Atmos. Chem. Phys. Discuss., 12, 2259–2302, 2012 www.atmos-chem-phys-discuss.net/12/2259/2012/ doi:10.5194/acpd-12-2259-2012 © Author(s) 2012. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

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

A. J. Kwan^{1,*}, A. W. H. Chan^{2,**}, N. L. Ng^{2,***}, H. G. Kjaergaard³, J. H. Seinfeld^{1,2}, and P. O. Wennberg^{1,4}

¹Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, USA

²Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

³Copenhagen Center for Atmospheric Chemistry, Department of Chemistry, University of Copenhagen, 2100 Copenhagen Ø, Denmark

⁴Division of Geology and Planetary Science, California Institute of Technology, Pasadena, CA 91125, USA



*now at: Energy Storage Division, NEXT ENERGY EWE-Forschungszentrum für Energietechnologie e.V., 26129 Oldenburg, Germany

**now at: Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, CA 94720, USA

***now at: School of Chemical and Biomolecular Engineering and School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA

Received: 20 December 2011 – Accepted: 6 January 2012 – Published: 24 January 2012

Correspondence to: A. J. Kwan (alan.j.kwan@gmail.com)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Diecueeion Da	ACPD 12, 2259–2302, 2012 RO ₂ chemistry during isoprene + NO ₃ reaction A. J. Kwan et al. <u>Title Page</u>		
nor Diecue			
icion Danc			
	Abstract	Introduction	
_	Conclusions	References	
	Tables	Figures	
200	I.∎	►I.	
u D D D r	•	•	
_	Back	Close	
	Full Scre	en / Esc	
	Printer-friendly Version		
D			
Dr	6		

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

further see evidence of significant hydroxyl radical (OH) formation in this system, which we propose comes from RO₂ + HO₂ reactions with a yield of ~42–62 %. 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 dimer-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 dimer compounds (ROOR). The nitrooxy, allylic, and C₅ peroxy radicals present in this system exhibit different behavior than the limited suite of peroxy radicals that have been studied to date.

1 Introduction

The global emissions of isoprene (440–660 Tg yr⁻¹ (Guenther et al., 2006)) are larger than any other non-methane hydrocarbon. Because of its high abundance and reactiv-

- ity 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., 2009b) 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 ¹⁵ (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. 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, ²⁰ 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 \sim 6–7% of

²⁵ 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 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 shortlived peroxynitrate 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 (and low under our experimental conditions (Sect. 2) due to the rapid reaction NO₃ + NO \rightarrow 2NO₂).
- In a previous study (Ng et al., 2008), we show that the SOA yield from the reaction of isoprene with NO₃ radicals is higher when experimental conditions favor RO₂ + RO₂ reactions over RO₂ + NO₃ reactions. This phenomenon is explained in part by the formation of low vapor pressure ROOR dimers from RO₂ + RO₂ reactions, a product channel that had previously been considered insignificant. In light of the potential importance
 of RO₂ + RO₂ reactions, we present here a detailed product study of the RO₂ + RO₂ reactions from the NO₃-initiated oxidation of isoprene.

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 NO₃ radicals. N₂O₅ is synthesized by mixing streams of nitric oxide (\geq 99.5%, Matheson Tri Gas) and ozone in a glass bulb, which forms N₂O₅ via the following reactions (Davidson et al., 1978):



 $NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + O_3 \rightarrow NO_3 + O_2$ $NO_2 + NO_3 \leftrightarrow N_2O_5$

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 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 m^3 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 (~20–21 °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



(R1)

(R2)

(R3)

(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 3methylfuran. The GC-FID, equipped with a bonded polystyrene-divinylbenzene based column (HP-Plot Q, $15 \text{ m} \times .53 \text{ mm}$, $40 \mu \text{m}$ thickness, J&W Scientific), is held at 60° C for 0.5 min, then ramped at 35° C min⁻¹ to 200°C, after which the temperature is held steady for 3.5 min.

¹⁰ 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., 2009a; St. Clair et al., 2010), 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).

- ¹⁵ 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., 2009a,b), it represents the largest source of uncertainty (±25%) for the CIMS data.

10 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 yields in Table 1 vary slightly from those reported in Ng et al. (2008) due to refinements in the estimated CIMS

¹⁵ 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 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 behavior is likely because these compounds have low vapor 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 nitrooxy-hydroperoxide. 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 dimer ROOR products at *m/z* 332, 377, and 393

¹⁵ (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 %.



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 – prob-⁵ ably 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 C₅hydroxycarbonyl 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, our yield estimate should be 10 considered a lower limit because there are also 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 NO_3 is consistent with the substantial yields determined by other studies: ~95% (under NO-free conditions) (Berndt and Boge, 1997), 57±11% (Perring et al., 2009), and 70±8% (Rollins et al., 2009). Vari-

- ¹⁵ Boge, 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
- ²⁰ 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;
- ²⁵ since δ -nitrooxyperoxy (i.e., primary) radicals react faster than β -nitrooxyperoxy (secondary) radicals (Lightfoot et al., 1992), this would mean that some β -nitrooxyperoxy radicals that form in the initial isoprene+NO₃ reaction will convert to δ -nitrooxyperoxy radicals by Le Chatelier's principle. Therefore, the distribution of isomers – which defines the final product distribution – may also be sensitive to specific experimental



conditions.

10

15

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 Ta-5 ble 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 \sim 130 ppb of isoprene reacted, and a nitrate yield of \sim 80 %. 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 $65 \pm 12\%$ (Perring et al., 2009).

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

Hydroxyl radical (OH) formation 3.2

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 com-20 pounds are analogous to those depicted in Figs. 1 and 2, only with oxidation initiated by the hydroxyl radical (OH) instead of NO₃ (Surratt et al., 2010). Some of the signal at m/z 201 may also be attributable to C₅-hydroperoxyaldehydes (Crounse et al., 2011), which also results from OH oxidation. Perring et al. (2009) report PTR-MS signals at m/z 101, 103, 119, and 117, which could be the protonated clusters of these 25

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 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) O_3 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). Hypotheses (i) and (ii) are unlikely to occur. Not only does our O_3 monitor not 10 detect any ozone during the experiment (limit of detection $\sim 2 \text{ ppb}$), but we also see no evidence in the CIMS data of significant organic acid or peroxide formation, which would result from the reaction of O_3 with isoprene (Hasson et al., 2001; Orzechowska and Paulson, 2005). Furthermore, for hypothesis (ii) to be feasible, $HO_2 + O_3$ reactions $(k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, Sander et al. (2006)) must be significantly faster than 15 $HO_2 + HO_2$ reactions (k = 2.48 × 10⁻¹² cm³ molec⁻¹ s⁻¹ at 1 atm and 298 K, Sander et al. (2006)), which produce ppb levels of H_2O_2 in the system (Table 1). This would require O_3 to be more than three orders of magnitude more abundant than HO₂, 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 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, [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 injec-



tion method. As discussed later (Sect. 3.4), 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 in Eq. (1) of Table 2; our final concentration of peroxides (i.e., $[ROOH] + 2 \times [H_2O_2]$) is ~29 ppb, much less than the ~109–125 ppb of RO_2 that is formed (Sect. 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 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 (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.

- ¹⁵ 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 + 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. 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 isoprene+NO₃ rate constant would lead to significantly more production of OH via NO₃ + HO₂ (Fig. 4). These simulations are consistent with Atkinson et al. (1988)'s observation during hydrocarbon+NO₃ kinetics studies that there is OH formation when slower reacting hydrocarbons are studied. The reaction of iso-



prene with NO₃ is sufficiently fast under our experimental conditions, however, that

such behavior should not occur.

5

We therefore suggest 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 are four documented pathways for the $RO_2 + HO_2$ reaction:

 $RO_2 + HO_2 \rightarrow ROOH$ (R4)

$$RO_2 + HO_2 \rightarrow ROH + O_3$$
 (R5)

$$RO_2 + HO_2 \rightarrow RO + OH + O_2 \tag{R6}$$

 $RO_2 + HO_2 \rightarrow R'CHO + H_2O + O_2$

- ¹⁰ 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 hydrotetroxide intermediate that only yields O_3 if RO_2 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
- ¹⁵ the C₅ hydroxycarbonyl can come from either OH or NO₃, which leads to uncertainty in this quantity. Similarly, the nitrooxycarbonyl can come directly from Reaction (R7), indirectly from the RO formed in Reaction (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 $RO_2 + HO_2$ but emphasize that our assumptions and results must be verified by further studies. We assume channel (R7) is negligible, as well as OH from $RO_2 + HO_2$ reactions where the RO_2 originates from isoprene + OH (Paulot et al., 2009b), and ignore any $RO_2 + HO_2$ reactions from the isometrized nitroever RO_2 . We thus constrain the react of OH formation

tions from the isomerized nitrooxy RO₂. We thus constrain the range of OH formation (channel 1c) to 9–20.5 ppb, with the upper limit incorporating all the hydroxy products



(R7)

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 nitrooxyhydoperoxide at m/z 248, so obtain a range for (R6)/[(R6) + (R4)] of between 9/(9 + 12.5) and 20.5/(20.5 + 12.5), or 42–62 %.

⁵ 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 only been found for acylperoxy, methoxymethylperoxy (CH₃OCH₂O₂), and β -carbonylperoxy (RC(O)CH₂OO) radicals, while alkylperoxy and hydroxyalkylperoxy radicals have exhibited minimal yields (Hasson et al., 2004; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008). Perhaps the presence of the nitrooxy group conjugated through the double bond stabilizes the alkoxy radical, thereby enabling the radical propagating channel.

3.2.1 OH formation from 2nd generation dinitrooxyepoxide formation

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., 2009b). 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

- ²⁰ 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., 2009b). 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. 5). In the OH system, (1,2) and (4,3) additions in the first oxidation step are most common (Paulot et al., 2009a), which means that the epoxide forming channel involves a second OH addition to the more favored 4- or 1-carbon, respectively.

3.3 RO₂ + RO₂ branching ratio

 $RO_2 + RO_2$ reactions have three product channels (Fig. 1):

 $RO_2 + RO_2 \rightarrow R'CHO + ROH + O_2$

¹⁰
$$\operatorname{RO}_2 + \operatorname{RO}_2 \rightarrow \operatorname{ROOR} + \operatorname{O}_2$$

 $RO_2 + RO_2 \rightarrow 2RO + O_2$

15

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 dimer 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 $RO_2 + HO_2$ or $RO_2 + RO_2$.

- ²⁰ 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 $RO_2 + RO_2$, and



(R8)

(R9)

(R10)

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 $RO_2 + RO_2$ reactions involving the hydroxyperoxy RO_2), we derive ranges for the $RO_2 + RO_2$ 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).

5

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 (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 $RO_2 + RO_2$ reactions from the NO_3 -initiated oxidation of 1,3-butadiene and 1,4-pentadiene (for the latter case, ROOR is only apparent in the aerosol phase,

- ¹⁵ M. N. Chan, personal communication), as well as the OH-initiated oxidation of 1,3butadiene 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 radi-
- ²⁰ cals we have studied are more likely to form ROOR than the smaller radicals that are the subject of most previous work because larger RO_2 have more vibrational modes with which to distribute collisional energy and prevent breaking apart upon combination with another RO_2 radical. Thus, ROOR formation from $RO_2 + RO_2$ reactions may be analogous to organic nitrate (RONO₂) yield from $RO_2 + NO$ reactions, which tends to increases with increasing RO_2 airs (O'Prion et al. 1008; Area et al. 2001; Mateuroge
- ²⁵ 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 HO_2 . From the amount of excess hydroxycarbonyl formed, we estimate that 18 ppb of HO_2 forms from O_2

⁵ 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 O_2 abstraction from RO is the sole source of excess nitrooxycarbonyl, and that direct formation from $RO_2 + HO_2$ reactions (Reaction R7) is negligible.

This is lower than the total sum of HO_2 derived from peroxide measurements in our system (29 ppb, Sect. 3.2). Additional HO_2 comes from O_2 abstraction from minor alkoxy radicals (the isomerized nitrooxyalkoxy and hydroxyalkoxy radicals) and formation of the C_5 -hydroperoxyaldehyde (Crounse et al., 2011), 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 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, $RO_2 + HO_2$ derived alkoxy radicals that do not undergo abstraction, and from nitrooxycarbonyls formed directly from $RO_2 + HO_2$ 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 Kwok and Atkinson (1995)'s structure-activity relationship, 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 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., $RO_2 + RO_2$, $RO_2 + HO_2$, $RO_2 + NO_3$) 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 depends on the reaction

¹⁰ enthalpy (and the values of the reaction enthalpies in our system), we have assumed in the above analysis that every RO behaves the same, regardless of source.

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.

- ¹⁵ 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
- ²⁰ 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. 6). 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
- ²⁵ 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.

4 Implications

5

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.

 $_{\rm 10}$ 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-¹⁵ 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 adduct (Fig. 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 NO₃ sinks and/or OH ²⁰ 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 $RO_2 + HO_2$ reactions which likely dominate in the ambient environment. Recent field studies suggest that the radical propagating channels of $RO_2 + HO_2$ reactions Discussion Paper ACPD 12, 2259–2302, 2012 RO₂ chemistry during isoprene + NO₃ reaction Discussion Paper A. J. Kwan et al. **Title Page** Introduction Abstract Conclusions References **Discussion** Paper **Tables Figures** Back **Discussion** Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

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; Faloona 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 (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.

- 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.,
- ¹⁵ 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 he
- ²⁰ 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,
²⁵ 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, though during this time NO

concentrations may still be high enough to react with a significant amount of RO₂. 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 5 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 the presence of electron withdrawing groups has been shown to significantly increase RO₂ + RO₂ reaction rates (Lightfoot et al., 1992). As noted by other investigators (Brown et al., 2009; Fry et al., 2009), SOA formed from the reaction of biogenic compounds with NO_3 – an anthropogenic oxidant – is consistent the common find-

ing 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 an-15 thropogenic emissions (de Gouw et al., 2005, 2008; Quinn et al., 2006; Sullivan et al., 2006; Weber et al., 2007).

10

Most of the RO_2 formed from isoprene + NO_3 reactions are primary radicals, however, whereas a significant amount of the RO₂ derived from terpenes are likely to be secondary or tertiary. Primary RO_2 tend to undergo significantly faster $RO_2 + RO_2$

- 20 reactions than secondary or tertiary RO₂ (Lightfoot et al., 1992). Reactivity trends are less certain for $RO_2 + NO_3$, $RO_2 + NO_3$, 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 terpenes are generally more reactive with NO₃ than isoprene (i.e., 25 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 $RO_2 + RO_2$ rate constants compared to competing reactions. On the other hand, if ROOR formation is analogous to RONO₂ formation from



 $RO_2 + NO$ reactions, then the ROOR yield from terpene $RO_2 + RO_2$ reactions may be higher, particularly for secondary RO_2 . $RONO_2$ yields for secondary RO_2 are about a factor of 2 higher than for primary or tertiary RO_2 , 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 quan-

tification. 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 sythesis (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.



Acknowledgements. This research is funded by the US Department of Energy Biological and Environmental Research Program DE-FG02-05ER63983. Also, this material is based upon work supported by the National Science Foundation (NSF) under grant ATM-0432377 and an NSF Graduate Research Fellowship (AJK). The authors would like to thank C. D. Vecitis,

J. Cheng, M. R. Hoffmann, K. Takematsu, and M. Okumura for experimental assistance, and 5 J. D. Crounse, N. H. Donahue, N. C. Eddingsaas, F. Paulot, and H. O. T. Pye for helpful discussions.

References

15

Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate, hydroxyalkyl nitrate,

- and hydroxycarbonyl formation from the NO_x-air photooxidations of C-5-C-8 n-alkanes, J. 10 Phys. Chem. A. 105, 1020-1027, 2001, 2275
 - Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, J. Phys. Chem. Ref. Data, 26, 215-290, 1997. 2262, 2275

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, Supplement 2, 197-219, 2003. 2280

Atkinson, R. and Arey, J.: Mechanisms of the gas-phase reactions of aromatic hydrocarbons and PAHs with OH and NO₃ radicals, Polycyclic Aromat. Compd., 27, 15–40, 2007. 2276, 2277

Atkinson, R., Aschmann, S., and Winer, A.: Alkyl Nitrate Formation from the Reaction of a

- Series of Branched RO₂ Radicals with NO as a Function of Temperature and Pressure, J. 20 Atmos. Chem., 5, 91–102, 1987. 2281
 - Atkinson, R., Aschmann, S. M., and Pitts, J. N.: Rate constants for the gas-phase reactions of the NO₃ radical with a series of organic compounds at 296 +/- 2 K, J. Phys. Chem., 92, 3454-3457, 1988, 2271
- ²⁵ Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, doi:10.5194/acp-6-3625-2006, 2006, 2280

Barnes, I., Bastian, V., Becker, K. H., and Tong, Z.: Kinetics and products of the reactions

Discussion Pa	ACPD 12, 2259–2302, 2012 RO ₂ chemistry during isoprene + NO ₃ reaction A. J. Kwan et al.		
per Discussion			
Pape	Title Page		
er	Abstract	Introduction	
D	Conclusions	References	
iscussi	Tables	Figures	
on Pa	14	►I	
aper	•	•	
_	Back	Close	
Discussio	Full Screen / Esc Printer-friendly Version		
n Paper	Interactive Discussion		

of NO_3 with monoalkenes, dialkenes, and monoterpenes, J. Phys. Chem., 94, 2413–2419, 1990. 2263, 2265, 2269

- Bench, G., Fallon, S., Schichtel, B., Malm, W., and McDade, C.: Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for
- ⁵ Protection of Visual Environments (IMPROVE) network sites, J. Geophys. Res.-Atmos., 112, D10205, doi:10.1029/2006JD007708, 2007. 2280
 - Berndt, T. and Boge, O.: Gas-phase reaction of NO₃ radicals with isoprene: A kinetic and mechanistic study, Int. J. Chem. Kinet., 29, 755–765, 1997. 2263, 2265, 2267, 2268, 2269, 2277
- ¹⁰ Bey, I., Aumont, B., and Toupance, G.: The nighttime production of OH radicals in the continental troposphere, Geophys. Res. Lett., 24, 1067–1070, 1997. 2279
 - Bey, I., Aumont, B., and Toupance, G.: A modeling study of the nighttime radical chemistry in the lower continental troposphere 2. Origin and evolution of HO_x, J. Geophys. Res.-Atmos., 106, 9991–10001, 2001a. 2279
- Bey, I., Jacob, D., Yantosca, R., Logan, J., Field, B., Fiore, A., Li, Q., Liu, H., Mickley, L., and Schultz, M.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106, 23073–23096, 2001b. 2279
 - Brown, S. S., Osthoff, H. D., Stark, H., Dube, W. P., Ryerson, T. B., Warneke, C., de Gouw, J. A., Wollny, A. G., Parrish, D. D., Fehsenfeld, F. C., and Ravishankara, A. R.: Aircraft
- $_{\rm 20}$ observations of daytime NO_3 and N_2O_5 and their implications for tropospheric chemistry, J. Photoch. Photobio. A, 176, 270–278, 2005. 2262
 - Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dube, W. P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67–70, 2006, 2262
- ²⁵ **311**, 67–70, 2006. 2262
 - Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dubé, W. P., Atlas, E., Weber, R. J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S. A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Nocturnal isoprene oxidation over the Northeast United States in summer and its impact
- on reactive nitrogen partitioning and secondary organic aerosol, Atmos. Chem. Phys., 9, 3027–3042, doi:10.5194/acp-9-3027-2009, 2009. 2262, 2263, 2280
 - Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987–5005, doi:10.5194/acp-9-4987-2009,



2009. 2261

- Carslaw, N., Carpenter, L. J., Plane, J. M. C., Allan, B. J., Burgess, R. A., Clemitshaw, K. C., Coe, H., and Penkett, S. A.: Simultaneous observations of nitrate and peroxy radicals in the marine boundary layer, J. Geophys. Res.-Atmos., 102, 18917–18933, 1997. 2262
- 5 Carter, W. and Atkinson, R.: Atmospheric Chemistry of Alkanes, J. Atmos. Chem., 3, 377–405, 1985. 2281
 - Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S.: The role of biogenic hydrocarbons in urban photochemical smog Atlanta as a case study, Science, 241, 1473–1475, 1988. 2261
- ¹⁰ Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173–1176, 2004. 2261 Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: State-of-the-art chamber facility for studying

atmospheric aerosol chemistry, Environ. Sci. Technol., 35, 2594–2601, 2001. 2264

¹⁵ Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry, Anal. Chem., 78, 6726–6732, 2006. 2265

Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, Phys. Chem. Chem. Phys., 13, 13607–13613, 2011. 2269, 2276

Davidson, J. A., Viggiano, A. A., Howard, C. J., Dotan, I., Fehsenfeld, F. C., Albritton, D. L., and Ferguson, E. E.: Rate constants for reactions of O₂⁺, NO₂⁺, NO⁺, H₃O⁺, CO₃⁻, NO₂⁻, and halide ions with N₂O₅ AT 300 K, J. Chem. Phys., 68, 2085–2087, 1978. 2263

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted

- Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res.-Atmos., 110, D16305, doi:10.1029/2004JD005623, 2005. 2279, 2280
 - de Gouw, J. A., Brock, C. A., Atlas, E. L., Bates, T. S., Fehsenfeld, F. C., Goldan, P. D., Holloway, J. S., Kuster, W. C., Lerner, B. M., Matthew, B. M., Middlebrook, A. M., Onasch, T. B., Peltier,
- R. E., Quinn, P. K., Senff, C. J., Stohl, A., Sullivan, A. P., Trainer, M., Warneke, C., Weber, R. J., and Williams, E. J.: Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes, J. Geophys. Res.-Atmos., 113, D08301, doi:10.1029/2007JD009243, 2008. 2280



- Dibble, T. S.: Failures and limitations of quantum chemistry for two key problems in the atmospheric chemistry of peroxy radicals, Atmos. Environ., 42, 5837–5848, 2008. 2275
- Dillon, T. J. and Crowley, J. N.: Direct detection of OH formation in the reactions of HO₂ with CH₃C(O)O₂ and other substituted peroxy radicals, Atmos. Chem. Phys., 8, 4877–4889, doi:10.5194/acp-8-4877-2008, 2008. 2270, 2273
- doi:10.5194/acp-8-4877-2008, 2008. 2270, 2273
 Donahue, N. M., Robinson, A. L., and Pandis, S. N.: Atmospheric organic particulate matter: From smoke to secondary organic aerosol, Atmos. Environ., 43, 94–106, 2009. 2279
 - Faloona, I., Tan, D., Brune, W., Hurst, J., Barket, D., Couch, T. L., Shepson, P., Apel, E., Riemer, D., Thornberry, T., Carroll, M. A., Sillman, S., Keeler, G. J., Sagady, J., Hooper, D.,
- and Paterson, K.: Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, J. Geophys. Res.-Atmos., 106, 24315–24333, 2001. 2279
 Fan, J. W. and Zhang, R. Y.: Atmospheric Oxidation Mechanism of Isoprene, Environ. Chem., 1, 140–149, 2004. 2263
 - Fiore, A. M., Horowitz, L. W., Purves, D. W., Levy, H., Evans, M. J., Wang, Y. X., Li, Q. B.,
- and Yantosca, R. M.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, J. Geophys. Res.-Atmos., 110, D12303, doi:10.1029/2004JD005485, 2005. 2263
 - Forkel, R., Klemm, O., Graus, M., Rappengluck, B., Stockwell, W. R., Grabmer, W., Held, A., Hansel, A., and Steinbrecher, R.: Trace gas exchange and gas phase chemistry in a Norway
- ²⁰ spruce forest: A study with a coupled 1-dimensional canopy atmospheric chemistry emission model, Atmos. Environ., 40, S28–S42, 2006. 2262
 - Francisco-Marquez, M., Alvarez-Idaboy, J. R., Galano, A., and Vivier-Bunge, A.: A Possible Mechanism for Furan Formation in the Tropospheric Oxidation of Dienes, Environ. Sci. Technol., 39, 8797–8802, 2005. 2299
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dubé, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.-P., Brauers, T., and Cohen, R. C.: Organic nitrate and secondary organic aerosol yield from NO₃ oxidation of β-pinene evaluated using a gas-phase kinetics/aerosol partitioning model, Atmos. Chem. Phys., 9, 1431–1449, doi:10.5194/acp-9-1431-2009, 2009. 2280
- ³⁰ Fuentes, J. D., Wang, D., Bowling, D. R., Potosnak, M., Monson, R. K., Goliff, W. S., and Stockwell, W. R.: Biogenic hydrocarbon chemistry within and above a mixed deciduous forest, J. Atmos. Chem., 56, 165–185, 2007. 2262

Garden, A. L., Paulot, F., Crounse, J. D., Maxwell-Cameron, I. J., Wennberg, P. O., and



Kjaergaard, H. G.: Calculation of conformationally weighted dipole moments useful in ionmolecule collision rate estimates, Chem. Phys. Lett., 474, 45-50, 2009. 2266

- Geyer, A. and Stutz, J.: Vertical profiles of NO₃, N₂O₅, O₃, and NO_y in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry, J.
- Geophys. Res.-Atmos., 109, D12307, doi:10.1029/2003JD004211, 2004. 2279 5 Gever, A., Alicke, B., Ackermann, R., Martinez, M., Harder, H., Brune, W., di Carlo, P., Williams, E., Jobson, T., Hall, S., Shetter, R., and Stutz, J.: Direct observations of daytime NO₃: Implications for urban boundary layer chemistry, J. Geophys. Res.-Atmos., 108, 4368, doi:10.1029/2002JD002967, 2003a. 2262
- Geyer, A., Bachmann, K., Hofzumahaus, A., Holland, F., Konrad, S., Klupfel, T., Patz, H. W., 10 Perner, D., Mihelcic, D., Schafer, H. J., Volz-Thomas, A., and Platt, U.: Nighttime formation of peroxy and hydroxyl radicals during the BERLIOZ campaign: Observations and modeling studies, J. Geophys. Res.-Atmos., 108, 8249, doi:10.1029/2001JD000656, 2003b. 2279

Golz, C., Senzig, J., and Platt, U.: NO₃-initiated oxidation of biogenic hydrocarbons, Chemosphere, 3, 339-352, 2001, 2279

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res.-Atmos., 104, 3555-3567, 1999. 2280

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates

- of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and 20 Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, doi:10.5194/acp-6-3181-2006, 2006. 2261
 - Hallguist, M., Wangberg, I., Ljungstrom, E., Barnes, I., and Becker, K. H.: Aerosol and product yields from NO3 radical-initiated oxidation of selected monoterpenes, Environ. Sci. Technol.,

33, 553-559, 1999. 2280 25

15

- Harley, P., Vasconcellos, P., Vierling, L., Pinheiro, C. C. D., Greenberg, J., Guenther, A., Klinger, L., De Almeida, S. S., Neill, D., Baker, T., Phillips, O., and Malhi, Y.: Variation in potential for isoprene emissions among Neotropical forest sites, Global Change Biol., 10, 630-650, 2004. 2262
- Harrison, R. M., Shi, J. P., and Grenfell, J. L.: Novel nighttime free radical chemistry in severe nitrogen dioxide pollution episodes, Atmos. Environ., 32, 2769-2774, 1998. 2279
 - Hasson, A. S., Ho, A. W., Kuwata, K. T., and Paulson, S. E.: Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 2. Asymmetric and



biogenic alkenes, J. Geophys. Res.-Atmos., 106, 34143–34153, 2001. 2270 Hasson, A. S., Tyndall, G. S., and Orlando, J. J.: A product yield study of the reaction of HO₂ radicals with ethyl peroxy (C₂H₅O₂), acetyl peroxy (CH₃C(O)O₂), and acetonyl peroxy (CH₃C(O)CH₂O₂) radicals, J. Phys. Chem. A, 108, 5979–5989, 2004. 2270, 2273

⁵ Hasson, A. S., Kuwata, K. T., Arroyo, M. C., and Petersen, E. B.: Theoretical studies of the reaction of hydroperoxy radicals (HO₂) with ethyl peroxy (CH₃CH₂O₂), acetyl peroxy (CH₃C(O)O₂) and acetonyl peroxy (CH₃C(O)CH₂O₂) radicals, J. Photoch. Photobio. A, 176, 218–230, 2005. 2270, 2272

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and

- Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, L18809, doi:10.1029/2005GL023831, 2005. 2279
 - Heintz, F., Platt, U., Flentje, H., and Dubois, R.: Long-term observation of nitrate radicals at the tor station, Kap Arkona (Rugen), J. Geophys. Res.-Atmos., 101, 22891–22910, 1996. 2262
 Horowitz, L. W., Liang, J. Y., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen
- from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res.-Atmos., 103, 13451–13476, 1998. 2261, 2263
 - Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J. F.: Observational constraints on the chemistry of isoprene nitrates over the eastern United States, J. Geophys. Res.-Atmos., 112, D12S08, doi:10.1029/2006JD007747, 2007. 2262, 2263, 2277, 2278
 - Jay, K. and Stieglitz, L.: The gas-phase addition of NO_x to olefins, Chemosphere, 19, 1939–1950, 1989. 2263

20

25

- Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the CH₃C(O)O₂+HO₂ reaction in the gas phase, Phys. Chem. Chem. Phys., 9, 3149–3162, 2007. 2270, 2273
- Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the CH₃C(O)CH₂O₂+HO₂ reaction in the gas phase, Phys. Chem. Chem. Phys., 10, 4274–4280, 2008. 2270, 2273
- Jenkin, M. E., Hurley, M. A., and Wallington, T. J.: Investigation of the Radical Product Channel
- ³⁰ of the CH₃OCH₂O₂ + HO₂ Reaction in the Gas Phase, J. Phys. Chem. A, 114, 408–416, 2010. 2270, 2273
 - Johnson, D., Jenkin, M. E., Wirtz, K., and Martin-Reviejo, M.: Simulating the Formation of Secondary Organic Aerosol from the Photooxidation of Aromatic Hydrocarbons, Environ.



Chem., 2, 35-48, 2005. 2279

10

20

25

30

- Keywood, M. D., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds, Environ. Sci. Technol., 38, 4157–4164, 2004. 2264
- ⁵ Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, Geophys. Res. Lett., 32, L18808, doi:10.1029/2005GL023637, 2005. 2261
 - Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, Environ. Sci. Technol., 40, 1869–1877, 2006. 2261
- Kwok, E. S. C. and Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-activity relationship an update, Atmos. Environ., 29, 1685–1695, 1995. 2276

Kwok, E. S. C., Aschmann, S. M., Arey, J., and Atkinson, R.: Product formation from the

- reaction of the NO₃ radical with isoprene and rate constants for the reactions of methacrolein and methyl vinyl ketone with the NO₃ radical, Int. J. Chem. Kinet., 28, 925–934, 1996. 2263, 2265
 - Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, 2008. 2279
 - Lesclaux, R.: Combination of Peroxyl Radicals in the Gas Phase, in: Peroxyl Radicals, edited by: Alfassi, Z., pp. 81–112, Wiley, 1997. 2280
 - Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F.: Organic peroxy radicals kinetics, spectroscopy and tropospheric chemistry, Atmos. Environ. A-Gen., 26, 1805–1961, 1992. 2268, 2280
 - Matsunaga, A. and Ziemann, P. J.: Yields of beta-Hydroxynitrates and Dihydroxynitrates in Aerosol Formed from OH Radical-Initiated Reactions of Linear Alkenes in the Presence of NO_x, J. Phys. Chem. A, 113, 599–606, 2009. 2275
 - Mayo, F. R.: Free radical autoxidations of hydrocarbons, Acc. Chem. Res., 1, 193–201, 1968. 2278
 - Mellouki, A., Talukdar, R. K., Bopegedera, A., and Howard, C. J.: Study of the kinetics of the reactions of NO₃ with HO₂ and OH, Int. J. Chem. Kinet., 25, 25–39, 1993. 2270 Neeb, P. and Moortgat, G. K.: Formation of OH radicals in the gas-phase reaction of propene.



isobutene, and isoprene with $\rm O_3$: Yields and mechanistic implications, J. Phys. Chem. A, 103, 9003–9012, 1999. 2270

- Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and
- Seinfeld, J. H.: Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys., 7, 5159–5174, doi:10.5194/acp-7-5159-2007, 2007. 2265
 - Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic
- aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), Atmos. Chem.
 Phys., 8, 4117–4140, doi:10.5194/acp-8-4117-2008, 2008. 2262, 2263, 2266, 2273, 2277, 2279
 - O'Brien, J. M., Czuba, E., Hastie, D. R., Francisco, J. S., and Shepson, P. B.: Determination of the hydroxy nitrate yields from the reaction of C-2-C-6 alkenes with OH in the presence of

¹⁵ NO, J. Phys. Chem. A, 102, 8903–8908, 1998. 2275

25

30

Orzechowska, G. E. and Paulson, S. E.: Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under dry and humid conditions using SPME, J. Phys. Chem. A, 109, 5358–5365, 2005. 2270

Osborne, D. A. and Waddington, D. J.: Reactions of oxygenated radicals in the gas phase:

 7. Reactions of methylperoxyl radicals and alkenes, J. Chem. Soc. Perk. T. 2, pp. 925–930, 1980. 2278

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009a. 2265, 2266, 2274

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730–733, 2009b. 2261, 2266, 2272, 2273

Peeters, J., Nguyen, T. L., and Vereecken, L.: HO_x radical regeneration in the oxidation of isoprene, Phys. Chem. Chem. Phys., 11, 5935–5939, 2009. 2268

Penkett, S. A., Burgess, R. A., Coe, H., Coll, I., Hov, O., Lindskog, A., Schmidbauer, N., Solberg, S., Roemer, M., Thijsse, T., Beck, J., and Reeves, C. E.: Evidence for large average concentrations of the nitrate radical (NO₃) in Western Europe from the HANSA hydrocarbon



database, Atmos. Environ., 41, 3465-3478, 2007. 2262

5

- Perring, A. E., Wisthaler, A., Graus, M., Wooldridge, P. J., Lockwood, A. L., Mielke, L. H., Shepson, P. B., Hansel, A., and Cohen, R. C.: A product study of the isoprene+NO₃ reaction, Atmos. Chem. Phys., 9, 4945–4956, doi:10.5194/acp-9-4945-2009, 2009. 2263, 2265, 2268, 2269
- Platt, U. and Janssen, C.: Observation and role of the free radicals NO₃, CIO, BrO and IO in the troposphere, Faraday Discuss., 100, 175–198, 1995. 2262
- Platt, U., Perner, D., Schroder, J., Kessler, C., and Toennissen, A.: The diurnal variation of NO₃,
 J. Geophys. Res.-Oc. Atm., 86, 1965–1970, 1981. 2262
- Quinn, P. K., Bates, T. S., Coffman, D., Onasch, T. B., Worsnop, D., Baynard, T., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E., Roberts, J. M., Lerner, B., Stohl, A., Pettersson, A., and Lovejoy, E. R.: Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine, J. Geophys. Res., 111, D23S36, doi:10.1029/2006JD007582, 2006. 2280
- ¹⁵ Ren, X. R., Harder, H., Martinez, M., Lesher, R. L., Oliger, A., Shirley, T., Adams, J., Simpas, J. B., and Brune, W. H.: HO_x concentrations and OH reactivity observations in New York City during PMTACS-NY2001, Atmos. Environ., 37, 3627–3637, 2003. 2279
 - Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., Hubler, G., Kuster, W. C., McKeen, S. A., Ryerson, T. B., Trainer, M., Williams, E. J., Fehsenfeld,
- F. C., Bertman, S. B., Nouaime, G., Seaver, C., Grodzinsky, G., Rodgers, M., and Young, V. L.: Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: Implications for regional ozone production from biogenic hydrocarbons, J. Geophys. Res.-Atmos., 103, 22473–22490, 1998. 2261

Rollins, A. W., Kiendler-Scharr, A., Fry, J. L., Brauers, T., Brown, S. S., Dorn, H.-P., Dubë, W.

- P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R., Wooldridge, P. J., and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields, Atmos. Chem. Phys., 9, 6685–6703, doi:10.5194/acp-9-6685-2009, 2009. 2263, 2265, 2268, 2269, 2277
- Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M.,
 Milford, J., and Guenther, A.: Monoterpene and sesquiterpene emission estimates for the United States, Environ. Sci. Technol., 42, 1623–1629, 2008. 2280
 - Sander, S., Golden, D., Kurylo, M., Moortgat, G. K., Wine, P., Ravishankara, A., Kolb, C., Molina, M. J., Finlayson-Pitts, B., Huie, R., Orkin, V., Friedl, R., and Keller-Rudek, H.: Chem-



2291

ical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 15, Jet Propulsion Laboratory, 2006. 2270

- Schichtel, B., Malm, W., Bench, G., Fallon, S., McDade, C., Chow, J., and Watson, J.: Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United
- States, J. Geophys. Res., 113, D02311, doi:10.1029/2007JD008605, 2008. 2280
 Seeley, J. V., Meads, R. F., Elrod, M. J., and Molina, M. J.: Temperature and pressure dependence of the rate constant for the HO₂ + NO reaction, J. Phys. Chem., 100, 4026–4031, 1996. 2270

Sharkey, T. D., Singsaas, E. L., Vanderveer, P. J., and Geron, C.: Field measurements of

- isoprene emission from trees in response to temperature and light, Tree Physiol., 16, 649– 654, 1996. 2262
 - Simmons, K. E. and van Sickle, D.: Addition abstraction competition of acylperoxy radicals reacting with alkenes cooxidation of cyclohexene and valeraldehyde, J. Am. Chem. Soc., 95, 7759–7763, 1973. 2278
- ¹⁵ Simpson, D., Yttri, K. E., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencser, A., Pio, C., Puxbaum, H., and Legrand, M.: Modeling carbonaceous aerosol over Europe: Analysis of the CARBOSOL and EMEP EC/OC campaigns, J. Geophys. Res.-Atmos., 112, D23S14, doi:10.1029/2006JD008158, 2007. 2279

Sinha, A., Lovejoy, E. R., and Howard, C. J.: Kinetic study of the reaction of HO₂ with ozone, J.

²⁰ Chem. Phys., 87, 2122–2128, 1987. 2270

30

- Skov, H., Hjorth, J., Lohse, C., Jensen, N. R., and Restelli, G.: Products and mechanisms of the reactions of the nitrate radical (NO₃) with isoprene, 1,3-butadiene and 2,3-dimethyl-1,3butadiene in air, Atmos. Environ. A-Gen., 26, 2771–2783, 1992. 2263, 2265, 2267
- Smith, N., Plane, J. M. C., Nien, C. F., and Solomon, P. A.: Nighttime radical chemistry in the San Joaquin Valley, Atmos. Environ., 29, 2887–2897, 1995. 2262
 - Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., and Wirtz, K.: Reactions of NO₃ radicals with limonene and alpha-pinene: Product and SOA formation, Atmos. Environ., 40, S116–S127, 2006. 2280

Stark, M. S. and Waddington, D. J.: Oxidation of propene in the gas-phase, Int. J. Chem. Kinet., 27, 123–151, 1995. 2278

Starn, T. K., Shepson, P. B., Bertman, S. B., Riemer, D. D., Zika, R. G., and Olszyna, K.: Nighttime isoprene chemistry at an urban-impacted forest site, J. Geophys. Res.-Atmos., 103, 22437–22447, 1998. 2262



- 2292
- Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Martinez, M., Harder, H., Brune, W. H., Williams, E. J., Roberts, J. M., Fehsenfeld, F. C., Hall, S. R., Shetter, R. E., Wert, B. P., and Fried, A.: Ozone production rates as a function of NO_x abundances and HO_x production rates in the Nashville urban plume, J. Geophys. Res.-Atmos., 107, D12, doi:10.1029/2001JD000932, 2002. 2279
- Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, Proc. Natl. Acad. Sci. USA, 107, 6640-6645, 2010. 2261
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110, 9665–9690, 2006. 2261
- 15 Sullivan, A. P., Peltier, R. E., Brock, C. A., de Gouw, J. A., Holloway, J. S., Warneke, C., Wollny, A. G., and Weber, R. J.: Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: Method development and an investigation into water-soluble organic carbon sources, J. Geophys. Res.-Atmos., 111, D23S46, doi:10.1029/2006JD007072, 2006. 2280 20
- Suh. I., Lei, W. F., and Zhang, R. Y.: Experimental and theoretical studies of isoprene reaction with NO3, J. Phys. Chem. A. 105, 6471-6478, 2001, 2263, 2267
- forested site during the 1999 Southern Oxidant Study, J. Geophys. Res.-Atmos., 107, D16, doi:10.1029/2001JD000959.2002.2262 Su, T. and Chesnavich, W. J.: Parameterization of the ion-polar molecule collision rate constant by trajectory calculations, J. Chem. Phys., 76, 5183-5185, 1982. 2266
- Stroud, C. A., Roberts, J. M., Williams, E. J., Hereid, D., Angevine, W. M., Fehsenfeld, F. C., Wisthaler, A., Hansel, A., Martinez-Harder, M., Harder, H., Brune. W. H.. Hoenninger, G., Stutz, J., and White, A. B.: Nighttime isoprene trends at an urban
- Steinbacher, M., Dommen, J., Ordonez, C., Reimann, S., Gruebler, F., Staehelin, J., Andreani-Aksoyoglu, S., and Prevot, A. S. H.: Volatile organic compounds in the Po Basin. part B: Biogenic VOCs, J. Atmos. Chem., 51, 293-315, 2005. 2262

5

10

30

Rev. Sci. Instrum., 81, 094102, 2010. 2265

Discussion St. Clair, J. M., McCabe, D. C., Crounse, J. D., Steiner, U., and Wennberg, P. O.: Chemical ionization tandem mass spectrometer for the in situ measurement of methyl hydrogen peroxide. ACPD 12, 2259–2302, 2012 Paper RO₂ chemistry during isoprene + NO₃ reaction **Discussion** Paper

Discussion Paper

Discussion Paper





- van Sickle, D., Mayo, F. R., and Arluck, R. M.: Liquid-phase oxidation of cyclopentene, J. Amer. Chem. Soc., 87, 4832–4837, 1965a. 2278
- van Sickle, D., Mayo, F. R., and Arluck, R. M.: Liquid-phase oxidations of cyclic alkenes, J. Amer. Chem. Soc., 87, 4824–4832, 1965b. 2278
- ⁵ Vaughan, S., Canosa-Mas, C. E., Pfrang, C., Shallcross, D. E., Watson, L., and Wayne, R. P.: Kinetic studies of reactions of the nitrate radical (NO₃) with peroxy radicals (RO₂): an indirect source of OH at night?, Phys. Chem. Chem. Phys., 8, 3749–3760, 2006. 2279, 2280
 - Vereecken, L. and Peeters, J.: Decomposition of substituted alkoxy radicals-part I: a generalized structure-activity relationship for reaction barrier heights, Phys. Chem. Chem. Phys., 11, 9062–9074, 2009, 2268
- 10 9062–9074, 2009. 2268
 - Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, Geophys. Res. Lett., 33, L17811, doi:10.1029/2006GL026899, 2006. 2279
- von Friedeburg, C., Wagner, T., Geyer, A., Kaiser, N., Vogel, B., Vogel, H., and Platt, U.: Derivation of tropospheric NO3 profiles using off-axis differential optical absorption spectroscopy measurements during sunrise and comparison with simulations, J. Geophys. Res.-Atmos., 107, D13, doi:10.1029/2001JD000481, 2002. 2262

von Kuhlmann, R., Lawrence, M. G., Pöschl, U., and Crutzen, P. J.: Sensitivities in global scale

- ²⁰ modeling of isoprene, Atmos. Chem. Phys., 4, 1–17, doi:10.5194/acp-4-1-2004, 2004. 2263 Wallington, T., Nielsen, O., and Sehested, J.: Reactions of Organic Peroxy Radicals in the Gas Phase, in: Peroxyl Radicals, edited by: Alfassi, Z., pp. 113–172, Wiley, 1997. 2280
 - Warneke, C., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E. J., Lerner, B. M., Jakoubek, R., Brown, S. S., Stark, H., Aldener, M., Ravishankara, A. R., Roberts, J. M.,
- Marchewka, M., Bertman, S., Sueper, D. T., McKeen, S. A., Meagher, J. F., and Fehsenfeld, F. C.: Comparison of daytime and nighttime oxidation of biogenic and anthropogenic VOCs along the New England coast in summer during New England Air Quality Study 2002, J. Geophys. Res.-Atmos., 109, D10309, doi:10.1029/2003JD004424, 2004. 2262, 2263 Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. P., Canosamas, C. E., Hjorth, J., Lebras, G.,
- Moortgat, G. K., Perner, D., Poulet, G., Restelli, G., and Sidebottom, H.: The nitrate radical physics, chemistry, and the atmosphere, Atmos. Environ. A-Gen., 25, 1–203, 1991. 2262
 - Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary



organic aerosol formation in the anthropogenic-influenced southeastern United States, J. Geophys. Res.-Atmos., 112, D13302, doi:10.1029/2007JD008408, 2007. 2280

- Williams, J., Roberts, J. M., Fehsenfeld, F. C., Bertman, S. B., Buhr, M. P., Goldan, P. D., Hubler, G., Kuster, W. C., Ryerson, T. B., Trainer, M., and Young, V.: Regional ozone from biogenic bydrosorbono deduced from airborne measurements of PAN. PPN, and MPAN. Coophys.
- ⁵ hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, Geophys. Res. Lett., 24, 1099–1102, 1997. 2261
 - Zhang, D. and Zhang, R. Y.: Unimolecular decomposition of nitrooxyalkyl radicals from NO₃-isoprene reaction, J. Chem. Phys., 116, 9721–9728, 2002. 2263
 - Ziemann, P.: Evidence for Low-Volatility Diacyl Peroxides as a Nucleating Agent and Major
- ¹⁰ Component of Aerosol Formed from Reactions of O₃ with Cyclohexene and Homologous Compounds, J. Phys. Chem. A, 106, 4390–4402, 2002. 2275

Jierneeinn Da	ACPD 12, 2259–2302, 2012			
aner I Diecheeinr	RO ₂ chemistry during isoprene + NO ₃ reaction A. J. Kwan et al.			
כמס	Title Page			
D	Abstract	Introduction		
_	Conclusions	References		
	Tables	Figures		
	I	►I.		
ע ססר	•	•		
_	Back	Close		
	Full Screen / Esc			
	Printer-friendly Version			
Dung	Interactive Discussion			
Ť.				

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

Compound	Method	m/z (CIMS)	Final concentration	
			(ppb)	
C ₄ non-nitrate compounds				
MACR	GC-FID	-	3	
MVK	GC-FID	-	6	
C ₄ -hydroxy carbonyl	CIMS 171	<0.5		
C ₅ Nitrates				
C5-nitrooxycarbonyl	CIMS	230	45.7	
C ₅ -hydroxynitrate	CIMS	232	27.5	
C ₅ -nitrooxyhydroperoxide	CIMS	248	12.5	
C ₄ /C ₅ Isomerized nitrates				
C _∈ nitrooxvhvdroxvcarbonvl	CIMS	246	5.5	
C _∈ nitrooxvdiol	CIMS	248	3.3	
C ₅ -nitrooxyhydroxyhydroperoxide	CIMS	264	2.1	
C ₄ -nitrooxy carbonyl	CIMS	216	0.6	
C ₅ Hydroxy compounds				
C _e -hvdroxvcarbonvl	CIMS	185	2.6	
C₅-diol	CIMS	187	2.3	
C ₅ -hydroxyhydroperoxide	CIMS	203	4.2	
C ₅ Isomerized hydroxy compounds				
C ₅ -dihydroxycarbonyl	CIMS	201	1.5	
C ₅ -triol	CIMS	203	1.3	
C ₅ -dihydroxyhydroperoxide	CIMS	219	<0.5	
Dimer compounds				
C ₁₀ -dinitrooxy ROOR	CIMS	377	1.0	
C ₁₀ -isomerized dinitrooxy ROOR	CIMS	393	0.6	
C ₁₀ -nitrooxycarbonyl ROOR	CIMS	330	<0.5	
C ₁₀ -hydroxynitrate ROOR	CIMS	332	0.6	
C ₁₀ -nitrooxyhydroperoxide ROOR	CIMS	348	<0.5	
C9-nitrooxycarbonyl ROOR	CIMS	316	<0.5	
Other				
3-MF	GC-FID	-	4.5	
hydroxyacetone	CIMS	159	0.5	
hydrogen peroxide	CIMS	119	5.5	
glycolaldehyde	CIMS	145	0.9	
Total ^b			128.4	

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

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



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

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

^a At 1 atm and 298 K. Units are cm³ molec⁻¹ s⁻¹, except k_7 and k_{10} , 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.



2296



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





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.

Printer-friendly Version

Interactive Discussion



Fig. 3. Formation mechanisms 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 uncertain (Francisco-Marquez et al., 2005).





Fig. 4. Box model simulations for OH production in isoprene + NO₃ 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 10; Pink: isoprene + NO_3 rate constant reduced by factor of 10; Light Blue: isoprene + NO_3 rate constant reduced by factor of 10; Light Blue: isoprene + NO_3 rate constant reduced by factor of 10; Light Blue: isoprene, 50 ppb N_2 .





Fig. 5. Formation mechanism of dinitrooxyepoxide and hydroxyl radical from oxidation of nitrooxyhydroperoxide.





Fig. 6. Proposed formation mechanisms of products detected by CIMS at m/z 316, 330, 332, and 348. Other isomers are possible.

