements of NO2 and temperature to derive HO2 levels from eq 5. HO2NO2 data were excluded during precipitation events, as they perturbed the equilibrium, or if they were below the LOD. All NO2 data were well above the LOD. We applied different averaging times to derive HO2 at different temperatures. Temperature ranged from ~4.7 to 24.5 °C during the winter observation and 18.8 to 37.6 °C during the summer observation. The lifetime of HO2NO2 and thus the time scale to approach equilibrium varied. Also, NO2 emitted by traffic (especially traffic on the highway nearby) fluctuated, which can perturb the HO2NO2 equilibrium on short time scales.

We used a time-dependent model21 to determine the appropriate averaging times. The model setup highlighted the appropriate averaging times to derive HO2 from simulated HO2NO2 using eq 5. Both model simulated and experimentally derived HO2 concentrations were averaged on different time scales and compared. The comparisons are shown in Figure 1. At ~5 °C, 10 min averages of derived and simulated HO2 agree within 10% (slope = 0.989, r = 0.976); at 5 °C, 5 min averages of derived and simulated HO2 agree within 5% (slope = 0.955, r = 0.988); at 15 °C, 1 min averages of derived and simulated HO2 agree within 3% (slope = 0.975, r = 0.985). Thus, we select the average time of 10 min for ~5 °C ≤ T < 5 °C, 5 min for 5 °C ≤ T < 15 °C, and 1 min for T ≥ 15 °C.

The uncertainty for HO2 derived from HO2NO2 observations has multiple sources. The equilibrium constant K in eq 5 has a 30% uncertainty in the temperature range of our
Table 3. Species and Parameters for the Steady-State Model Prediction of HO2

<table>
<thead>
<tr>
<th>species/parameters</th>
<th>constrained (measured)</th>
<th>constrained (modeled/assumed)</th>
<th>predicted by the model</th>
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<tr>
<td></td>
<td>T, p, O3, H2O2, CO, NO, NO2, HO2NO2, N2O5</td>
<td>j values</td>
<td>OH, HO2, CH3O2, C2H6O2, CH2 OH2, CH3O2, CH3C(O)CH3, CH3C(O)CHO2, CH3C(O)CH3, CH3C(O)CH2OH, CH3C(O)CHO, isoprene, CH3C(O)CH=CH2 (MKV), CH3=C(CH3)CHO (MACR), benzene, toluene, HONO, CH2O, CH3CHO, peroxyacetyl nitrate (PAN), CH3C(O)CH2OH, CH3C(O)CHO, isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), benzene, toluene, HONO, and H2O2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>constrained (measured)</td>
<td>Predicted by the steady-state model in Run_1; constrained by measurements in Run_2 (see text).</td>
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<tr>
<td></td>
<td></td>
<td>Predicted by the REAM model in the summer observation.</td>
<td>Estimated using the REAM model in the summer observation.</td>
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<tr>
<td></td>
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<td>Estimated using the NCAR TUV model, scaled using the measured UV radiation.</td>
<td>Estimated using the REAM model.</td>
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<tr>
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<td>Constrained by measurement in the winter</td>
<td>Hydroxylperoxy radicals derived from the OH-initiated oxidation of isoprene.</td>
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<tr>
<td></td>
<td></td>
<td>Oxidation of benzene and toluene.</td>
<td>Hydroxyperoxy radicals derived from the OH-initiated oxidations of MACR/MVK.</td>
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<tr>
<td></td>
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<td>Estimated using the REAM model.</td>
<td>Panel 4-D Regional chEmical and tRansport Model (REAM).</td>
</tr>
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</table>

HO2 ranged from 1.4 to 64.6 ppbv (average 11.3 ppbv), and derived HO2 was up to 89.3 pptv (daytime average 10.4 pptv). Figure 2 shows mean diurnal profiles of HO2. Peak values of HO2 profiles were 0.19 pptv in winter and 20.0 pptv in summer. These HO2 levels are close to those observed in the same seasons at polluted sites. Low HO2 associated with high NO was oftentimes observed in both seasons, during the day and night. Diurnal profiles of HO2 at high NO peaks. Figure 2. Diurnal profiles of derived HO2, NO, and solar radiation in both winter and summer observations. NO suppressed HO2 during morning rush hours. Diurnal profiles of HO2 are also plotted in dotted lines. Low HO2 was 0.19 pptv in winter and 20.0 pptv in summer. These HO2 levels are close to those observed in the same seasons at polluted sites. In the following sections, we look at two test cases and model comparisons to determine if the derived HO2 is reasonable. Suppression of HO2 at High NO. HO2 can be efficiently suppressed at high NO due to the fast reaction of HO2 with NO. The most obvious suppression of HO2 occurred during morning rush hour, as seen in Figure 2. In both seasons, the peak of NO in the morning depressed HO2, resulting in asymmetric diurnal profiles, although the radical production is expected to be symmetric as it follows the solar radiation. A similar behavior was observed in urban areas by Holland et al. and Martinez et al.

Low HO2 associated with high NO was oftentimes observed in both seasons, during the day and night. Figure 3 displays two examples of the suppression of HO2 at high NO peaks. On December 26 and 27, 2014, HO2 decreased accordingly to high NO multiple times (20:00 to 23:00, 03:00 to 06:00, 07:40 to 08:30, 09:00 to 14:00). On June 20, 2015, HO2 was around 1 pptv during 17:00 to 18:00 while NO was high up to 12 ppbv; then, HO2 recovered to ~6 pptv after NO dropped to ~1 ppbv. In all, our derived HO2 responded to NO accordingly. This indicates that there are no significant interference when NOx is high that lead to an obvious over estimation.
of HO₂. However, very low levels of HO₂ were still observed at high NO.

**Relationship between HO₂ and O₃/NO₃ at Night.**

Nighttime HO₂ has been reported in several locations. Here, we examine the correlation between nighttime HO₂ and O₃ in both seasons and the correlation between nighttime HO₂ and NO₃ in winter when N₂O₅ was measured, which allowed for an estimate of [NO₃]:

$$\text{[NO}_3\text{]} \approx \frac{k_{N_2O_5}[N_2O_5] + k_{NO_3+O_3}[NO_3][O_3]}{k_{NO_3+NO_3}[NO_2] + k_{NO_3+NO_3}[NO]}$$

where $k_{N_2O_5}$ is the unimolecular thermal decomposition rate of N₂O₅.

HO₂ was moderately correlated to O₃ at night for the both seasons. $r(\text{HO}_2−\text{O}_3) = 0.68$ in the winter observation and 0.67 in summer. The correlation with NO₃ was found to be less, $r(\text{HO}_2−\text{NO}_3) = 0.27$ in winter. However, if a filter of NO < 1 ppbv is applied, as high NO can suppress HO₂, O₃, and NO₃, then $r(\text{HO}_2−\text{O}_3) = 0.59$ in winter and $r(\text{HO}_2−\text{NO}_3) = 0.67$ in winter.

Strong correlations between HO₂ and O₃/NO₃ were also observed on individual nights. For instance, as seen in Figure 4, during 18:30−01:30 on the night of December 1 to 2, 2014, most of the time NO < 1 ppbv, HO₂, O₃ and NO₃ all showed similar temporal patterns, $r(\text{HO}_2−\text{O}_3) = 0.89$, and $r(\text{HO}_2−\text{NO}_3) = 0.86$. Also, as seen in Figure 5, during 20:00−05:00 on the night of June 30 to July 1, 2015, NO was mostly <1 ppbv and $r(\text{HO}_2−\text{O}_3) = 0.90$. These strong correlations suggest that O₃ and NO₃ were driving the production of HO₂ on these nights.

**Comparison of Observation-Derived and Model-Predicted HO₂.**

Figure 6 compares the derived HO₂ with model predicted HO₂ (Run_1 and Run_2). (See Figures S7 and S8 for day-to-day variations of derived/model predicted HO₂ and other species.) As the model was not constrained by measured VOC, H₂O₂, HONO, and j values, discrepancies between model simulated and derived HO₂ are expected. Nevertheless, Run_1 still captures the features of HO₂. The average model-to-observed ratio (M/O) of Run_1 is 1.27 ($r = 0.54$) for winter and 0.70 ($r = 0.80$) for summer. For the summer observations, Run_1 tends to underestimate midday (e.g., June 15−18, 2015) and nighttime HO₂, which suggests that more sources of HO₂ may exist than are included in the model.
With the constraint of HO$_2$NO$_2$, Run_2 predicted HO$_2$ with average M/O = 1.13 ($r = 0.77$) for winter and average M/O = 0.90 ($r = 0.97$) for summer. Run_2 slightly improved M/O for the winter season and improved M/O for the summer season. Both model runs predicted peak midday HO$_2$ levels on several winter days, such as December 21–24, that were significantly higher than the observations. One likely explanation for this is the overprediction of HONO levels by the REAM model. HONO has heterogeneous sources, which are difficult to parametrize. The photolysis of HONO becomes a more important source of HO$_x$ in winter, as other sources such as the photolysis of ozone contribute less. As a result, predicted HONO has a larger impact on HO$_2$ prediction in winter. This also suggests the importance of better observational constraints in future studies. Nevertheless, considering the few observational constraints available, both model runs are in reasonable agreement with the derived HO$_2$.

**Future Studies.** Our study shows the feasibility of deriving HO$_2$ from HO$_2$NO$_2$ measurements in warm environments. Future work should focus on: (1) model calculation of HO$_2$ with a better constrained observational data set and (2) inter-comparison with HO$_2$ measurement techniques such as laser-induced fluorescence (LIF). In addition, a direct CIMS HO$_2$ measurement technique using Br$^-$ as the reagent ion has recently been developed. We plan on further comparisons with this method as well.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05169.

Synthesis of HO$_2$NO$_2$ ion chemistry of HO$_2$NO$_2$ with $\Gamma^-(\text{H}_2\text{O})_n$; calibration of HO$_2$NO$_2$ assessment of the
CIMS NO$_3^-$ channel; chemistry scheme for the time-dependent and steady-state models; time series of observed HO$_2$NO$_2$, temperature, NO, NO$_2$, solar radiation, derived and model-predicted HO$_2$ (PDF)

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**Notes**
The authors declare no competing financial interest.

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