Chapter 3

Products of peroxy radical reactions from the NO_3-initiated oxidation of isoprene[2]

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[2] Adapted from Kwan, A. J., Chan, A. W. H., Ng, N. L., Kjaergaard, H.G., Seinfeld, J. H., and Wennberg, P. O.: Products of peroxy radical reactions from the NO_3-initiated oxidation of isoprene, in preparation.

Abstract

Peroxy radical reactions (RO_2-RO_2) in the NO_3-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 RO_2-HO_2 reactions with a yield of 44-64%. The branching ratio of the radical propagating, carbonyl and alcohol forming, and dimer forming channels of the RO_2-RO_2 reaction are found to be 18-38%, 59-75%, and 7-10%, respectively. HO_2 formation in this system is lower than has been previously assumed. Reaction of RO_2 with isoprene is suggested as a possible route to the formation of several isoprene dimer compounds (ROOR). The nitrooxy, allylic, and C_5 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 ~ 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 ~ 1 pptv and be responsible for ~ 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 1st 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 NO_3 radicals is higher when experimental conditions favor RO_2-RO_2 reactions over RO_2-NO_3 reactions. This phenomenon is explained in part by the formation of low vapor pressure ROOR dimers from RO_2- RO_2 reactions, a product channel that had previously been considered insignificant. In light of the potential importance of RO_2-RO_2 reactions, we present here a detailed product study of the RO_2-RO_2 reactions from the NO_3-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 N_2O_5 serves as the source of NO_3 radicals. N_2O_5 is synthesized by mixing streams of nitric oxide (≥99.5%, Matheson Tri Gas) and ozone in a glass bulb, which forms N_2O_5 via the following reactions (Davidson et al., 1978):

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2+O_3 \rightarrow NO_3 + N_2O_5$

$NO_2+NO_3 \leftrightarrow N_2O_5$

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 N_2O_5 is trapped for 2 hours in an acetone-dry ice bath at approximately -80°C, cold enough to trap N_2O_5 but not O_3, as condensed O_3 can explode upon warming. After synthesis, the bulb containing the N_2O_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_2O_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_2O_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_2O_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_2O_5 concentration is ~ 150 ppb. The large excess of hydrocarbon with respect to N_2O_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_2O_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 .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 CF_3O^- 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-NO_3 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_3O^- 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 $\mu g/m^3$ 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

C_5 nitrooxycarbonyls, hydroxynitrates, and nitrooxyhydroperoxides, the major products of the isoprene-NO_3 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 NO_3 addition to the x carbon and subsequent N_2O_5 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 RO_2-RO_2 reactions is identical for both the non-isomerized and isomerized nitrooxyperoxy radical (the branching ratio of RO_2-RO_2 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_2O_5 during this reaction. Lacking a quantitative measurement of N_2O_5, we use the change in NO_2 concentration after the addition of isoprene (~ 125 ppb) as a proxy. Each conversion of N_2O_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_2O_5 or reaction of N_2O_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 NO_3 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: δ-nitrooxyperoxy radicals tend to maintain their nitrate functionality (with the exception of the possible formation of hydroxycarbonyl or 3-MF), while β-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 NO_3 consumption (by up to 20% depending on the sources of NO_2) 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 NO_3 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 NO_3 (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-NO_3 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_2O_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_2O_5] = 125 ppb, and [NO_2] = 50 ppb (the NO_2 likely results from decomposition of N_2O_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 HO_2 sources and magnitudes, so for the purposes of assessing possible OH sources, we assume as an upper limit that the formation rate of HO_2 is the same as that of RO_2; the final concentration of peroxides (i.e., [ROOH] + 2 x $[H_2O_2]$) is ~ 23 ppb, much less than the ~ 109-128 ppb of RO_2 that is formed (section 3.3.1), suggesting that the formation of HO_2 is significantly less than that of RO_2.

The box model shows that the NO levels in the chamber are too low to sustain substantial OH formation via hypothesis (iii). The NO_x 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 N_2O_5) reacts quickly with NO_3 after N_2O_5 injection; the NO lifetime is ~ 1 s with the N_2O_5 loading. Although NO may be generated as a minor channel of the $NO_2 + NO_3$ reaction, the rapid reaction of NO and NO_3 limits the steady state concentration of NO to < ~ 4 ppt, so HO_2 + 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 (RO_2, HO_2, NO_3, and NO_2) reacting with HO_2.

The box model also suggests that hypothesis (iv) is not feasible because of the substantial difference in the rates of the NO_3-isoprene and NO_3-HO_2 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 HO_2 and underestimates the concentration of isoprene, less than 1% of the NO_3 reacts with HO_2, while 94% reacts with isoprene and the rest with RO_2. Therefore, while there is significant uncertainty with the RO_2-HO_2, RO_2-RO_2, and RO_2-NO_3 rate constants, the frequency of the NO_3-

HO_2 reaction predicted by the model is quite insensitive to these rates. Even if we favor NO_3-HO_2 reactions by reducing the RO_2-HO_2 and RO_2-NO_3 rate constants by a factor of 100, we obtain ~ 5 ppb of OH formation; in contrast, lowering the isoprene-NO_3 rate constant leads to significantly more production of OH via NO_3-HO_2 (Figure 3.4). These simulations reflect the observations of Atkinson et al. (1988) during hydrocarbon-NO_3 kinetics studies that there is apparent OH formation when slower reacting hydrocarbons are studied. The reaction of isoprene with NO_3 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 RO_2 and HO_2 radicals. Quantifying the branching ratio of the RO_2-HO_2 reaction, however, is not trivial. There there are four documented pathways for the RO_2-HO_2 reaction:

$$RO_2 + HO_2 \rightarrow ROOH \qquad (3.1a)$$

$$\rightarrow ROH + O_3 \qquad (3.1b)$$

$$\rightarrow RO + OH + O_2 \qquad (3.1c)$$

$$\rightarrow R'CHO + H_2O + O_2 \qquad (3.1d)$$

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 O_3 only if RO_2 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 C_5

hydroxycarbonyl can come from either OH or NO_3, 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 RO_2-RO_2. Because multiple pathways share common products, and lacking more knowledge about these individual pathways, we cannot unambiguously constrain the RO_2-HO_2 branching ratios with the available data.

Recognizing the uncertainties, we estimate the OH yield from RO_2-HO_2 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 RO_2-HO_2 reactions where the RO_2 originates from isoprene + OH (Paulot et al., 2009a), and ignore any RO_2-HO_2 reactions from the isomerized nitrooxy RO_2. 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 RO_2-HO_2 reaction channels. Thus far, significant OH yields (15-67%) have been found only for acylperoxy, methoxymethylperoxy ($CH_3OCH_2O_2$), and β-carbonylperoxy ($RC(O)CH_2OO$) 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 RO_2 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 RO_2-RO_2 branching ratio

Using the data and assumptions described above, we derive a master equation for RO_2-RO_2 reactions. An estimated 55 ppb of RO_2 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 RO_2-HO_2 or RO_2-RO_2. 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-NO_3 reactions). Of this, 9-20.5 ppb comes from RO_2-HO_2, depending on the true provenance of MVK, MACR, and the hydroxycarbonyl.

Each pathway to RO (e.g., RO_2-RO_2, RO_2-HO_2, RO_2-NO_3) 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 RO_2-RO_2 reactions involving the hydroxyperoxy RO_2.

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 RO_2-RO_2, and between 73.5 and 96 ppb (i.e., between 55 + 5 + 13.5 and 55 + 5 + 36) of RO_2 undergoing RO_2-RO_2 reactions. From this, we derive ranges for the RO_2-RO_2 branching ratio:

$$RO_2 + RO_2 \rightarrow 2RO + O_2 \qquad (3.2a)$$

$$\rightarrow R'CHO + ROH + O_2 \qquad (3.2b)$$

$$\rightarrow ROOR + O_2 \qquad (3.2c)$$

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 RO_2-RO_2 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 RO_2-RO_2 reactions from the NO_3-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 RO_2-RO_2 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 RO_2 radical. This may be analogous to trends in organic nitrate ($RONO_2$) yields from RO_2-NO reactions, which tend to increase with increasing RO_2 size (O'Brien et al., 1998; Arey et al., 2001; Matsunaga and Ziemann, 2009).

3.3.4 RO radical fate and 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 HO_2. From the amount of excess hydroxycarbonyl formed, we estimate that 18 ppb of HO_2 forms from O_2 abstraction of RO (33.5-45 ppb; Section 3.3.3), or 40-54% of RO. This assumes that O_2 abstraction from RO is the sole source of excess nitrooxycarbonyl, and that direct formation from RO_2-HO_2 reactions (equation 3.1d) is negligible. This HO_2 estimate is somewhat lower than the total sum of HO_2 derived from peroxide measurements in our system (23 ppb, section 3.3.2). Additional HO_2 comes from O_2 abstraction from minor alkoxy radicals (the isomerized nitrooxyalkoxy and hydroxyalkoxy radicals), but it is not trivial to attempt an HO_2 balance because of the uncertainties in both the CIMS calibration and the sources and sinks of HO_2. HO_2 can result from the conversion of the nitrooxyalkoxy radical to a nitrooxycarbonyl, or MVK and MACR if the latter are from OH + isoprene; sinks of HO_2 include peroxide formation, RO_2-HO_2 derived alkoxy radicals that do not undergo abstraction, and from nitrooxycarbonyls formed directly from RO_2-HO_2 via channel (3.4c).

Because the δ-nitrooxyalkoxy radical, the dominant alkoxy radical in the system, can isomerize via a 1,5-H shift, the large HO_2 yield is somewhat surprising because isomerization reactions are typically faster than abstraction by O_2 (Atkinson, 2007). It is possible that the nitrooxy group limits isomerization when the δ-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 α 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 peroxy 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 N_2O_5 (~ 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 N_2O_5 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 NO_3 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 NO_3 system is likely lower because the dominant first-generation peroxy radical is from the (1,4) addition of NO_3. Therefore, to form an epoxide the second NO_3 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 RO_2-RO_2 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 RO_2 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 RO_2-RO_2 reactions in general, is difficult to predict because of the large uncertainties in the rates of all the relevant competing pathways (RO_2-RO_2, RO_2-NO_3, RO_2-NO, RO_2-HO_2, RO_2-alkene) as well as the large variation in ambient mixing ratios of the relevant species. It is clear, though, that RO_2-RO_2 reactions are most favored when the concentration of hydrocarbon is greater than that of oxidant. For the case of isoprene-NO_3 reactions, this most likely would occur in the early evening, as OH concentrations drop and NO_3 concentrations are still low, though during this time NO concentrations may still be high enough to react with a significant amount of RO_2.

Situations favoring nighttime RO_2-RO_2 (or RO_2-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 NO_3 suitable for chamber studies, so chemical transformations occur the instant the NO_3 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 RO_2 reaction pathways in chamber studies of OH oxidation (i.e., RO_2+NO for high NO_x conditions and RO_2+HO_2 for low NO_x conditions), this is currently not feasible for NO_3 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 NO_3 oxidation kinetics and mechanisms offers promise to significantly advance our understanding of nighttime atmospheric chemistry, but will require overcoming challenges such as reagent sythesis (including isomeric specificity), finding suitable radical precursors, and limiting secondary and competing reactions. Many of our results (e.g., OH yield from RO_2-HO_2, RO yield from RO_2-RO_2, HO_2 formation from RO, ROOR formation, RO_2-HO_2 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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Compound	Method	m/z (CIMS)	final concentration (ppb)
C4 compounds			
MACR	GC-FID	--------	3
MVK	GC-FID	--------	6
C4 hydroxy carbonyl	CIMS	171	< 0.5
C5 Nitrates			
C5 nitrooxycarbonyl	CIMS	230	45.7
C5 hydroxynitrate	CIMS	232	27.5
C5 nitrooxy hydroperoxide	CIMS	248	11.6
C5 Isomerized Nitrates			
C5 nitrooxy hydroxy carbonyl	CIMS	246	5.5
C5 nitrooxy diol	CIMS	248	3.0
C5 nitrooxy hydroxy hydroperoxide	CIMS	264	2.1
C4 nitrooxy carbonyl	CIMS	216	0.6
C5 Hydroxy compounds			
C5 hydroxy carbonyl	CIMS	185	2.6
C5 diol	CIMS	187	2.3
C5 hydroxy hydroperoxide	CIMS	203	4.2
C5 Isomerized hydroxy compounds			
C5 dihydroxy carbonyl	CIMS	201	1.5
C5 triol	CIMS	203	1.3
C5 dihydroxy hydroperoxide	CIMS	219	< 0.5
Dimer compounds			
dinitrooxy ROOR	CIMS	377	1.4
isomerized dinitrooxy ROOR	CIMS	393	0.9
nitrooxy carbonyl ROOR	CIMS	330	< 0.5
hydroxy nitrate ROOR	CIMS	332	0.9
nitrooxy hydroperoxide ROOR	CIMS	348	< 0.5
C9 nitrooxy ROOR carbonyl	CIMS	316	< 0.5
Other			
3-MF	GC-FID	--------	4.5
hydroxyacetone	CIMS	159	0.5
hydrogen peroxide	CIMS	119	2.4
glycolaldehyde	CIMS	145	0.9

Table 3.1: Products detected by GC-FID and CIMS. Products with small but non-zero signals are noted as < 0.5 ppb.

No.	Reaction	Rate constant	Source
1	$NO_3 + isoprene \longrightarrow RO_2 + HO_2$	6.6E-13	Atkinson, 1997
2	$RO_2 + RO_2 \longrightarrow products$	1.0E-13	Atkinson et al., 2006, and references therein
3	$RO_2 + NO_3 \longrightarrow products$	3.0E-12	Biggs et al., 1994; Daele et al., 1995; Canosa-Mas et al., 1996; Vaughan et al., 2006
4	$RO_2 + HO_2 \longrightarrow products$	2.2E-11	Atkinson et al., 2006, and references therein
5	$NO_3 + HO_2 \longrightarrow OH + NO_2 + O_2$	3.5E-12	Sander et al., 2006, and references therein
6	$NO_2 + NO_3 \longrightarrow N_2O_5$	6.7E-12	Sander et al., 2006, and references therein
7	$N_2O_5 \longrightarrow NO_2 + NO_3$	2.2E-01	Sander et al., 2006, and references therein
8	$HO_2 + HO_2 \longrightarrow H_2O_2$	2.5E-12	Sander et al., 2006, and references therein
9	$HO_2 + NO_2 \longrightarrow HO_2NO_2$	2.8E-12	Sander et al., 2006, and references therein
10	$HO_2NO_2 \longrightarrow HO_2 + NO_2$	1.7E-01	Sander et al., 2006, and references therein
11	$NO_3 + NO_2 \longrightarrow NO + NO_2 + O_2$	6.6E-16	Sander et al., 2006, and references therein
12	$NO_3 + NO \longrightarrow 2NO_2$	2.6E-11	Sander et al., 2006, and references therein
13	$HO_2 + NO \longrightarrow NO_2 + OH$	8.1E-12	Sander et al., 2006, and references therein

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.

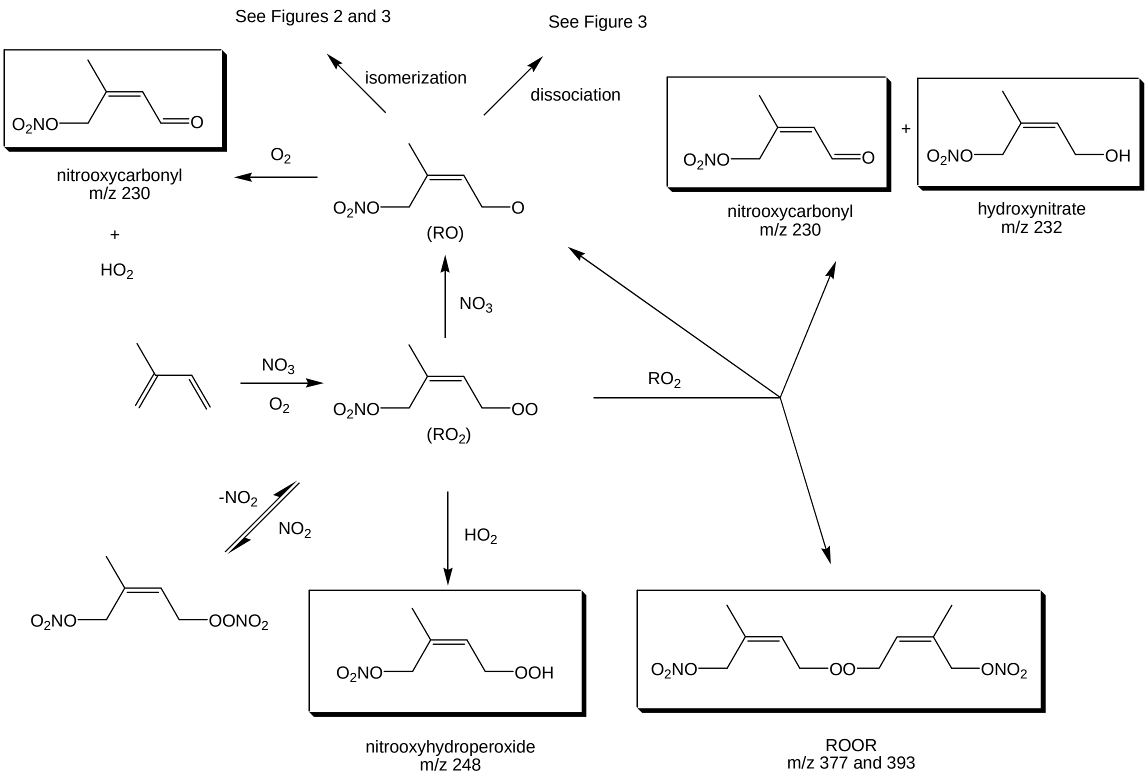

Figure 3.1. Generalized reaction mechanism in the isoprene-NO_3 system. Boxed compounds are detected by CIMS instrument at the indicated m/z values.

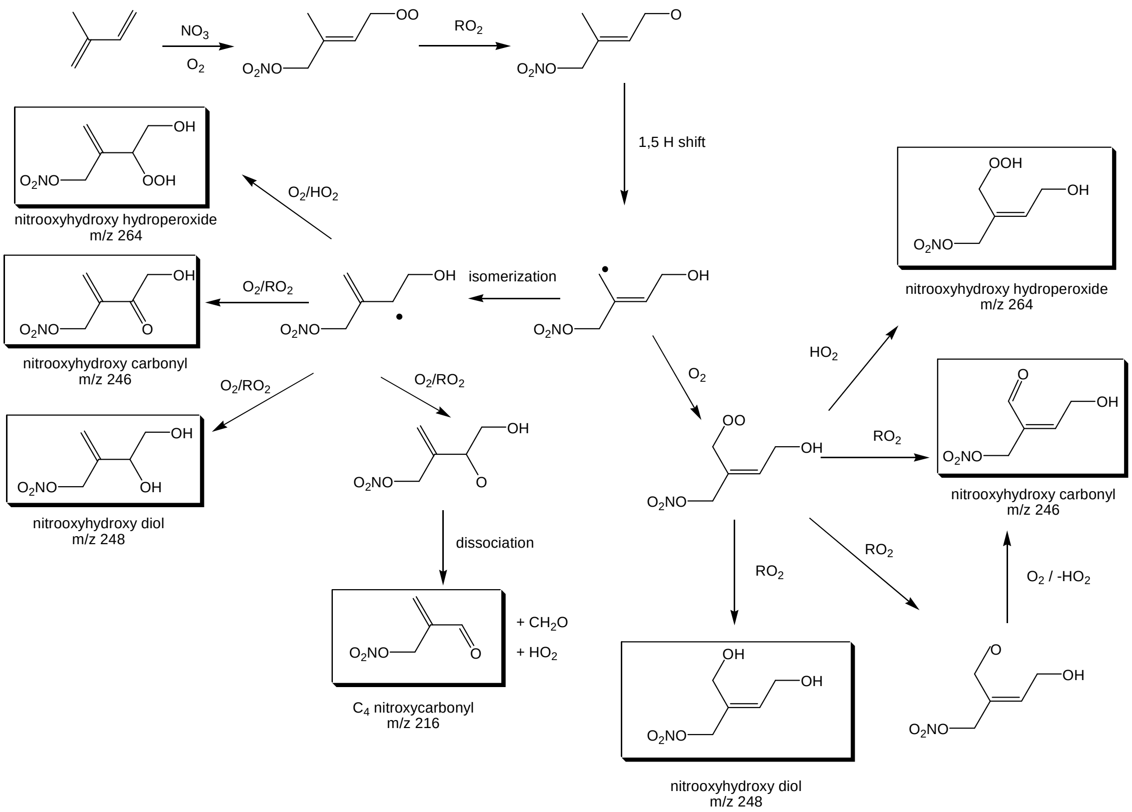

Figure 3.2. Formation of compounds resulting from the isomerization of alkoxy radicals and seen by CIMS instruments at m/z 216, 246, 248, and 264. This figure assumes initial NO_3 attachment to the 1-carbon and formation of an (E)-δ-peroxy radical, but other isomers are possible.

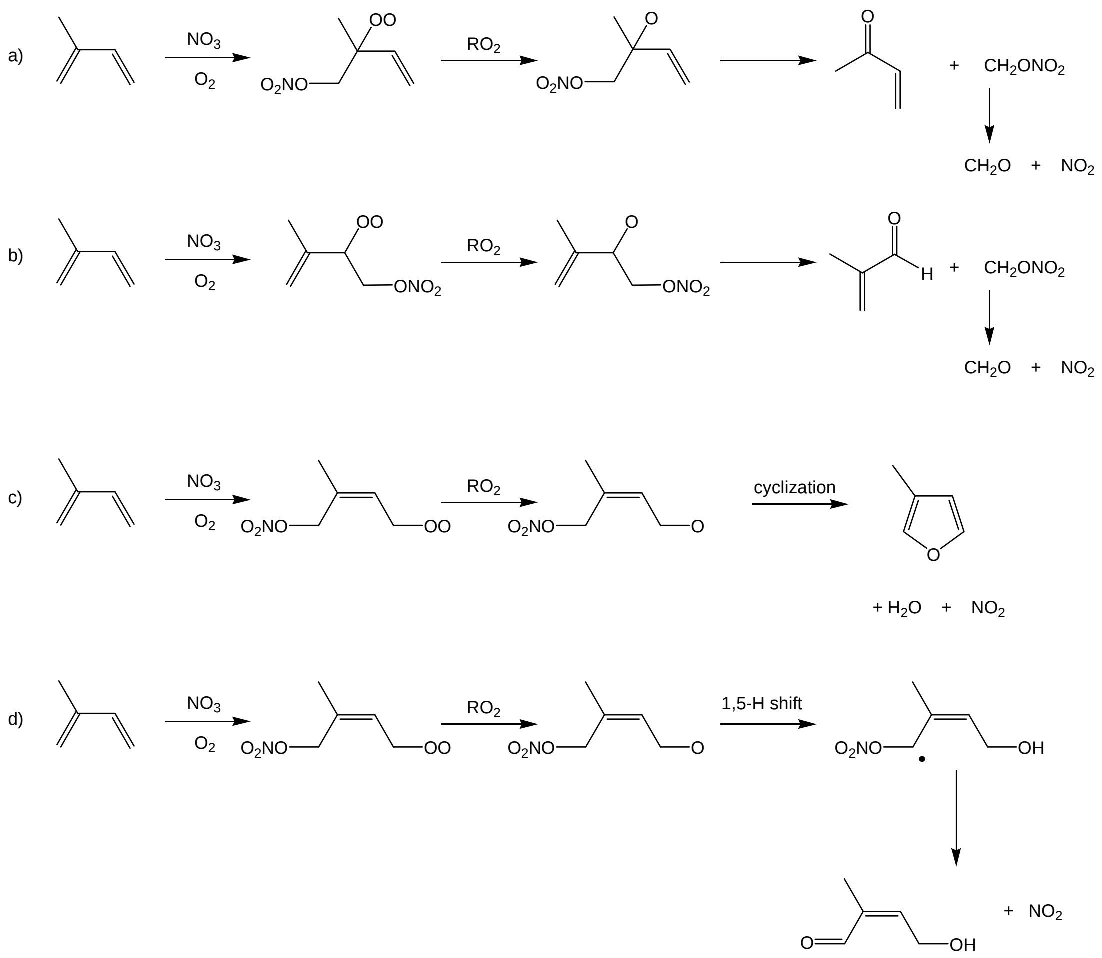

Figure 3.3. Formation mechanism of methyl vinyl ketone (a), methacrolein (b), 3-methylfuran (c), and hydroxycarbonyl (d), leading to release of NO_2. The exact mechanism of 3-methylfuran formation is still unknown (Francisco-Márquez et al., 2005).

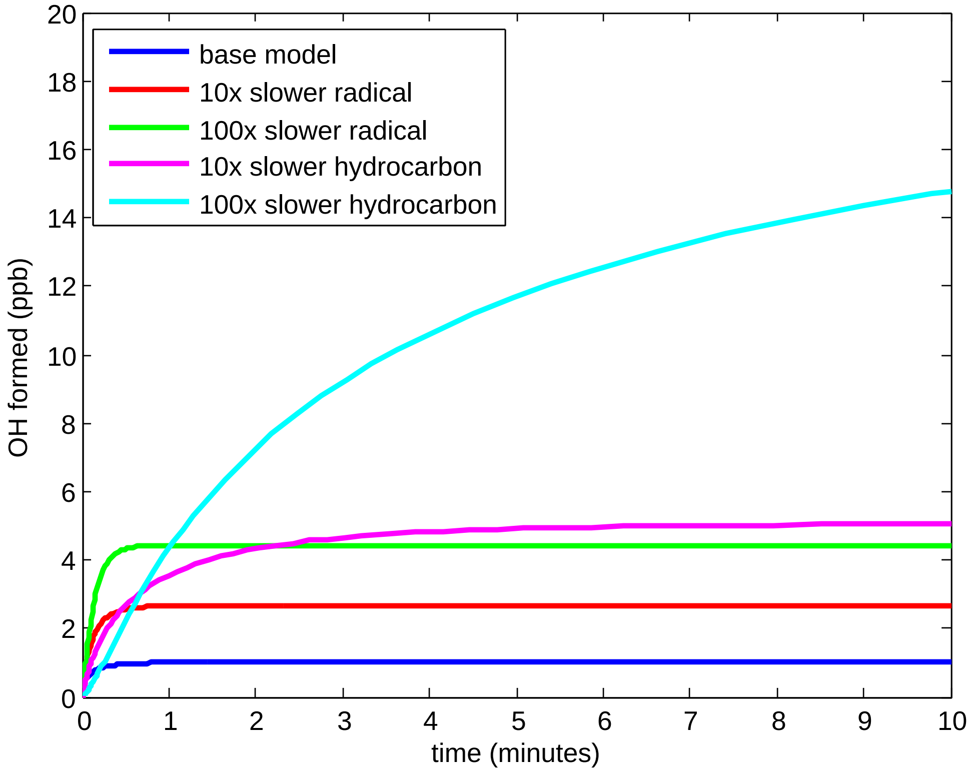

Figure 3.4. Box model simulations for OH production in isoprene-NO_3 system. Blue: base case described in Table 2; Red: RO_2-HO_2 and RO_2-NO_3 rate constants reduced by factor of 10; Green: RO_2-HO_2 and RO_2-NO_3 rate constants reduced by factor of 100; Pink: isoprene-NO_3 rate constant reduced by factor of 100; Light Blue: isoprene-NO_3 rate constant reduced by factor of 100. Initial conditions: 150 ppb N_2O_5, 800 ppb isoprene, 50 ppb NO_2.

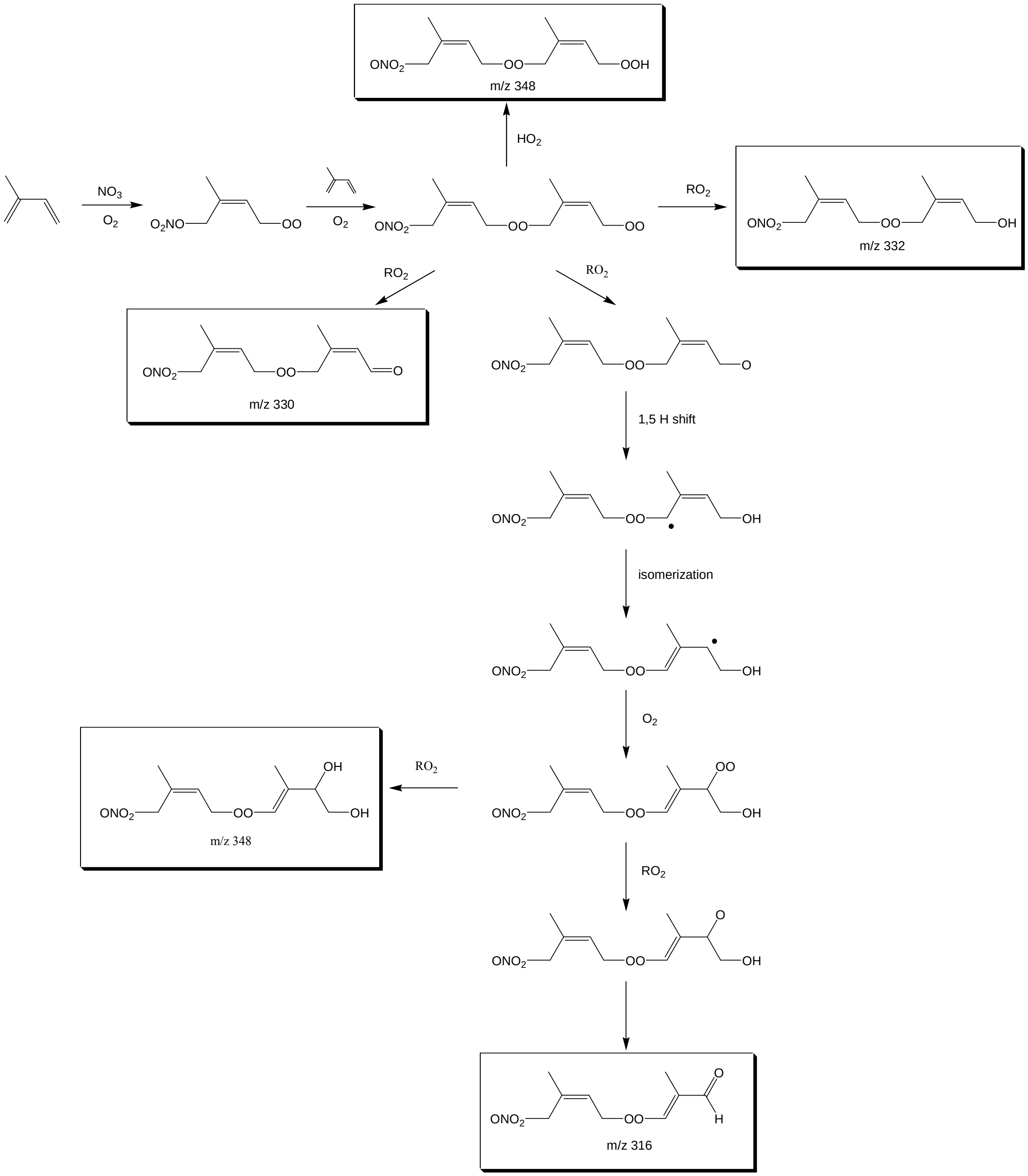

Figure 3.5. Proposed formation mechanisms of products detected by CIMS at m/z 316, 330, 332, and 348. Other isomers are possible.

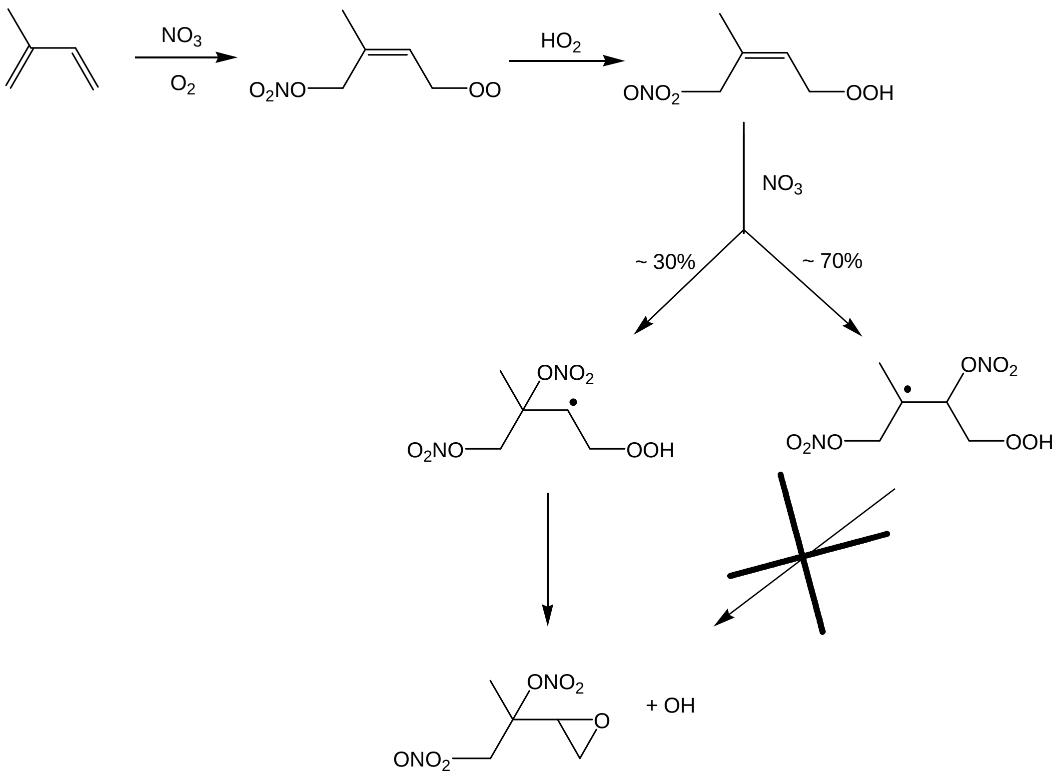

Figure 3.6. Formation mechanism of dinitrooxyepoxide and hydroxyl radical from oxidation of nitrooxyhydroperoxide.