



Peroxy radical chemistry and OH radical production during the NO₃-initiated oxidation of isoprene

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Abstract. Peroxy radical reactions (RO₂+RO₂) from 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 hydroxyl radical (OH) formation in this system, which we propose comes from RO₂+HO₂ reactions with a yield of ~38–58%. An additional OH source is the second generation oxidation of the nitrooxyhydroperoxide, which produces OH and a dinitrooxyepoxide with a yield of ~35%. The branching ratio of the radical propagating, carbonyl- and alcohol-forming, and organic peroxide-forming channels of the RO₂+RO₂ reaction are found to be ~18–38%, ~59–77%, and ~3–4%, respectively. HO₂ formation in this system is lower than has been previously assumed. Addition of RO₂ to isoprene is suggested as a possible route to the formation of several isoprene C₁₀-organic peroxide 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.

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 (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) (Claeys et al., 2004; Kroll et al., 2005, 2006; Surratt et al., 2006, 2010; Carlton et al., 2009).

Nitrate radicals (NO₃), which form primarily from the reaction of NO₂ and O₃, 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 (Starn et al., 1998; Stroud et al., 2002; Warneke et al., 2004; Steinbacher et al., 2005; Brown et al., 2009). The rate constant for isoprene's reaction with NO₃ is ~50 000 times higher than that of its reaction

with O₃, the other major nighttime oxidant (Atkinson, 1997). Assuming an NO₃ mixing ratio of 10 ppt and an O₃ mixing ratio of 40 ppb, oxidation of isoprene by NO₃ will proceed more than an order of magnitude faster than that by O₃. Mixing ratios of NO₃ 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, NO₃ 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 = O₃ + NO₂) and low actinic flux. NO₃ has been shown to reach concentrations of ~1 ppt 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 O₃, NO₃ concentrations between 5–30 ppt in the hours before sunset have been measured (Geyer et al., 2003a).

The reaction of isoprene and NO₃ can be significant to atmospheric carbon and nitrogen budgets – and subsequently ozone formation – particularly on a regional scale. Globally, it is estimated that the isoprene + NO₃ 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 air-masses advected offshore within the marine boundary layer, and ~73% of NO₃ consumption can be attributed to this reaction (Warneke et al., 2004; Brown et al., 2009). In addition, the isoprene + NO₃ 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 + NO₃ 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 and Zhang, 2002; Fan and Zhang, 2004; Ng et al., 2008; Perring et al., 2009; Rollins et al., 2009). The initial step in the reaction is NO₃ addition to one of the double bonds, followed by addition of O₂ to make a nitrooxyalkyl peroxy radical (RO₂). The RO₂ radicals then react with NO₂ (to make short-lived peroxyxynitrate compounds), NO₃, HO₂, NO₂, or another RO₂, leading to a variety of 1st generation products (Fig. 1). We neglect RO₂ reactions with NO as NO concentrations are generally very low at night in the remote environments where this reaction is most likely to occur (and low under our experimental conditions (Sect. 2) due to the rapid reaction NO₃ + NO → 2NO₂).

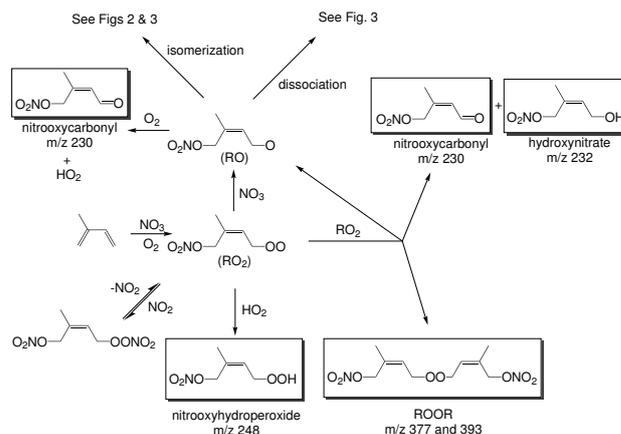


Fig. 1. Generalized reaction mechanism of the isoprene + NO₃ reaction. Boxed compounds are detected by CIMS instrument as CF₃O⁻ adducts at the indicated *m/z* values.

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 C₁₀-organic peroxides (ROOR), 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.

Our study also requires analysis of RO₂ + HO₂ reactions, which inevitably occur in this system. Such reactions are generally considered to form peroxides (ROOH), but there is a growing body of work showing that, for certain RO₂, other product channels are significant, in particular the channel leading to the formation of hydroxyl radical (OH) (Hasson et al., 2004, 2012; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008; Birdsall et al., 2010; Birdsall and Elrod, 2011). Since isoprene + NO₃ reactions occur when there is limited photochemical production of OH, such a channel may play an important role in determining the oxidative capacity of the nighttime atmosphere.

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):





Ozone is generated by flowing oxygen through an ozonizer (OREC V10-0); its mixing ratio is found to be $\sim 2\%$ 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 h in an acetone-dry ice bath at approximately -80°C , cold enough to trap N₂O₅ but not O₃, as condensed O₃ can explode upon warming. After synthesis, the bulb containing the N₂O₅, a white solid, is stored in a liquid nitrogen dewar.

Experiments are performed in the Caltech dual 28 m³ Teflon chambers (Cocker et al., 2001; Keywood et al., 2004). O₃ (Horiba, APOA 360), NO and NO₂ (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 ($\sim 20\text{--}21^\circ\text{C}$) under dry conditions (RH < 10%). Prior to an experiment, the chambers are continuously flushed for at least 24 h. The N₂O₅ 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 N₂O₅ has been achieved in the bulb, the bulb's contents are flushed into the chamber with a 5 l min⁻¹ air stream. After waiting ~ 1 h to allow the N₂O₅ 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 dry air stream, which initiates the reaction.

The amount of isoprene added corresponds to a mixing ratio in the chamber of ~ 800 ppb, while the N₂O₅ concentration is ~ 150 ppb. The large excess of hydrocarbon with respect to N₂O₅ maximizes peroxy radical self- and cross-reactions and minimizes NO₃ 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 N₂O₅ 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 \times .53 mm, 40 μm thickness, J&W Scientific), is held at 60 $^\circ\text{C}$ for 0.5 min, then ramped at 35 $^\circ\text{C min}^{-1}$ to 200 $^\circ\text{C}$, 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; St. Clair et al., 2010), 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 (Crouse 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 Boge, 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 analogs. In contrast, the CIMS technique 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 of Su and Chesnavich (1982). This method estimates the collision rate of CF₃O⁻ and an analyte based on the analyte's dipole moment and polarizability. We calculate the conformationally averaged dipole moment and polarizability of the analytes with the Spartan06 quantum package using 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., 2009b,a), it represents the largest source of uncertainty ($\pm 25\%$) for the CIMS data.

3 Results and discussion

Because the isoprene + NO₃ reaction is rapid, the low time resolution of our measurements (one measurement every ~ 12 min for the GC-FID and ~ 8 min for the CIMS) allows us to determine only the final product distribution (Table 1). The molar yields in Table 1 vary slightly 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 cost of estimating the conformationally averaged dipole and polarizability of large molecules, we have assumed that the CIMS has the same sensitivity to all of the C₉ and C₁₀ compounds.

The only species for which we see time dependent signals are the ROOR C₁₀-organic peroxide 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 behavior is likely because these compounds have low vapor

Table 1. Products detected by GC-FID and CIMS.

Compound	Method	<i>m/z</i> (CIMS)	Final concentration (ppb) ^a	Percent Yield (%) ^b
C ₄ non-nitrate compounds				
MACR	GC-FID	–	3	2.3
MVK	GC-FID	–	6	4.7
C ₄ -hydroxycarbonyl	CIMS	171	<0.5	~0
C ₅ Nitrates				
C ₅ -nitrooxycarbonyl	CIMS	230	45.7	35.6
C ₅ -hydroxynitrate	CIMS	232	27.5	21.4
C ₅ -nitroxyhydroperoxide	CIMS	248	12.5	9.7
C ₄ /C ₅ Isomerized nitrates				
C ₅ -nitroxyhydroxycarbonyl	CIMS	246	5.5	4.3
C ₅ -nitroxydiol	CIMS	248	3.3	2.6
C ₅ -nitroxyhydroxyhydroperoxide	CIMS	264	2.1	1.6
C ₄ -nitrooxycarbonyl	CIMS	216	0.6	0.5
C ₅ Hydroxy compounds				
C ₅ -hydroxycarbonyl	CIMS	185	2.6	2.0
C ₅ -diol	CIMS	187	2.3	1.8
C ₅ -hydroxyhydroperoxide	CIMS	203	4.2	3.3
C ₅ Isomerized hydroxy compounds				
C ₅ -dihydroxycarbonyl	CIMS	201	1.5	1.2
C ₅ -triol	CIMS	203	1.3	1.0
C ₅ -dihydroxyhydroperoxide	CIMS	219	<0.5	~0
Organic peroxides				
C ₁₀ -dinitrooxy ROOR	CIMS	377	1.0	0.8
C ₁₀ -isomerized dinitrooxy ROOR	CIMS	393	0.6	0.5
C ₁₀ -nitrooxycarbonyl ROOR	CIMS	330	<0.5	~0
C ₁₀ -hydroxynitrate ROOR	CIMS	332	0.6	0.5
C ₁₀ -nitroxyhydroperoxide ROOR	CIMS	348	<0.5	~0
C ₉ -nitrooxycarbonyl ROOR	CIMS	316	<0.5	~0
Other				
3-MF	GC-FID	–	4.5	3.5
hydroxyacetone	CIMS	159	0.5	0.4
hydrogen peroxide	CIMS	119	5.5	4.3
glycolaldehyde	CIMS	145	0.9	0.7
Total ^c			128.4	

^a Products with small but non-zero signals are noted as <0.5 ppb.

^b Molar yield.

^c Sum of all products except hydrogen peroxide and minor signals. C₁₀ compounds are counted twice as they comprise two isoprene molecules.

pressures and thus interact significantly with instrument tubing or condense into secondary organic aerosol (~ 10 μg m⁻³ of SOA forms rapidly in this experiment). For these compounds, the reported values are the peak mixing ratios seen during the experiment.

3.1 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 nitrate

products resulting from the isomerization of the alkoxy (RO) radical originating from the δ -nitrooxyperoxy radical formed by (1,4) or (4,1) addition (the notation (x,y) indicates NO₃ addition to the x carbon and subsequent O₂ addition to the y carbon) (Fig. 2). Previous studies have shown that (1,4) additions are dominant in this system (Skov et al., 1992; Berndt and Boge, 1997; Suh et al., 2001). Isomerization also leads to a nitrate 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 Sect. 3.4). Finally, we see C₁₀-organic peroxides at m/z 332, 377, and 393 (further discussed in Sect. 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 can 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 NO₃ radical consumed, which is equivalent to the loss of N₂O₅ during this reaction. Lacking a quantitative measurement of N₂O₅, we use the change in NO₂ concentration after the addition of isoprene (~ 125 ppb) as a proxy. Every conversion of N₂O₅ to NO₃ releases NO₂, but the total change in NO₂ may be an overestimate of total NO₃ reacted because NO₂ can also be released in the formation of methyl vinyl ketone (MVK), methacrolein (MACR), 3-methylfuran (3-MF), and the C₅ hydroxycarbonyl (Fig. 3), though in Sect. 3.2 we discuss alternative formation pathways for these compounds. Subtracting these additional NO₂ sources to get a lower limit for NO₃ consumption leads to an NO₃ consumption range of 109–125 ppb and a corresponding nitrate yield of ~ 80 –90 % (all percentage yields in this work are calculated on a molar basis).

This high yield suggests that the NO₃ radical reacts with isoprene predominantly, if not exclusively, via addition to a double bond. The CIMS does not see a detectable rise in HNO₃, indicating that hydrogen abstraction is not a significant pathway for this reaction (our sensitivity to HNO₃, however, is hampered by a large background – probably from impurities in the N₂O₅ or reaction of N₂O₅ with trace water on the surface of the chamber). Assuming most of the 16.1 ppb of MVK, MACR, 3-MF, and the C₅-hydroxycarbonyl originates from nitrooxyperoxy radicals, we can account for ~ 100 % of the reacted NO₃. Additionally, although our experimental design seeks to minimize reactions of NO₃ with species other than isoprene, there are possible (likely small) losses of NO₃ 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 Boge, 1997),

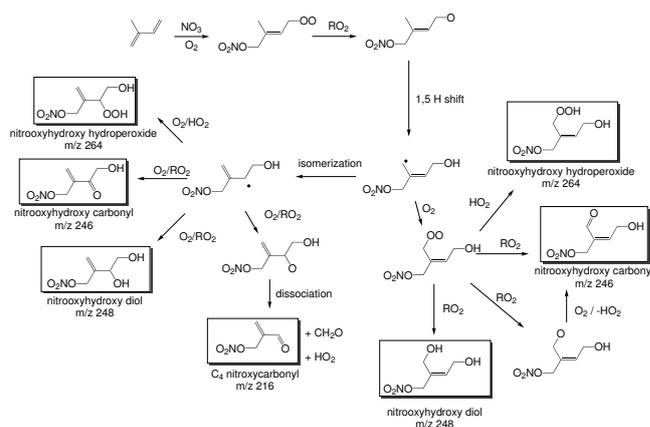


Fig. 2. Formation mechanism of compounds resulting from the isomerization of alkoxy radicals and measured by the CIMS at m/z 216, 246, 248, and 264. This figure assumes initial NO₃ attachment to the 1-carbon and formation of an (E)- δ -peroxy radical, but other isomers are possible.

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 Boge (1997) and Peeters et al. (2009) suggest that peroxy radical isomers formed from isoprene oxidation are continuously interconverting. If this is true, the degree of interconversion is affected by the rate at which RO₂ become stable products relative to the interconversion rate, i.e., the magnitudes of k_1 and k_2 with respect to $k_{\text{int}1}$ and $k_{\text{int}2}$ in Fig. 4. These rates are specific to the unique experimental conditions of each study, such as temperature, pressure, the degree of mixing, and hydrocarbon and oxidant concentrations. Therefore, the distribution of isomers – which defines the final product distribution – may 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, we do not know the exact starting isoprene concentration. Therefore, we assume that each of the products listed in Table 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 ~ 130 ppb of isoprene reacted, and a nitrate yield of ~ 80 %.

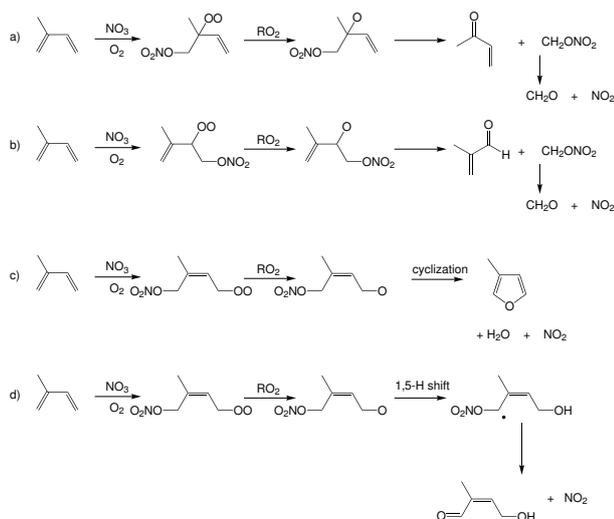


Fig. 3. Formation mechanisms of methyl vinyl ketone (a), methacrolein (b), 3-methylfuran (c), and hydroxycarbonyl (d), leading to release of NO₂. The exact mechanism of 3-methylfuran formation is still uncertain (Francisco-Marquez et al., 2005).

As with the nitrogen-based yield, this result too is consistent with other studies: ~80% (Barnes et al., 1990), ~90% (Berndt and Boge, 1997), 70 ± 8% (Rollins et al., 2009), and 65 ± 12% (Perring et al., 2009).

Much of the discrepancy between our estimates of isoprene and NO₃ consumption is likely due to our lack of an empirical calibration for the CIMS. Some of it, however, is due to an additional loss process of isoprene besides oxidation by NO₃, which we discuss in the following section.

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 Figs. 1 and 2, only with oxidation initiated by the hydroxyl radical (OH) (Fig. 5) (Surratt et al., 2010); the relative contribution of isobaric species is determined in the same manner as in Sec. 3.1. Some of the signal at *m/z* 201 may also be attributable to C₅-hydroperoxyaldehydes, which have recently been reported to result from OH oxidation (Crouse et al., 2011). 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, our 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 that most of the 3-MF comes

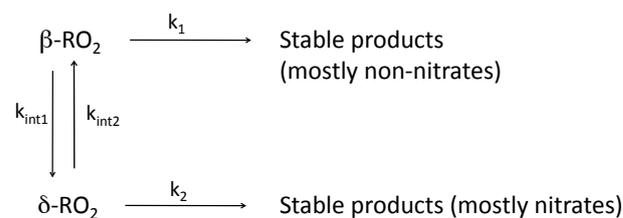


Fig. 4. Schematic of the relationship between the interconversion of peroxy radical isomers and nitrate yields.

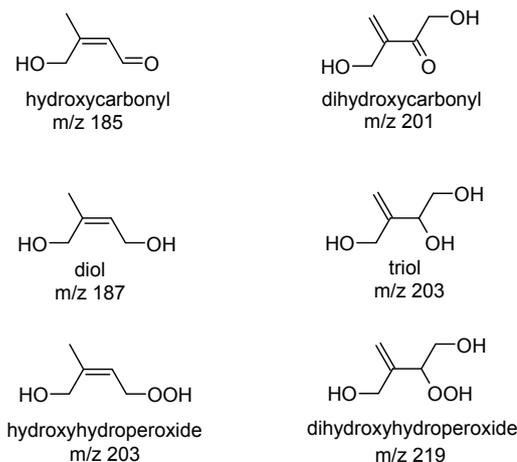


Fig. 5. Products detected by CIMS that may result from the OH-initiated oxidation of isoprene. Other isomers are possible.

from isoprene + NO₃ reactions because its yield in the isoprene + OH system is low (Ruppert and Becker, 2000; Paulot et al., 2009b).

We evaluate five possible routes to OH formation in our system: reactions of (i) O₃ and isoprene (Neeb and Moortgat, 1999), (ii) HO₂ and O₃ (Sinha et al., 1987), (iii) HO₂ and NO (Seeley et al., 1996), (iv) HO₂ and NO₃ (Mellouki et al., 1993), and (v) RO₂ and HO₂ (Hasson et al., 2004, 2005; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008). Routes (i) and (ii) are unlikely to be significant sources of OH in our experiments. Not only does our O₃ monitor not detect any ozone during the experiment (limit of detection ~2 ppb), but we also see no evidence in the CIMS data of significant organic acid or peroxide formation, which would result from the reaction of O₃ with isoprene (Hasson et al., 2001; Orzechowska and Paulson, 2005). Furthermore, for route (ii) to be feasible, HO₂ + O₃ reactions ($k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K, Sander et al., 2011) must be significantly faster than HO₂ + HO₂ reactions ($k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 1 atm and 298 K, Sander et al., 2011), which produce ppb levels of H₂O₂ in the system (Table 1). This would require O₃ to be more than three orders of magnitude more abundant than HO₂, i.e.,

Table 2. Reactions considered for box model assessment of OH sources in the isoprene + NO₃ system.

No.	Reaction	Rate constant ^a	Source
1 ^b	NO ₃ + isoprene → RO ₂ + HO ₂	6.6 × 10 ⁻¹³	Atkinson (1997)
2	RO ₂ + RO ₂ → products	1 × 10 ⁻¹³	Atkinson et al. (2006), and references therein
3	RO ₂ + NO ₃ → products	3 × 10 ⁻¹²	Biggs et al. (1994); Daele et al. (1995); Canosa-Mas et al. (1996); Vaughan et al. (2006)
4	RO ₂ + HO ₂ → products	2.2 × 10 ⁻¹¹	Atkinson et al. (2006), and references therein
5	RO ₂ + NO ₂ → RO ₂ NO ₂	5 × 10 ⁻¹¹	Sander et al. (2011), and references therein
6	RO ₂ NO ₂ → RO ₂ + NO ₂	20	Sander et al. (2011), and references therein
7	NO ₃ + HO ₂ → OH + NO ₂ + O ₂	3.5 × 10 ⁻¹²	Sander et al. (2011), and references therein
8	NO ₂ + NO ₃ → N ₂ O ₅	6.7 × 10 ⁻¹²	Sander et al. (2011), and references therein
9	N ₂ O ₅ → NO ₂ + NO ₃	2.2 × 10 ⁻¹	Sander et al. (2011), and references therein
10	HO ₂ + HO ₂ → H ₂ O ₂	2.3 × 10 ⁻¹²	Sander et al. (2011), and references therein
11	HO ₂ + NO ₂ → HO ₂ NO ₂	2.8 × 10 ⁻¹²	Sander et al. (2011), and references therein
12	HO ₂ NO ₂ → HO ₂ + NO ₂	1.8 × 10 ⁻¹	Sander et al. (2011), and references therein
13	NO ₃ + NO ₂ → NO + NO ₂ + O ₂	6.6 × 10 ⁻¹⁶	Sander et al. (2011), and references therein
14	NO ₃ + NO → 2NO ₂	2.6 × 10 ⁻¹¹	Sander et al. (2011), and references therein
15	HO ₂ + NO → NO ₂ + OH	8.0 × 10 ⁻¹²	Sander et al. (2011), and references therein

^a At 1 atm and 298 K. Units are cm³ molec⁻¹ s⁻¹, except *k*₆, *k*₉ and *k*₁₂, which are s⁻¹. Reaction rates involving RO₂ are approximated from values found in the literature.

^b HO₂ yield is an upper limit to facilitate model analysis.

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 2 lists the parameters of this box model; for rate constants that have not been experimentally determined, we use estimates based on the rate constants of similar reactions found in 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, [N₂O₅] = 125 ppb, and [NO₂] = 50 ppb (the NO₂ likely results from decomposition of N₂O₅ 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 (Sect. 3.4), 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 in Eq. (1) of Table 2; our final concentration of peroxides (i.e., [ROOH] + 2 × [H₂O₂]) is ~ 29 ppb, much less than the ~ 109–125 ppb of RO₂ that is formed (Sect. 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 route (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 N₂O₅) reacts quickly

with NO₃ after N₂O₅ injection; the NO lifetime is ~ 1 s with our 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; at this concentration, NO cannot compete with other radicals reacting with HO₂ (i.e., RO₂, HO₂, NO₃, and NO₂). Therefore, HO₂ + NO is unlikely to contribute significantly to the ~ 12–21 ppb of OH that is formed in our system.

The box model also suggests that route (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 our box model in Table 2, which significantly overestimates the prevalence of HO₂ and underestimates the concentration of isoprene in the plume, 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 very insensitive to these rates because NO₃ reactivity is dominated by its reaction with isoprene. Even if we favor NO₃ + HO₂ reactions by reducing the RO₂ + HO₂ and RO₂ + NO₃ rate constants by a factor of 100, we only obtain ~ 5 ppb of OH formation; in contrast, lowering the NO₃ + isoprene rate constant would lead to significantly more production of OH via NO₃ + HO₂ (Fig. 6). These simulations are consistent with the observation of Atkinson et al. (1988) during hydrocarbon + NO₃ kinetics studies that there is OH formation when slower reacting hydrocarbons are studied. The reaction of isoprene with NO₃ is sufficiently fast under our

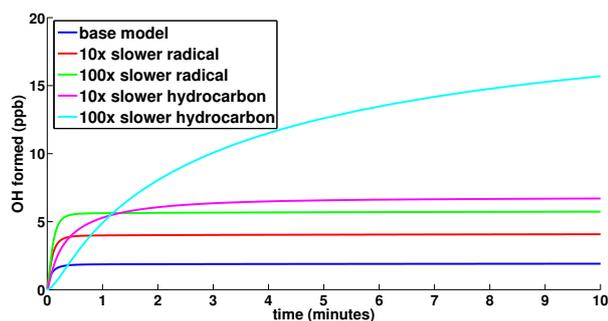


Fig. 6. Box model simulations for OH production in isoprene + NO₃ system. Blue: base case described in Table 2; Red: RO₂ + HO₂ and RO₂ + NO₃ rate constants reduced by factor of 10; Green: RO₂ + HO₂ and RO₂ + NO₃ rate constants reduced by factor of 100; Pink: isoprene + NO₃ rate constant reduced by factor of 10; Light Blue: isoprene + NO₃ rate constant reduced by factor of 100. Initial conditions: 150 ppb N₂O₅, 800 ppb isoprene, 50 ppb NO₂.

experimental conditions, however, that such behavior should not occur.

We therefore suggest 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:



Channel (R4) can be quantified with CIMS measurements of peroxides. We neglect channel (R5), first because we don't see any evidence for ozone formation, and also because this channel is believed to proceed via a hydroperoxide intermediate that only yields O₃ if RO₂ is an acylperoxy radical (RC(O)OO) (Hasson et al., 2005). To quantify channel (R6), 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 come directly from channel (R7), indirectly from the RO formed in channel (R6), or from 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 (R7) is negligible, as well as OH from RO₂ + HO₂ reactions where the RO₂ originates from isoprene + OH (Paulot

et al., 2009a). We thus constrain the range of OH formation to 9–20.5 ppb, with the upper limit incorporating 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 (R4) by the concentration of the nitrooxyhydroperoxides at *m/z* 248 and *m/z* 264, so obtain a range for (R6)/[(R6)+(R4)] of between 9/(9 + 12.5 + 2.1) and 20.5/(20.5 + 12.5 + 2.1), or 38–58%. Because this analysis assumes that RO₂ + HO₂ reactions are the exclusive source of OH radicals and also ignores channel (R7), this yield should be considered an upper limit. Also, this yield is for the isomeric mix of RO₂ in this system, which is dominated by RO₂ from (1,4) additions, but also contains other isomers.

To our knowledge, this is the first study that has attempted to quantify the OH yield from RO₂ + HO₂ reactions involving the nitrooxyperoxy radicals in our system. Thus far, significant OH yields (15–80%) have been found for acylperoxy (RC(O)OO), methoxymethylperoxy (CH₃OCH₂OO), and α -carbonylperoxy (RC(O)CH₂OO) radicals, and evidence for OH formation also exists for bicyclic hydroxyperoxy radicals derived from toluene; in contrast, alkylperoxy and hydroxyalkylperoxy radicals have exhibited minimal yields (Hasson et al., 2004, 2012; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008; Birdsall et al., 2010; Birdsall and Elrod, 2011). For the peroxy radicals in this study, the high OH yields may result from the presence of the electron-withdrawing nitrooxy group conjugated through the double bond, which may stabilize (i.e., lower the enthalpy of) the alkoxy radical formed by the radical propagating channel (R6), thereby making this channel more thermodynamically favored.

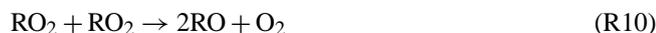
3.2.1 OH formation from 2nd generation dinitrooxyepoxide formation

While this study focuses on the first generation products from the isoprene + NO₃ 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 ~6 ppb, while the signal for the dinitrooxyepoxide (at *m/z* 293) rises ~2.3 ppb, indicating that the epoxide (and OH) yield from the NO₃ oxidation of the nitrooxyhydroperoxide is ~35%, compared

to ~75 % for OH oxidation of isoprene hydroxyhydroperoxides (Paulot et al., 2009a). 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 (Fig. 7). 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. Another factor which may contribute to a lower yield in our experiment is the presence of large amounts of nitric acid, which may increase heterogeneous loss processes for the epoxide, either on the surface of the SOA or the chamber walls. Epoxides have been shown to undergo significant reactive uptake by acidic aerosol (Eddingsaas et al., 2010; Surratt et al., 2010).

3.3 RO₂ + RO₂ branching ratio

RO₂ + RO₂ reactions have three product channels (Fig. 1):



The C₅-hydroxynitrate at *m/z* 232 comes exclusively from channel (R8), so we estimate that 55 ppb of RO₂ passes through this channel, leading to 27.5 ppb of hydroxynitrate and 27.5 ppb of the C₅-nitrooxycarbonyl at *m/z* 230. Similarly, we see that ~3 ppb of RO₂ follows channel (R9) to become ROOR (the sum of *m/z* 377 and 393, multiplied by 2 because each ROOR comprises two RO₂), although some ROOR is likely in the aerosol phase as well, which we are unable to quantify.

For channel (R10), we assume that the nitrooxycarbonyl yield in excess of the hydroxynitrate yield arises from RO-forming channels of either RO₂ + HO₂ or RO₂ + RO₂. Thus, the total RO formation is estimated to be 33.5–45 ppb; the lower limit comprises the sum of the excess nitrooxycarbonyl, isomerized nitrates, and 3-MF, while the upper limit includes the lower limit plus MVK, MACR, and hydroxycarbonyl (assumed to come exclusively from isoprene+NO₃ reactions). Of the RO formation, 9–20.5 ppb comes from RO₂ + HO₂ (Sect. 3.2), depending on the true provenance of MVK, MACR, and the hydroxycarbonyl. Taking into account the uncertainties involving RO, we get between 13 (i.e., 33.5–20.5) and 36 (i.e., 45–9) ppb of RO coming from RO₂ + RO₂, and summing up all the product channels yields a range of between 71 (i.e., 55 + 3 + 13) and 94 (i.e., 55 + 3 + 36) ppb of RO₂ undergoing RO₂ + RO₂ reactions.

With the above analysis (and neglecting possible RO₂ + RO₂ reactions involving the hydroxyperoxy RO₂), we

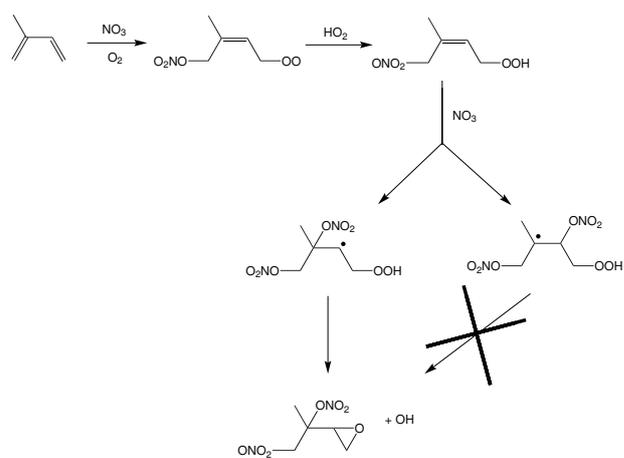


Fig. 7. Formation mechanism of dinitrooxyepoxide and hydroxyl radical from oxidation of nitrooxyhydroperoxide.

derive ranges for the RO₂ + RO₂ branching ratio of 59–77 % (i.e., 55/94–55/71) for (R8), 3–4 % (i.e., 3/94–3/71) for (R9), 19–38 % (i.e., 13.5/71–36/94) for (R10).

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 (R10) is typically more than 50 %, while channel (R9) 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 and 1,4-pentadiene (for the latter compound, ROOR is only apparent in the aerosol phase, M. N. Chan, personal communication, 2010), 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 the smaller radicals that have been the subject of most previous work because larger RO₂ have more vibrational modes with which to distribute collisional energy and prevent breaking apart upon combination with another RO₂ radical. Thus, ROOR formation from RO₂ + RO₂ reactions may be analogous to organic nitrate (RONO₂) yield from RO₂ + NO reactions, which tends to increase with increasing RO₂ size (O'Brien et al., 1998; Arey et al., 2001; Matsunaga and Ziemann, 2009).

3.4 RO radical fate and HO₂ 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 HO₂. From the amount of excess hydroxycarbonyl formed, we estimate that 18 ppb of HO₂ forms from O₂ abstraction of RO (the formation of which we constrain to 33.5–45 ppb, Sect. 3.3), or 40–54 % of RO. This assumes that O₂ abstraction from RO is the sole source of excess nitrooxycarbonyl, and that direct formation from RO₂ + HO₂ reactions (R7) is negligible.

This is lower than the total sum of HO₂ derived from peroxide measurements in our system (29 ppb, Sect. 3.2). Additional HO₂ comes from O₂ abstraction from minor alkoxy radicals (the isomerized nitrooxyalkoxy and hydroxyalkoxy radicals) and formation of the C₅-hydroperoxyaldehyde (Crouse et al., 2011), but it is not trivial to attempt an HO₂ balance because of the uncertainties in both the CIMS calibration and the sources and sinks of HO₂. HO₂ can come from the conversion of the nitrooxyalkoxy radical to a nitrooxycarbonyl, or MVK and MACR if the latter are from OH + isoprene; sinks of HO₂ include peroxide formation, RO₂ + HO₂ derived alkoxy radicals that do not undergo abstraction, and from nitrooxycarbonyls formed directly from RO₂ + HO₂ via channel (R7).

Because the δ -nitrooxyalkoxy radical, the dominant alkoxy radical in our system, can isomerize via a 1,5-H shift, the large HO₂ yield is somewhat surprising because isomerization reactions are typically faster than abstraction by O₂ (Atkinson and Arey, 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 NO₃ group on isomerization rate. Large HO₂ yields would also be possible if O₂ abstractions are faster for the alkoxy radicals in this system.

While our HO₂ yield is higher than expected based on the alkoxy radical structure, it is lower than the value of 80 % of RO₂ that has been used in modeling studies (Horowitz et al., 2007; Rollins et al., 2009). Therefore, models may overestimate the impact of isoprene + NO₃ reactions on nighttime HO_x chemistry in this respect.

Each pathway to RO (e.g., RO₂ + RO₂, RO₂ + HO₂, RO₂ + NO₃) has a different heat of reaction, which may affect the RO fate (Berndt and Boge, 1997; Atkinson and Arey, 2007). Lacking any specific knowledge about how the RO fate in our system depends on the reaction enthalpy (and the values of the reaction enthalpies in our system), we have as-

sumed in the above analysis that every RO behaves the same, regardless of source.

3.5 Formation of C₁₀-organic peroxides

In Ng et al. (2008), we report the formation of ROOR C₁₀-organic peroxide at m/z 377 and 393. Further examination of the CIMS data reveals other isoprene-based C₁₀-organic peroxides. 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 RO₂ + RO₂ reaction where one RO₂ comes from NO₃ and the other from OH. The abundance of OH is much less than that of NO₃, 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 RO₂ radical to isoprene, creating a C₁₀-alkyl (and subsequently alkylperoxy) radical, which undergoes an RO₂ + RO₂ reaction to create the C₁₀-hydroxynitrate ROOR (Fig. 8). This mechanism for creating a C₁₀ RO₂ 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 an apparent C₉ compound at m/z 316 that can result from isomerization of a C₁₀-nitrooxyalkoxy radical; isomerization may also lead to a diol at m/z 348, the same mass as the hydroperoxide.

We are not aware of any previous work that has examined external RO₂ addition to alkenes under atmospheric conditions, though it has been reported in both gas phase combustion (Osborne and Waddington, 1980; Stark and Waddington, 1995) and liquid phase studies (van Sickle et al., 1965a,b; Mayo, 1968; Simmons and van Sickle, 1973), producing both epoxides and polymeric peroxy radicals. This pathway may be another source of large peroxides in the ambient atmosphere.

4 Implications

The observed high nitrate yields, in general agreement with previous results, support the modeling results of Horowitz et al. (2007) that isoprene + NO₃ 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. The nitrogen-based yield (i.e., [nitrates]/[NO₃ consumed]) is non-unity due to competing reactions of NO₃ (e.g., reactions with RO₂, HO₂, and walls) and loss of the nitrate functionality by the initial isoprene-NO₃

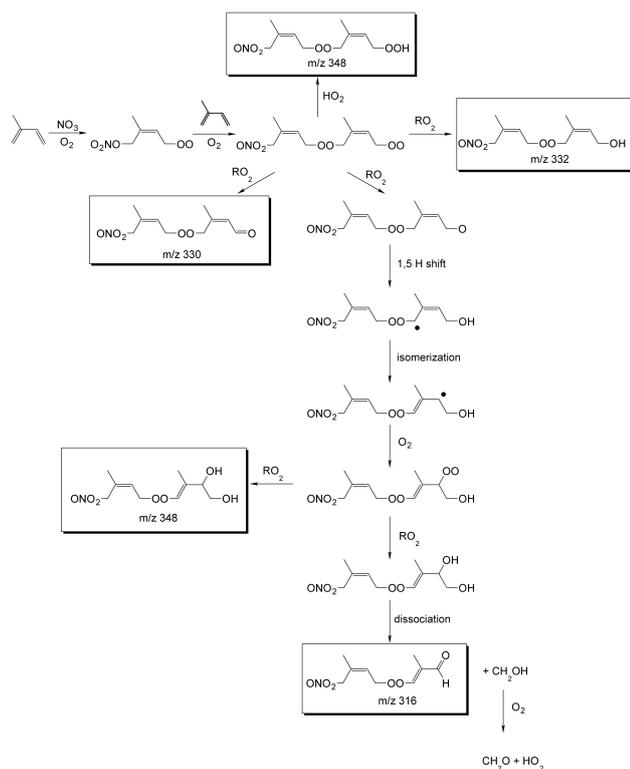


Fig. 8. Proposed formation mechanisms of products detected by CIMS at m/z 316, 330, 332, and 348. Other isomers are possible.

adduct (Fig. 3); 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 NO₃ 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 yield of products produced from reaction of OH with isoprene is potentially very important for nighttime chemistry, particularly because we propose that the source of OH is from RO₂ + HO₂ reactions which likely dominate in the ambient environment (Beaver et al., 2012). Recent field studies suggest that the radical propagating channels of RO₂ + HO₂ reactions must be significant to explain observations (Thornton et al., 2002; Lelieveld et al., 2008). Previous studies of nighttime chemistry have only considered alkene ozonolysis and HO₂ + NO, HO₂ + O₃, and NO₃ + HO₂ reactions as sources of OH (Bey et al., 1997, 2001a,b; Harrison et al., 1998; Faloon et al., 2001; Golz 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 (Faloon 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.

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., 2005; Volkamer et al., 2006; Simpson et al., 2007), a discrepancy that may be explained by SOA formation pathways, such as ROOR, that are missing from models. In this work, we see evidence of an additional ROOR formation pathway, possibly 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 in the atmosphere 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 apparent, 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, or during the daytime under clouds or in forest canopies, when isoprene concentrations are high and small amounts of NO₃ can also exist.

Although the isoprene : NO₃ ratio in our experiment varies both temporally and spatially within the chamber, our box model (Sect. 3.2) shows that the ratios achieved during the experiment may be plausible in the ambient atmosphere. During the base case simulation, the peak NO₃ concentration is ~ 1.5 ppb, which represents an isoprene:NO₃ ratio of ~ 500. If we increase the initial isoprene level to 3 ppm (to account for the fact that our concentrated plume contains more than 800 ppb isoprene) the peak NO₃ concentration is ~ 0.5 ppb, for a ratio of ~ 6000. Thus, the isoprene:NO₃ ratios during the experiment, while variable, are likely on the order of ~ 1000 when most of the reaction takes place. Apel et al. (2002) and Brown et al. (2009) find isoprene concentrations ~ 1 ppb at sunset in Northern Michigan and New England, respectively, so NO₃ levels of ~ 1 ppt would yield similar ratios. Studies of daytime NO₃ oxidation find even higher ratios, with isoprene concentrations ~ 10 ppb and NO₃ concentrations ~ 0.5 ppt, or a ratio of ~ 20 000 (Brown et al., 2005; Fuentes et al., 2007). Thus, it is likely that our experimental conditions, which favor RO₂ + RO₂ reactions over

RO₂ + NO₃ reactions, can occur in the ambient atmosphere, but the ambient atmosphere will also likely have higher HO₂ and NO levels (due to additional sources of these radicals such as soil emissions and pernitric acid decomposition) which will also influence the final product yield and must also be considered.

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 RO₂ + RO₂ reactions in nighttime SOA formation is worthy of further study, particularly because the nitrooxy group is electron withdrawing, and the presence of electron withdrawing groups has been shown to significantly increase RO₂ + RO₂ reaction rates (Lightfoot et al., 1992). Resonance stabilization may also affect RO₂ reaction rates, though we know of no work that has examined this effect. As noted by other investigators (Brown et al., 2009; Fry et al., 2009), SOA formed from the reaction of biogenic compounds with NO₃ – an anthropogenic oxidant – is consistent with the common finding that while SOA is largely composed of contemporary carbon, even in urban areas (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 RO₂ formed from isoprene + NO₃ reactions are primary radicals, however, whereas a significant amount of the RO₂ derived from terpenes are likely to be secondary or tertiary. Primary RO₂ tend to undergo significantly faster RO₂ + RO₂ reactions than secondary or tertiary RO₂ (Lightfoot et al., 1992). Reactivity trends are less certain for RO₂ + NO, RO₂ + NO₃, and RO₂ + HO₂ reactions, but the variation in the available data is less pronounced than for RO₂ + RO₂ reactions (Lightfoot et al., 1992; Lesclaux, 1997; Wallington et al., 1997; Atkinson et al., 2006; Vaughan et al., 2006). So while terpenes are generally more reactive with NO₃ than isoprene (i.e., have higher RO₂ formation rates) (Atkinson and Arey, 2003), RO₂ + RO₂ reactions for these compounds may be less competitive than for isoprene under the same conditions because of the significantly lower RO₂ + RO₂ rate constants compared to competing reactions. On the other hand, if ROOR formation is analogous to RONO₂ formation from RO₂ + NO reactions, then the ROOR yield from terpene RO₂ + RO₂ reactions may be higher, particularly for secondary RO₂. RONO₂ yields for secondary RO₂ are about a factor of 2 higher than for primary or tertiary RO₂, which have similar yields (Carter and Atkinson, 1985; Atkinson et al., 1987).

Although we have gained insights into the isoprene + NO₃ system in this work, chamber studies such as ours 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. Therefore, because of our experimental conditions we are only able 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 NO_x conditions and RO₂ + HO₂ for low NO_x conditions), this is currently not feasible for NO₃ chamber studies. Also, while the CIMS can speciate 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; increased transferring 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) differ from what is 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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