Chapter 3

Products of peroxy radical reactions from the NO$_3$-initiated oxidation of isoprene$^2$

Abstract

Peroxy radical reactions (RO₂-RO₂) in the NO₃-initiated oxidation of isoprene are studied with both gas chromatography and a chemical ionization mass spectrometry technique that allows for more specific speciation of products than in previous studies of this system. We find high nitrate yields (> ~ 80%), consistent with other studies. We further see evidence of significant OH formation in this system, which we propose comes from RO₂-HO₂ reactions with a yield of 44-64%. The branching ratio of the radical propagating, carbonyl and alcohol forming, and dimer forming channels of the RO₂-RO₂ reaction are found to be 18-38%, 59-75%, and 7-10%, respectively. HO₂ formation in this system is lower than has been previously assumed. Reaction of RO₂ with isoprene is suggested as a possible route to the formation of several isoprene dimer compounds (ROOR). The nitrooxy, allylic, and C₅ peroxy radicals present in this system exhibit different behavior than the limited suite of peroxy radicals that have been studied to date.

3.1 Introduction

The global emissions of isoprene (440-660 Tg yr⁻¹ (Guenther et al., 2006)) are larger than those of any other non-methane hydrocarbon. Because of its high abundance and reactivity towards atmospheric radicals, isoprene plays a major role in the oxidative chemistry of the troposphere (e.g., Chameides et al., 1988; Williams et al., 1997; Roberts et al., 1998; Horowitz et al., 1998; Paulot et al., 2009a) and is an important precursor for secondary organic aerosol (SOA) (e.g., Claeys et al., 2004; Kroll et al., 2005, 2006; Surratt et al., 2006, 2010; Carlton et al., 2009).
Nitrate radicals (NO$_3$), which form primarily from the reaction of NO$_2$ and O$_3$, are likely the dominant oxidant of isoprene at night when photochemical production of hydroxyl radicals (OH) ceases. Although nighttime isoprene emissions are negligible (Sharkey et al., 1996; Harley et al., 2004), isoprene emitted late in the day, as OH concentrations drop, remains in the nighttime atmosphere (e.g., Starn et al., 1998; Stroud et al., 2002; Warneke et al., 2004; Steinbacher et al., 2005; Brown et al., 2009). The rate constant for the isoprene reaction with NO$_3$ is $\sim$ 50,000 times higher than that with O$_3$, the other major nighttime oxidant (Atkinson, 1997). Assuming an NO$_3$ mixing ratio of 10 ppt and an O$_3$ mixing ratio of 40 ppb, oxidation of isoprene by NO$_3$ will proceed more than an order of magnitude faster than by O$_3$. Mixing ratios of NO$_3$ in the nighttime continental boundary layer generally exceed 10 ppt, being in the range of 10-100 ppt (Platt and Janssen, 1995; Smith et al., 1995; Heintz et al., 1996; Carslaw et al., 1997), though concentrations on the order of several hundred ppt have been reported (Platt et al., 1981; von Friedeburg et al., 2002; Brown et al., 2006; Penkett et al., 2007).

During the day, NO$_3$ is efficiently destroyed by photolysis and reaction with NO (Wayne et al., 1991), but significant daytime concentrations have been measured under conditions of sufficient O$_x$ ($O_x = O_3 + NO_2$) and low actinic flux. NO$_3$ has been shown to reach concentrations of $\sim$ 1 pptv and be responsible for $\sim$ 10% of total isoprene oxidation in the daytime under clouds or in a forest canopy (Brown et al., 2005; Forkel et al., 2006; Fuentes et al., 2007). In Houston, with large concentrations of both NO$_x$ and O$_3$, NO$_3$ concentrations between 5-30 pptv in the hours before sunset have been measured (Geyer et al., 2003a).
The reaction of isoprene and NO$_3$ can be significant to atmospheric carbon and nitrogen budgets – and subsequently ozone formation – particularly on a regional scale. Globally, it is estimated the isoprene-NO$_3$ reaction is responsible for ~ 6-7% of total isoprene oxidation (Horowitz et al., 2007; Ng et al., 2008) and ~ 15% of oxidized nitrogen consumption (Brown et al., 2009). Field studies in the northeastern United States, which has a mix of NO$_x$ and isoprene sources, find that ~ 22% of isoprene oxidation in the residual daytime boundary layer, ~ 40% of isoprene oxidation in airmasses advected offshore within the marine boundary layer, and ~ 73% of NO$_3$ consumption can be attributed to this reaction (Warneke et al., 2004; Brown et al., 2009). In addition, the isoprene-NO$_3$ reaction is likely an important source of isoprene nitrates, which are significant NO$_x$-reservoir compounds affecting regional ozone formation (von Kuhlmann et al., 2004; Fiore et al., 2005; Horowitz et al., 1998, 2007).

The oxidation mechanism and products of the isoprene-NO$_3$ reaction have been the subject of numerous studies (Jay and Stieglitz, 1989; Barnes et al., 1990; Skov et al., 1992; Kwok et al., 1996; Berndt and Boge, 1997; Suh et al., 2001; Zhang et al., 2002; Fan et al., 2004; Ng et al., 2008, Perring et al., 2009; Rollins et al., 2009). The initial step in the reaction is addition to one of the double bonds, followed by addition of O$_2$ to make a nitrooxyalkyl peroxy radical (RO$_2$). The RO$_2$ radicals then react with NO$_2$ (to make short-lived peroxynitrate compounds), NO$_3$, HO$_2$, NO$_2$, or another RO$_2$, leading to a variety of 1$^{st}$ generation products (Figure 3.1). We neglect RO$_2$ reactions with NO, as NO concentrations are generally very low at night (and low in the chamber due to the rapid reaction NO$_3$ + NO $\rightarrow$ 2NO$_2$).
In a previous study (Ng et al., 2008), we show that the SOA yield from the reaction of isoprene with NO₃ radicals is higher when experimental conditions favor RO₂-RO₂ reactions over RO₂-NO₃ reactions. This phenomenon is explained in part by the formation of low vapor pressure ROOR dimers from RO₂-RO₂ reactions, a product channel that had previously been considered insignificant. In light of the potential importance of RO₂-RO₂ reactions, we present here a detailed product study of the RO₂-RO₂ reactions from the NO₃-initiated oxidation of isoprene.

3.2 Experimental

This work presents a detailed product study of the “excess isoprene” experiment discussed in Ng et al. (2008). The thermal decomposition of N₂O₅ serves as the source of NO₃ radicals. N₂O₅ is synthesized by mixing streams of nitric oxide (≥99.5%, Matheson Tri Gas) and ozone in a glass bulb, which forms N₂O₅ via the following reactions (Davidson et al., 1978):

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{N}_2\text{O}_5 \\
\text{NO}_2 + \text{NO}_3 & \leftrightarrow \text{N}_2\text{O}_5
\end{align*}
\]

Ozone is generated by flowing oxygen through an ozonizer (OREC V10-0); its mixing ratio is found to be ~2% as measured by a UV/VIS spectrometer (Hewlett-Packard 8453). The flow rate of nitric oxide into the glass bulb is adjusted until the brown color in the bulb disappears. The N₂O₅ is trapped for 2 hours in an acetone-dry ice bath at
approximately -80°C, cold enough to trap N$_2$O$_5$ but not O$_3$, as condensed O$_3$ can explode upon warming. After synthesis, the bulb containing the N$_2$O$_5$, a white solid, is stored in a liquid nitrogen dewar.

Experiments are performed in the Caltech dual 28 m$^3$ Teflon chambers (Cocker et al., 2001; Keywood et al., 2004). O$_3$ (Horiba, APOA 360), NO and NO$_2$ (Horiba, APNA 360), and temperature and relative humidity (RH) (Vaisala, HMP 233) are continuously monitored. The chambers are maintained in the dark at room temperature (~ 20-21°C) under dry conditions (RH<10%). Prior to an experiment, the chambers are continuously flushed for at least 24 hours. The N$_2$O$_5$ is removed from the liquid nitrogen and vaporizes into an evacuated 500 ml glass bulb, the pressure in which is continuously monitored by a capacitance manometer (MKS). Once a sufficient pressure of N$_2$O$_5$ has been achieved in the bulb, the bulb’s contents are flushed into the chamber with a 5L min$^{-1}$ air stream. After waiting ~ 1 hour to allow the N$_2$O$_5$ to become well-mixed in the chamber, a known volume of isoprene (Aldrich, 99%) is injected into a glass bulb and flushed into the chamber with a 5 L min$^{-1}$ air stream, which initiates the reaction.

The amount of isoprene added corresponds to a mixing ratio in the chamber of ~800 ppb, while the N$_2$O$_5$ concentration is ~ 150 ppb. The large excess of hydrocarbon with respect to N$_2$O$_5$ maximizes peroxy radical self- and cross- reactions and minimizes NO$_3$ reactions with both peroxy radicals and stable first generation products (i.e., species other than isoprene). This excess is magnified by adding the hydrocarbon after the N$_2$O$_5$ is well-mixed in the chamber: within the injected plume, hydrocarbon concentrations will be much greater than 800 ppb.
An Agilent 6890N gas chromatograph with flame ionization detector (GC-FID) measures isoprene and the oxidation products methyl vinyl ketone, methacrolein, and 3-methylfuran. The GC-FID, equipped with a bonded polystyrene-divinylbenzene based column (HP-Plot Q, 15 m x 0.53 mm, 40 μm thickness, J&W Scientific), is held at 60°C for 0.5 minutes, then ramped at 35°C min⁻¹ to 200°C, after which the temperature is held steady for 3.5 min.

The other gas-phase products reported here are monitored with a custom-modified Varian 1200 chemical ionization mass spectrometer (CIMS) (Ng et al., 2007; Paulot et al., 2009b), which selectively clusters CF₃O⁻ with compounds having a high fluoride affinity (e.g., acids, peroxides, and multifunctional nitrooxy- and hydroxy- compounds), forming ions detected at m/z MW + 85 (Crounse et al., 2006). The quadrupole mass filter scans from m/z 50 to m/z 425, with a dwell time of 0.5 s per mass. The CIMS enables more specific speciation of organic nitrates than other techniques that have been employed to study the isoprene-NO₃ system: Fourier transform infrared (FT-IR) (Barnes et al., 1990; Skov et al., 1992; Berndt and Böge, 1997), thermal dissociation-laser induced fluorescence (TD-LIF) (Perring et al., 2009; Rollins et al., 2009), and proton transfer reaction mass spectrometry (PTR-MS) (Kwok et al., 1996; Perring et al., 2009; Rollins et al., 2009). FT-IR and TD-LIF measure the amount of a certain functionality (e.g., nitrates), but in complex mixtures it is difficult to distinguish compounds sharing a common functional group (e.g., nitrooxycarbonyls and hydroxynitrates). The PTR-MS allows for identification of individual compounds, but does so with significant fragmentation and water clustering, which leads to complex mass spectra and an increased probability of mass analog confusion. In contrast, the CIMS does not lead to
significant fragmentation or water clustering under these experimental conditions, which simplifies interpretation of mass spectra.

Because authentic standards for the major products are unavailable, we estimate the sensitivity of the CIMS to these products using the empirical method described by Su and Chesnavich (1982) and Garden et al. (2009). This method estimates the collision rate of CF$_3$O$^-$ and an analyte based on the analyte’s dipole moment and polarizability, which are calculated with the Spartan06 quantum package based on molecular structures optimized with the B3LYP/6-31G(d) method. While this theoretical approach compares favorably with experimentally derived sensitivities for many compounds (Garden et al., 2009; Paulot et al., 2009ab), it represents the largest source of uncertainty (+/- 25%) for the CIMS data.

### 3.3 Results and Discussion

Because the isoprene-NO$_3$ reaction is rapid, the low time resolution of our measurements (one measurement every ~ 12 minutes for the GC-FID and ~ 8 minutes for the CIMS) allows us to determine only the final product distribution (Table 3.1). The yields in Table 3.1 vary from those reported in Ng et al. (2008) due to refinements in the estimated CIMS sensitivity, but these changes do not significantly alter the conclusions drawn in our earlier work. Due to the computational intensity of estimating the dipole and polarizability of large molecules, we have assumed that the CIMS has the same sensitivity to all of the C$_9$ and C$_{10}$ compounds.

The only species for which we see time dependent signals are the ROOR dimer compounds (CIMS m/z 332, 377, and 393), which reach peak signals 1-3 h after the
reaction is initiated, followed by a slow decay. This slow rise and decay is likely a result of the fact that these compounds have low vapor pressures and thus interact significantly with instrument tubing or condense into secondary organic aerosol (~ 10 µg/m³ of SOA forms rapidly in this experiment). For these compounds, the reported values are the peak mixing ratios seen during the experiment.

3.3.1 Nitrate yield

C5 nitrooxycarbonyls, hydroxynitrates, and nitrooxyhydroperoxides, the major products of the isoprene-NO₃ reaction, are detected by the CIMS at m/z 230, 232, and 248, respectively. In addition, we see compounds appearing at m/z 216, 246, and 264, which are consistent with products resulting from the isomerization of the alkoxy (RO) radical originating from the δ-nitrooxyperoxy radical from (1,4) or (4,1) addition (the notation (x,y) indicates NO₃ addition to the x carbon and subsequent N₂O₅ addition to the y carbon) (Figure 3.2). Previous studies have shown that (1,4) additions are dominant in this system (Skov et al., 1992; Berndt and Böge, 1997; Suh et al., 2001). Isomerization also leads to a product at m/z 248, the same mass as the nitrooxyhydroperoxide. To estimate the ratio of these two isobaric species, we assume that the alkoxy radical yield from RO₂-RO₂ reactions is identical for both the non-isomerized and isomerized nitrooxyperoxy radical (the branching ratio of RO₂-RO₂ is discussed further in section 3.3.4). Finally, we see dimer ROOR products at m/z 332, 377, and 393 (further discussed in section 3.3.6). Summing the concentrations of these nitrates (and noting that the ROOR compounds at m/z 377 and 393 sequester two nitrates), we find a total organic nitrate concentration of ~ 100 ppb.
We express the nitrate yield with respect to both reacted nitrogen or carbon. For the nitrogen-based yield, we divide the nitrate concentration by the amount of NO$_3$ radical consumed, which is equivalent to the loss of N$_2$O$_5$ during this reaction. Lacking a quantitative measurement of N$_2$O$_5$, we use the change in NO$_2$ concentration after the addition of isoprene (~125 ppb) as a proxy. Each conversion of N$_2$O$_5$ to NO$_3$ releases NO$_2$, but the total change in NO$_2$ may be an overestimate of total NO$_3$ reacted because NO$_2$ can also be released in the formation of methyl vinyl ketone (MVK), methacrolein (MACR), 3-methylfuran (3-MF), and the C$_5$ hydroxycarbonyl (Figure 3.3), though in section 3.3.2 we discuss alternative formation pathways for these compounds. Subtracting these additional NO$_2$ sources to get a lower limit for NO$_3$ consumption leads to an NO$_3$ consumption range of 109–125 ppb and a corresponding nitrate yield of ~80–90%.

This high yield suggests that the NO$_3$ radical reacts with isoprene predominantly, if not exclusively, via addition to a double bond. The CIMS does not see a detectable rise in HNO$_3$, indicating that hydrogen abstraction is not a significant pathway for this reaction (our sensitivity to HNO$_3$, however, is hampered by a large background – probably from impurities in the N$_2$O$_5$ or reaction of N$_2$O$_5$ with trace water). Assuming most of the 16.1 ppb of MVK, MACR, 3-MF, and the C$_5$ hydroxycarbonyl originates from nitrooxyperoxy radicals, we account for ~100% of the NO$_3$ reacted. Additionally, although our experimental design seeks to minimize reactions of NO$_3$ with species other than isoprene, our yield estimate should be considered a lower limit because there are also possible (likely small) losses of NO$_3$ from reaction with other radicals or first-generation products, or heterogeneously to the chamber walls or SOA.
The measured nitrate yield with respect to NO₃ is consistent with the substantial yields determined by other studies: ~95% (under NO-free conditions) (Berndt and Böge, 1997), 57 ± 11% (Perring et al., 2009), and 70 ± 8% (Rollins et al., 2009). Variance in yields with different experimental methods is not surprising because they depend on the relative concentrations of different radicals, as well as physical loss and mixing processes, which are unique to each work. Furthermore, the final product distribution is a strong function of the distribution of peroxy radical isomers: $\delta$-nitrooxyperoxy radicals tend to maintain their nitrate functionality (with the exception of the possible formation of hydroxycarbonyl or 3-MF), while $\beta$-nitrooxyperoxy radicals, if they become nitrooxyalkoxy radicals, are likely to lose the nitrate to form MVK or MACR (Vereecken and Peeters, 2009). Berndt and Böge (1997) and Peeters et al. (2009) suggest that peroxy radical isomers formed from isoprene oxidation are continuously interconverting, so the distribution of isomers that defines the final product distribution may also be sensitive to specific experimental conditions.

To calculate the nitrate yield with respect to carbon, we divide the concentration of nitrates by the amount of isoprene reacted. Because a portion of the isoprene reacts immediately upon introduction into the chamber, the exact starting isoprene concentration is uncertain. Therefore, we assume that each of the products listed in Table 3.1 comes from one isoprene molecule, with the exception of the ROOR compounds (which comprise two isoprene molecules) and hydrogen peroxide (which comprises zero). This leads to an estimate of ~128 ppb of isoprene reacted, and a nitrate yield of ~80%. As with the nitrogen-based yield, this result too is consistent with other studies: ~
80% (Barnes et al., 1990), ~ 90% (Berndt and Böge, 1997), 70 ± 8% (Rollins et al., 2009), and 65 ± 12% (Perring et al., 2009).

That our CIMS-derived estimate of isoprene consumption is higher than our independent estimate of NO₃ consumption (by up to 20% depending on the sources of NO₂) suggests that our reported nitrate yields may be overestimated slightly, and should therefore be considered upper limits. The discrepancy between our estimates of isoprene and NO₃ consumption is likely attributable to the lack of an empirical calibration for the CIMS.

### 3.3.2 Hydroxyl radical (OH) formation

The CIMS detects the formation of products at m/z 185, 187, 203, and 201, which are indicative of compounds at MW 100, 102, 118, and 116, respectively. These compounds are analogous to those depicted in Figures 3.1 and 3.2, only with oxidation initiated by the hydroxyl radical (OH) instead of NO₃ (Surratt et al., 2010). Perring et al. (2009) report PTR-MS signals at m/z 101, 103, 119, and 117, which could be the protonated clusters of these compounds, though they attribute the latter three m/z to water clusters of other major product ions. Under the dry conditions of our experiment, however, we do not typically observe water clusters with, or significant fragmentation of, the product ions, so we are confident that the signals on the CIMS in fact represent hydroxy compounds. OH formation may also contribute to some or all of the MVK and MACR produced in our system, though it is likely most of the 3-MF comes from isoprene-NO₃ reactions because its yield in the isoprene-OH system is low (Ruppert and Becker, 2000; Paulot et al., 2009b).
We consider the following five possible routes to OH formation in our system:

- reactions of (i) O$_3$ and isoprene (Neeb and Moortgat, 1999),
- (ii) HO$_2$ and O$_3$ (Sinha et al., 1987),
- (iii) HO$_2$ and NO (Seeley et al., 1996),
- (iv) HO$_2$ and NO$_3$ (Mellouki et al., 1993),
- and (v) RO$_2$ and HO$_2$ (Hasson et al., 2004, 2005; Jenkin et al., 2007, 2008, 2010; Crowley and Dillon, 2008).

Hypotheses (i) and (ii) are unlikely to occur. Not only is no O$_3$ detected during the experiment (limit of detection ~ 2 ppb), but there is no evidence in the CIMS data of significant organic acid or peroxide formation, which would result from the reaction of O$_3$ with isoprene (Hasson et al., 2001; Orzechowska and Paulson, 2005). Furthermore, for hypothesis (ii) to be feasible, HO$_2$-O$_3$ reactions ($k = 1.9 \times 10^{-15}$ cm$^3$ molec$^{-1}$ s$^{-1}$, Sander et al., 2006) must be significantly faster than HO$_2$-HO$_2$ reactions ($k = 2.48 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ at 1 atm and 298K, Sander et al., 2006), which produce ppb levels of H$_2$O$_2$ in the system (Table 3.1). This would require O$_3$ to be more than three orders of magnitude more abundant than HO$_2$, i.e., at ppm levels, that cannot come from trace contamination of the chamber.

To examine the remaining hypotheses, we create a box model incorporating the major reactions in the system for developing a qualitative understanding of which processes may be important for the final product yield. Table 3.2 lists the parameters of this box model; for rate constants that have not been experimentally determined, we use estimates based on the literature, but caution that the actual rate constants may differ significantly. Initial conditions reflect the nominal concentration of reagents in the chamber: [isoprene] = 800 ppb, [N$_2$O$_5$] = 125 ppb, and [NO$_2$] = 50 ppb (the NO$_2$ likely results from decomposition of N$_2$O$_5$ prior to isoprene injection). In reality, though, the isoprene concentration is higher than 800 ppb during the reaction because of our injection...
method. As discussed later, there are major uncertainties in the HO₂ sources and magnitudes, so for the purposes of assessing possible OH sources, we assume as an upper limit that the formation rate of HO₂ is the same as that of RO₂; the final concentration of peroxides (i.e., [ROOH] + 2 x [H₂O₂]) is ~ 23 ppb, much less than the ~ 109-128 ppb of RO₂ that is formed (section 3.3.1), suggesting that the formation of HO₂ is significantly less than that of RO₂.

The box model shows that the NO levels in the chamber are too low to sustain substantial OH formation via hypothesis (iii). The NOₓ monitor measures < 1 ppb of NO throughout our experiment, and any NO that may exist prior to the experiment (or as a trace impurity in the N₂O₅) reacts quickly with NO₃ after N₂O₅ injection; the NO lifetime is ~ 1 s with the N₂O₅ loading. Although NO may be generated as a minor channel of the NO₂ + NO₃ reaction, the rapid reaction of NO and NO₃ limits the steady state concentration of NO to < ~ 4 ppt, so HO₂ + NO is unlikely to contribute to significantly to the 12-21 ppb of OH that is formed in the system. In the simulation, NO at its maximum concentration cannot compete with other radicals (RO₂, HO₂, NO₃, and NO₂) reacting with HO₂.

The box model also suggests that hypothesis (iv) is not feasible because of the substantial difference in the rates of the NO₃-isoprene and NO₃-HO₂ reactions, both of which are well established experimentally. Under the base conditions of the box model in Table 3.2, which significantly overestimates the prevalence of HO₂ and underestimates the concentration of isoprene, less than 1% of the NO₃ reacts with HO₂, while 94% reacts with isoprene and the rest with RO₂. Therefore, while there is significant uncertainty with the RO₂-HO₂, RO₂-RO₂, and RO₂-NO₃ rate constants, the frequency of the NO₃-
HO₂ reaction predicted by the model is quite insensitive to these rates. Even if we favor NO₃-HO₂ reactions by reducing the RO₂-HO₂ and RO₂-NO₃ rate constants by a factor of 100, we obtain ~ 5 ppb of OH formation; in contrast, lowering the isoprene-NO₃ rate constant leads to significantly more production of OH via NO₃-HO₂ (Figure 3.4). These simulations reflect the observations of Atkinson et al. (1988) during hydrocarbon-NO₃ kinetics studies that there is apparent OH formation when slower reacting hydrocarbons are studied. The reaction of isoprene with NO₃ is sufficiently fast under our experimental conditions, however, that such behavior should not occur.

We therefore conclude that formation of OH radicals most likely results from the reaction of RO₂ and HO₂ radicals. Quantifying the branching ratio of the RO₂-HO₂ reaction, however, is not trivial. There are four documented pathways for the RO₂-HO₂ reaction:

\[
RO₂ + HO₂ \rightarrow ROOH \quad (3.1a)
\]

\[
\rightarrow ROH + O_3 \quad (3.1b)
\]

\[
\rightarrow RO + OH + O_2 \quad (3.1c)
\]

\[
\rightarrow R'CHO + H_2O + O_2 \quad (3.1d)
\]

Channel (3.1a) can be quantified with CIMS measurements of peroxides. We neglect channel (3.1b), first because there is no evidence for ozone formation, and also because this channel is believed to proceed via a hydrotetroxide intermediate that yields O₃ only if RO₂ is an acylperoxy radical (RC(O)OO) (Hasson et al., 2005). To quantify channel (3.1c), we can use the sum of OH products as a tracer, but MVK, MACR, and the C₅
hydroxycarbonyl can come from either OH or NO₃, which leads to uncertainty in this quantity. Similarly, the nitrooxycarbonyl can result directly from reaction (3.1d), indirectly from the RO formed in reaction (3.1c), or RO₂-RO₂. Because multiple pathways share common products, and lacking more knowledge about these individual pathways, we cannot unambiguously constrain the RO₂-HO₂ branching ratios with the available data.

Recognizing the uncertainties, we estimate the OH yield from RO₂-HO₂ but emphasize that our assumptions and results must be verified by further studies. We assume channel (3.1d) is negligible, as well as OH from RO₂-HO₂ reactions where the RO₂ originates from isoprene + OH (Paulot et al., 2009a), and ignore any RO₂-HO₂ reactions from the isomerized nitrooxy RO₂. We constrain the range of OH formation (channel 3.1c) to 9-20.5 ppb, with the upper limit being all the hydroxy products plus MVK and MACR, and the lower limit being the upper limit minus MVK, MACR, and the hydroxycarbonyl. We estimate channel (3.1a) by the concentration of the nitrooxyhydoperoxide at m/z 248, so obtain a range for (3.1c)/(3.1a)+(3.1c) of between 9/20.5 and 20.5/32.1, or 44-64%.

This high yield contrasts with the existing, albeit limited, literature on RO₂-HO₂ reaction channels. Thus far, significant OH yields (15-67%) have been found only for acylperoxy, methoxymethylperoxy (CH₃OCH₂O₂), and β-carbonylperoxy (RC(O)CH₂OO) radicals, while alkylperoxy and hydroxyalkylperoxy radicals have exhibited minimal yields (Hasson et al., 2004; Jenkin et al., 2007, 2008, 2010; Crowley and Dillon, 2008). Perhaps the presence of nitrooxy group or the additional double bond present in the RO₂ radicals in this study make the radical propagating channel more
favored than for the compounds previously studied. We also recognize that some entirely
different mechanism unknown to us is responsible for the formation of OH.

3.3.3 RO₂-RO₂ branching ratio

Using the data and assumptions described above, we derive a master equation for
RO₂-RO₂ reactions. An estimated 55 ppb of RO₂ passes through the channel forming
R’CHO and ROH, and 5 ppb becomes ROOR (Table 3.1). The nitrooxycarbonyl yield in
excess of the hydroxynitrate yield is assumed to arise from RO-forming channels of
either RO₂-HO₂ or RO₂-RO₂. Total RO formation is estimated to be 33.5-45 ppb, as
calculated from the sum of the isomerized nitrates, 3-MF, and the excess hydroxynitrate
(the upper limit includes MVK, MACR, and hydroxycarbonyl from isoprene-NO₃
reactions). Of this, 9-20.5 ppb comes from RO₂-HO₂, depending on the true provenance
of MVK, MACR, and the hydroxycarbonyl.

Each pathway to RO (e.g., RO₂-RO₂, RO₂-HO₂, RO₂-NO₃) has a different heat of
reaction, which may affect the RO fate (Bernt and Böge, 1997; Atkinson, 2007). Lacking
any specific knowledge about the dependence of RO fate on the reaction enthalpy,
however, we assume that every RO behaves the same, regardless of source. We also
neglect possible RO₂-RO₂ reactions involving the hydroxyperoxy RO₂.

Taking into account the uncertainties involving RO, we get between 13.5 (i.e.,
33.5-20.5) and 36 (i.e., 45-9) ppb of RO coming from RO₂-RO₂, and between 73.5 and 96
ppb (i.e., between 55 + 5 + 13.5 and 55 + 5 + 36) of RO₂ undergoing RO₂-RO₂ reactions.
From this, we derive ranges for the RO₂-RO₂ branching ratio:
RO₂ + RO₂ → 2RO + O₂  \hfill (3.2a)

→ R’CHO + ROH + O₂  \hfill (3.2b)

→ ROOR + O₂  \hfill (3.2c)

where the branching ratios of (3.2a), (3.2b), and (3.2c) are 18-38%, 59-75%, and 7-10%, respectively.

To our knowledge, this is the first study analyzing the branching ratio of RO₂-RO₂ reactions of isoprene nitrooxyperoxy radicals. For most peroxy radicals that have been studied, channel (3.2a) is typically more than 50%, while channel (3.2c) is generally considered negligible (Atkinson, 1997, and references therein). Ziemann (2002) proposes ROOR formation as the source of diacyl peroxides found in SOA from cycloalkene ozonolysis. Preliminary work in our laboratory has also detected ROOR compounds as products of RO₂-RO₂ reactions from the NO₃-initiated oxidation of 1,3-butadiene, as well as the OH-initiated oxidation of 1,3-butadiene and isoprene. There remain many uncertainties regarding the mechanism of RO₂-RO₂ reactions (Dibble, 2008), so it is difficult to assess whether reported ROOR formation (or lack thereof) is a result of the particular radicals studied or the analytical techniques employed to study their reaction. It is possible that the larger peroxy radicals we have studied are more likely to form ROOR than smaller radicals because they have more vibrational modes with which to distribute collisional energy and prevent breaking apart upon collision with another RO₂ radical. This may be analogous to trends in organic nitrate (RONO₂) yields from RO₂-NO reactions, which tend to increase with increasing RO₂ size (O’Brien et al., 1998; Arey et al., 2001; Matsunaga and Ziemann, 2009).
3.3.4 RO radical fate and \( \text{HO}_2 \) production

The fate of the alkoxy radical is important both for understanding the chamber studies and in nighttime chemistry as it leads to the production of \( \text{HO}_2 \). From the amount of excess hydroxycarbonyl formed, we estimate that 18 ppb of \( \text{HO}_2 \) forms from \( \text{O}_2 \) abstraction of RO (33.5-45 ppb; Section 3.3.3), or 40-54\% of RO. This assumes that \( \text{O}_2 \) abstraction from RO is the sole source of excess nitrooxycarbonyl, and that direct formation from \( \text{RO}_2\text{-HO}_2 \) reactions (equation 3.1d) is negligible. This \( \text{HO}_2 \) estimate is somewhat lower than the total sum of \( \text{HO}_2 \) derived from peroxide measurements in our system (23 ppb, section 3.3.2). Additional \( \text{HO}_2 \) comes from \( \text{O}_2 \) abstraction from minor alkoxy radicals (the isomerized nitrooxyalkoxy and hydroxyalkoxy radicals), but it is not trivial to attempt an \( \text{HO}_2 \) balance because of the uncertainties in both the CIMS calibration and the sources and sinks of \( \text{HO}_2 \). \( \text{HO}_2 \) can result from the conversion of the nitrooxyalkoxy radical to a nitrooxycarbonyl, or MVK and MACR if the latter are from \( \text{OH} + \text{isoprene} \); sinks of \( \text{HO}_2 \) include peroxide formation, \( \text{RO}_2\text{-HO}_2 \) derived alkoxy radicals that do not undergo abstraction, and from nitrooxycarbonyls formed directly from \( \text{RO}_2\text{-HO}_2 \) via channel (3.4c).

Because the \( \delta \)-nitrooxyalkoxy radical, the dominant alkoxy radical in the system, can isomerize via a 1,5-H shift, the large \( \text{HO}_2 \) yield is somewhat surprising because isomerization reactions are typically faster than abstraction by \( \text{O}_2 \) (Atkinson, 2007). It is possible that the nitrooxy group limits isomerization when the \( \delta \)-nitrooxyalkoxy radical is in a Z conformation. According to the structure-activity relationship of Kwok and Atkinson (1995), H-abstraction from a carbon with an attached nitrooxy group is an order
of magnitude slower than from a carbon with an attached methyl group. The nitrooxy group likely does not prevent isomerization – we see the analogous isomerized nitrates in experiments with 1,3-butadiene, for which the isomerization must abstract a hydrogen from the carbon $\alpha$ to the nitrooxy group – but more study is required to elucidate the effect of the NO$_3$ group on isomerization rate. It is also possible that O$_2$ abstractions are faster for the alkoxy radicals in this system.

While our HO$_2$ yield is higher than expected based on the alkoxy radical structure, it is lower than the value of 80% of RO$_2$ that has been used in modeling studies (Horowitz et al., 2007; Rollins et al., 2009). Therefore, models may overestimate the impact of isoprene-NO$_3$ reactions on nighttime HO$_x$ chemistry in this respect.

3.3.5 Formation of dimer compounds

In Ng et al. (2008), we report the formation of ROOR dimer compounds at m/z 377 and 393. Further examination of the CIMS data reveals other isoprene dimer compounds. The most abundant of these, with a signal similar in magnitude to that of m/z 393, appears at m/z 332, which indicates a hydroxynitrate ROOR. One possible source for this compound is an RO$_2$-RO$_2$ reaction where one RO$_2$ comes from NO$_3$ and the other from OH. The abundance of OH is much less than that of NO$_3$, however, so it would be surprising if such a reaction would produce almost as much ROOR as the reaction between nitrooxyperoxy radicals. Alternatively, this compound may result from addition of an RO$_2$ radical to isoprene, creating a C$_{10}$ alkyl (and subsequently alkyl peroxy) radical, which undergoes an RO$_2$-RO$_2$ reaction to create the C$_{10}$ hydroxynitrate ROOR (Figure 3.5). This mechanism for creating a C$_{10}$ RO$_2$ radical is analogous to the
formation of bicyclic radicals by aromatic peroxo radicals (Atkinson and Arey, 2007). Small amounts of the corresponding nitrooxycarbonyl and nitrooxyhydroperoxide at m/z 330 and 348, respectively, are seen, as well as a compounds at m/z 316 that can be a C$_9$ compound that results from isomerization of a C$_{10}$ nitrooxyalkoxy radical; isomerization may also lead to a diol at m/z 348, the same mass as the hydroperoxide.

We do not know of any previous work that has examined RO$_2$ addition to alkenes under atmospheric conditions, though it has been reported in both gas-phase combustion (e.g., Osborn and Waddington, 1980; Stark and Waddington, 1995) and liquid-phase studies (e.g., van Sickle et al., 1965ab; Mayo, 1968; Simmons and van Sickle, 1973), producing both epoxides and polymeric peroxy radicals.

### 3.4 Implications

The observed high nitrate yields, in general agreement with previous results, support the modeling results of Horowitz et al. (2007) that isoprene-NO$_3$ reactions, while a minor sink of isoprene, are a substantial source of isoprene nitrates in the atmosphere. The formation and fate of these nitrates, in turn, significantly influences tropospheric NO$_x$ and ozone.

Although we obtain similar nitrate yields relative to both reacted nitrogen and carbon, these two yields are fundamentally different quantities that coincidentally have similar magnitudes. Even in an ideal situation in which NO$_3$ reacts exclusively with isoprene (i.e., no reactions with RO$_2$, HO$_2$, walls, etc.), the nitrogen based yield (i.e., [nitrates]/[NO$_3$ consumed]) is non-unity solely due to loss of the nitrate functionality by the initial isoprene-NO$_3$ adduct (Figure 3.2); in contrast, the carbon-based yield (i.e.,
[nitrates]/[isoprene reacted] or [nitrates]/[total carbon products]) is non-unity from both nitrate losses by the initial adduct and isoprene reactions with OH. For systems with extensive amounts of competing NO$_3$ sinks and/or OH formation, the nitrogen- and carbon-based yields may vary considerably. Thus, when applying experimental yields to atmospheric models, care must be taken to choose the appropriate value, as well as to consider the conditions under which those yields are obtained.

The large yield of products from reaction of OH with isoprene is potentially very important for nighttime chemistry, particularly because we propose that the source of OH is from RO$_2$-HO$_2$ reactions which likely dominate in the ambient environment. Recent field studies suggest that the radical propagating channels of RO$_2$-HO$_2$ reactions must be significant to explain observations (Thornton et al., 2002; Leileveld et al., 2008).

Previous studies of nighttime chemistry have considered only alkene ozonolysis and HO$_2$-NO, HO$_2$-O$_3$, and NO$_3$-HO$_2$ reactions as sources of OH (Bey et al., 1997, 2001ab; Harrison et al., 1998; Faloona et al., 2001; Gölz et al., 2001; Geyer et al., 2003b; Ren et al., 2003; Geyer and Stutz, 2004; Vaughan et al., 2006). While a missing OH source may explain instances where models underestimate field measurements of OH (Faloona et al., 2001; Ren et al., 2003), Geyer et al. (2003b) overpredict measurements by a factor of two without such a source. Clearly, there remain many unresolved issues surrounding the abundance of oxidants in the nighttime atmosphere.

While this study focuses on the first-generation products from the isoprene-NO$_3$ reaction, another nighttime source of OH in the atmosphere would be the further oxidation of the nitrooxyhydroperoxide, which can produce a dinitrooxyepoxide and OH (Paulot et al., 2009a). In another experiment described in detail in Ng et al. (2008), we
first add 179 ppb of isoprene to the chamber followed by three additions of N₂O₅ (~ 120, 50, and 210 ppb). After the first two additions, isoprene is completely consumed, so the third aliquot leads primarily to the formation of second-generation products; some second-generation products may be oxidized by this third addition, but the amount of N₂O₅ added is similar to the concentration of first generation products (which is roughly equal to the starting isoprene concentration), so such tertiary chemistry is likely to be minimal. After this third addition, the nitrooxyhydroperoxide signal drops ~ 8 ppb, while the signal for the dinitrooxyepoxide (at m/z 293) rises ~ 2.5 ppb. This indicates that the epoxide (and OH) yield from the NO₃ oxidation of the nitrooxyhydroperoxide is ~ 30%, compared to ~ 75% for OH oxidation of isoprene hydroxyhydroperoxides (Paulot et al., 2009a), although heterogeneous loss of epoxide to the acidic aerosol is also possible (Surratt et al., 2010). The yield in the NO₃ system is likely lower because the dominant first-generation peroxy radical is from the (1,4) addition of NO₃. Therefore, to form an epoxide the second NO₃ must add to the 2-carbon, creating a secondary alkyl radical, whereas the more favored addition is likely to the 3-carbon creating a more stable tertiary alkyl radical (Figure 3.6). In the OH system, (1,2) and (4,3) additions in the first oxidation step are most common (Paulot et al., 2009b), which means that the epoxide-forming channel involves a second OH addition to the more favored 4- or 1- carbon, respectively.

As demonstrated by Ng et al. (2008), while ROOR compounds are minor products of RO₂-RO₂ reactions, they may be important in the atmosphere because they present a means of significantly increasing the mass of a molecule, thereby reducing its volatility and increasing its potential to form SOA. Currently, field measurements of SOA burdens
often exceed those predicted by models (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006; Simpson et al., 2007), a discrepancy that may be explained by SOA formation pathways, such as ROOR, that are not included in models. In this work, we see evidence of an additional ROOR formation pathway, the RO₂ addition to alkenes, that may be relevant to SOA formation. As SOA itself is a minor product of hydrocarbon oxidation (Donahue et al., 2009), pathways that are negligible in the context of gas-phase oxidation mechanisms may in fact be important if they represent efficient pathways to forming SOA.

The formation of ROOR compounds in the atmosphere, and the importance of RO₂-RO₂ reactions in general, is difficult to predict because of the large uncertainties in the rates of all the relevant competing pathways (RO₂-RO₂, RO₂-NO₃, RO₂-NO, RO₂-HO₂, RO₂-alkene) as well as the large variation in ambient mixing ratios of the relevant species. It is clear, though, that RO₂-RO₂ reactions are most favored when the concentration of hydrocarbon is greater than that of oxidant. For the case of isoprene-NO₃ reactions, this most likely would occur in the early evening, as OH concentrations drop and NO₃ concentrations are still low, though during this time NO concentrations may still be high enough to react with a significant amount of RO₂.

Situations favoring nighttime RO₂-RO₂ (or RO₂-alkene) reactions may be more prevalent for monoterpenes and sesquiterpenes, which, unlike isoprene, may be emitted at night (Sakulyanontvittaya et al., 2008). Many of these compounds have exhibited high SOA yields in laboratory studies, though there are still many uncertainties in the SOA formation mechanism (Griffin et al., 1999; Hallquist et al., 1999; Spittler et al., 2006; Fry et al., 2009). Based on our experience with isoprene, the role of monoterpene and
sesquiterpene RO$_2$-RO$_2$ reactions in nighttime SOA formation is worthy of further study, particularly because the nitrooxy group is electron withdrawing, and presence of electron withdrawing groups has been shown to significantly increase RO$_2$-RO$_2$ reaction rates (Lightfoot et al., 1992). As noted by other investigators (e.g., Brown et al., 2009; Fry et al., 2009), SOA formed from the reaction of biogenic compounds with NO$_3$ – an anthropogenic oxidant – is consistent with the common finding that while SOA is largely composed of biogenic carbon (Bench et al., 2007; Schichtel et al., 2008), its concentrations are correlated with anthropogenic emissions (de Gouw et al., 2005, 2008; Quinn et al., 2006; Sullivan et al., 2006; Weber et al., 2007).

Most of the RO$_2$ formed from isoprene-NO$_3$ reactions are primary radicals, however, whereas a significant amount of the RO$_2$ derived from monoterpenes are likely to be secondary or tertiary. Primary RO$_2$ tend to undergo significantly faster RO$_2$-RO$_2$ reactions than secondary or tertiary RO$_2$ (Lightfoot et al., 1992). Reactivity trends are less certain for RO$_2$-NO, RO$_2$-NO$_3$, and RO$_2$-HO$_2$ reactions, but the variation in the available data is less pronounced than for RO$_2$-RO$_2$ (Lightfoot et al., 1992; Lesclaux, 1997; Wallington et al., 1997; Atkinson et al., 2006; Vaughan et al., 2006). So while monoterpenes and sesquiterpenes are generally more reactive with NO$_3$ than isoprene (i.e., have higher RO$_2$ formation rates) (Atkinson and Arey, 2003), RO$_2$-RO$_2$ reactions for these compounds may be less competitive than for isoprene under the same conditions because of the significantly lower RO$_2$-RO$_2$ rate constants compared to competing reactions.

Although we have gained insights into the isoprene-NO$_3$ system in this work, chamber studies such as those we report here have limitations. There currently exists no
stable precursor of NO₃ suitable for chamber studies, so chemical transformations occur the instant the NO₃ precursor and hydrocarbon meet; for isoprene, the chemistry occurs on a much faster timescale than the mixing. Because of our experimental conditions, we are able only to do an end product analysis of our experiments, and are unable to perform kinetic modeling, which could provide deeper insights into the system. Furthermore, while we can constrain RO₂ reaction pathways in chamber studies of OH oxidation (i.e., RO₂+NO for high NOₓ conditions and RO₂+HO₂ for low NOₓ conditions), this is currently not feasible for NO₃ chamber studies. Also, while the CIMS can isolate oxidation products with greater specificity than other techniques, the lack of commercial or easily synthesizable standards leads to uncertainties in product quantification.

Up to now, most studies relating to hydrocarbon oxidation mechanisms and kinetics have focused on ozone or the OH radical; application of the techniques employed in those studies to NO₃ oxidation kinetics and mechanisms offers promise to significantly advance our understanding of nighttime atmospheric chemistry, but will require overcoming challenges such as reagent synthesis (including isomeric specificity), finding suitable radical precursors, and limiting secondary and competing reactions. Many of our results (e.g., OH yield from RO₂-HO₂, RO yield from RO₂-RO₂, HO₂ formation from RO, ROOR formation, RO₂-HO₂ reaction rates) differ from those suggested by previous work on different – mostly small alkylperoxy, acylperoxy, or hydroxyalkylperoxy – systems. More studies focused on nitrooxy and allylic peroxy radicals, as well as larger peroxy radicals, are warranted.

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</tbody>
</table>

Table 3.1: Products detected by GC-FID and CIMS. Products with small but non-zero signals are noted as < 0.5 ppb.
<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO$_3$ + isoprene $\rightarrow$ RO$_2$ + HO$_2$</td>
<td>6.6E-13</td>
<td>Atkinson, 1997</td>
</tr>
<tr>
<td>2</td>
<td>RO$_2$ + RO$_2$ $\rightarrow$ products</td>
<td>1.0E-13</td>
<td>Atkinson et al., 2006, and references therein</td>
</tr>
<tr>
<td>3</td>
<td>RO$_2$ + NO$_3$ $\rightarrow$ products</td>
<td>3.0E-12</td>
<td>Biggs et al., 1994; Daele et al., 1995; Canosa-Mas et al., 1996; Vaughan et al., 2006</td>
</tr>
<tr>
<td>4</td>
<td>RO$_2$ + HO$_2$ $\rightarrow$ products</td>
<td>2.2E-11</td>
<td>Atkinson et al., 2006, and references therein</td>
</tr>
<tr>
<td>5</td>
<td>NO$_3$ + HO$_2$ $\rightarrow$ OH + NO$_2$ + O$_2$</td>
<td>3.5E-12</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>6</td>
<td>NO$_2$ + NO$_3$ $\rightarrow$ N$_2$O$_5$</td>
<td>6.7E-12</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>7</td>
<td>N$_2$O$_5$ $\rightarrow$ NO$_2$ + NO$_3$</td>
<td>2.2E-01</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>8</td>
<td>HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$</td>
<td>2.5E-12</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>9</td>
<td>HO$_2$ + NO$_2$ $\rightarrow$ HO$_2$NO$_2$</td>
<td>2.8E-12</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>10</td>
<td>HO$_2$NO$_2$ $\rightarrow$ HO$_2$ + NO$_2$</td>
<td>1.7E-01</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>11</td>
<td>NO$_3$ + NO$_2$ $\rightarrow$ NO + NO$_2$ + O$_2$</td>
<td>6.6E-16</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>12</td>
<td>NO$_3$ + NO $\rightarrow$ 2NO$_2$</td>
<td>2.6E-11</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
<tr>
<td>13</td>
<td>HO$_2$ + NO $\rightarrow$ NO$_2$ + OH</td>
<td>8.1E-12</td>
<td>Sander et al., 2006, and references therein</td>
</tr>
</tbody>
</table>

Table 3.2: Reactions considered for assessment of OH sources in isoprene-NO$_3$ system. All rate constant units are cm$^3$ molec$^{-1}$ s$^{-1}$, except $k_7$ and $k_{10}$, which are s$^{-1}$. Rates of reactions involving RO$_2$ are based on an approximation of values found in the literature. HO$_2$ yield in reaction 1 is an upper limit to facilitate model analysis.
Figure 3.1. Generalized reaction mechanism in the isoprene-NO₃ system. Boxed compounds are detected by CIMS instrument at the indicated m/z values.
Figure 3.2. Formation of compounds resulting from the isomerization of alkoxy radicals and seen by CIMS instruments at m/z 216, 246, 248, and 264. This figure assumes initial NO$_3$ attachment to the 1-carbon and formation of an (E)-$\delta$-peroxy radical, but other isomers are possible.
Figure 3.3. Formation mechanism of methyl vinyl ketone (a), methacrolein (b), 3-methylfuran (c), and hydroxycarbonyl (d), leading to release of NO₂. The exact mechanism of 3-methylfuran formation is still unknown (Francisco-Márquez et al., 2005).
Figure 3.4. Box model simulations for OH production in isoprene-NO$_3$ system. Blue: base case described in Table 2; Red: RO$_2$-HO$_2$ and RO$_2$-NO$_3$ rate constants reduced by factor of 10; Green: RO$_2$-HO$_2$ and RO$_2$-NO$_3$ rate constants reduced by factor of 100; Pink: isoprene-NO$_3$ rate constant reduced by factor of 100; Light Blue: isoprene-NO$_3$ rate constant reduced by factor of 100. Initial conditions: 150 ppb N$_2$O$_5$, 800 ppb isoprene, 50 ppb NO$_2$. 
Figure 3.5. Proposed formation mechanisms of products detected by CIMS at m/z 316, 330, 332, and 348. Other isomers are possible.
Figure 3.6. Formation mechanism of dinitrooxyepoxide and hydroxyl radical from oxidation of nitrooxyhydroperoxide.