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A product study of the isoprene+NO_3 reaction

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Abstract. Oxidation of isoprene through reaction with NO_3 radicals is a significant sink for isoprene that persists after dark. The main products of the reaction are multifunctional nitrates. These nitrates constitute a significant NO_x sink in the nocturnal boundary layer and they likely play an important role in formation of secondary organic aerosol. Products of the isoprene+NO_3 reaction will, in many locations, be abundant enough to affect nighttime radical chemistry and to persist into daytime where they may represent a source of NO_x. Product formation in the isoprene + NO_3 reaction was studied in a smog chamber at Purdue University. Isoprene nitrates and other hydrocarbon products were observed using Proton Transfer Reaction-Mass Spectrometry (PTR-MS) and reactive nitrogen products were observed using Thermal Dissociation–Laser Induced Fluorescence (TD-LIF). The organic nitrate yield is found to be 65±12% of which the majority was nitrooxy carbonyls and the combined yield of methacrolein and methyl vinyl ketone (MACR+MVK) is found to be ∼10%. PTR-MS measurements of nitrooxy carbonyls and TD-LIF measurements of total organic nitrates agreed well. The PTR-MS also observed a series of minor oxidation products which were tentatively identified and their yields quantified These other oxidation products are used as additional constraints on the reaction mechanism.

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1 Introduction

Global isoprene emissions are estimated to be 440–660 Tg/yr (Guenther et al., 2006) and are larger than emissions for any other single organic molecule (Guenther et al., 1995; Bey et al., 2001). Thus even minor changes in the oxidation of isoprene have a major influence on the chemistry of the atmosphere. For example, isoprene nitrate (IN) production, the focus of this manuscript, is calculated to be a major sink of NO_x. The removal of NO_x and possible subsequent release (Perring et al., 2009) affects regional and global ozone and also the response of ozone to climate change (Horowitz et al., 2007; Wu et al., 2007). Isoprene is also likely a significant source of secondary organic aerosol (Kroll et al., 2006; Ng et al., 2006). The aerosol effects are due both to the role of INs as a NO_x sink and thus to the indirect role of INs as a regulator of available NO_x and more directly to the subsequent oxidation of INs leading to low vapor pressure and/or highly water soluble molecules. INs are produced during the daytime as a minor product of OH-initiated isoprene oxidation in the presence of NO (Tuazon and Atkinson, 1990; Werner et al., 1999) and at night as a major product of oxidation by NO_3 (Barnes et al., 1990; Skov et al., 1992; Berndt and Boge, 1997).

Nitrate product formation as a result of isoprene oxidation by NO_3 was first studied by Barnes et al. (1990) who report a nitrate yield of 80%. Isoprene emission occurs mostly during the daytime, increasing with temperature and radiation over the course of the morning and falling off in the afternoon (Fehsenfeld et al., 1992). Several studies have found reaction with NO_3 to be the dominant loss process for isoprene that remains during the early evening in moderately

polluted environments (∼15% of the total) (Stroud et al., 2002; Warneke et al., 2004), and that this can result in substantial conversion of NO_x to organic nitrates at night (Starn et al., 1998). Not only is NO_3 an important isoprene sink but, because of the high yield, INs formed by NO_3-initiated oxidation may represent a large fraction of the total IN source (Horowitz et al., 2007).

Kwok et al. (1996) studied the products of the NO_3+isoprene reaction using API-MS and observed the formation of C_5 carbonyl nitrates, C_5 hydroxy nitrates, C_5 hydroperoxy nitrates and C_5 hydroxy carbonyls. They also observed methacrolein ($CH_2C(CH_3)CHO$ or MACR) and methyl vinyl ketone ($CH_3C(O)CHCH_2$ or MVK) formation and found each produced with a 3.5% yield. A partial oxidation scheme that illustrates likely formation pathways and structures of the observed products is shown in Figure 1. Oxidation is initiated by addition of NO_3 to a double bond to produce an unstable radical adduct intermediate (step 1). This intermediate reacts with O_2 to produce a nitrooxy peroxy radical (step 2), which undergoes subsequent reactions to form a stable nitrate product (pathways $3a_1$, $3c_2$, $4a_1$) or dissociates to give NO_2 and an oxidized hydrocarbon (pathways 4b or 5) (Skov et al., 1992; Berndt and Boge, 1997). Both theoretical (Suh et al., 2001) and experimental (Skov et al., 1992; Kwok et al., 1996; Berndt and Boge, 1997) studies of the kinetics of NO_3 + isoprene have shown that addition of NO_3 at the C_2 or C_3 positions is negligible and that addition of NO_3 at the C_1 position (shown) dominates over addition at the C_4 position (not shown). Estimates range from 75–85% C_1 addition with the balance C_4 addition (Skov et al., 1992; Berndt and Boge, 1997). These estimates are consistent with structure-reactivity relationships described by Pfrang et al. (2006a, b) that indicate that the double bond between C_1 and $C_2$is almost an order of magnitude more reactive to NO_3 than the bond between C_3 and C_4 due to its increased substitution. Figure 1 shows those products resulting from initial NO_3 addition at the C_1 position. Pathways and products resulting from addition at other positions are similar to those shown here.

Due to the presence of conjugated double bonds in isoprene, the reaction of the alkyl radical with oxygen (step 2) forms both a δ-peroxy radical (pathway 2a) and a β-peroxy radical (pathway 2b) (Skov et al., 1992). Subsequent reactions of these peroxy radicals can lead to either keto or hydroxy nitrate products or to the release of NO_2 and production of an oxidized hydrocarbon via a short lived alkoxy radical intermediate. MVK and MACR are produced from reactions of the β-peroxy radicals. C_5 hydroxy carbonyls are thought to result from a cyclic hydrogen abstraction rearrangement of the δ-alkoxy radicals (pathway 5) (Kwok et al., 1996).

Here we report a product study of the NO_3 + isoprene reaction that incorporates comprehensive measurements of both the nitrogen and carbon containing products. This includes two independent, direct measurements of the nitrate product yield for the reaction of NO_3 with isoprene and a wide suite of oxidized hydrocarbon products.

2 Methods

The experiment was performed in a 5500 L PFA-Teflon-lined smog chamber at Purdue University. The chamber is described in detail elsewhere (Chen et al., 1998). NO_3 and N_2O_5 were produced in the chamber, via reactions 1 and 2, by injecting 400 ppbv of NO_2 and 145 ppbv of O_3 into dry zero air and allowing the mixture to react for ∼4 h.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (1)$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \quad (2)$$

38 L from a cylinder of 19.5±0.9 ppmv isoprene in nitrogen were injected into the smog chamber to give a calculated "initial" isoprene concentration of 134±7 ppbv. We define t=0 immediately prior to the isoprene addition. The full injection was completed by t=6 min and products were monitored for the subsequent half hour. Isoprene was consumed rapidly during the injection. O_3 was measured using a calibrated TECO Model42 UV absorption ozone monitor. The sampling flow was ∼50 sccm during the NO_3/N_2O_5 production phase and ∼3 L/min after isoprene injection, leading to an overall depletion of ∼3% in chamber volume by the end of the experiment (∼1 h after isoprene injection). Due to the low sampling rate, and to avoid dilution effects, no replenishment flow was supplied. The chamber volume varies by up to 8% with changes in internal pressure but has been routinely observed to be constant to within 1% over the course of a single-day experiment.

Alkyl and multifunctional nitrates (ΣANs), peroxy nitrates including N_2O_5 (ΣPNs), NO_2 and HNO_3 were measured by the Berkeley Thermal-Dissociation Laser Induced Fluorescence (TD-LIF) instrument (Thornton et al., 2000; Day et al., 2002). Briefly, gas is pulled simultaneously through each of 4 channels, one for each class of compounds listed above. Each channel consists of a section of heated quartz tube followed by detection of NO_2 using laser-induced fluorescence. Due to differing X-NO_2 bond strengths, ΣPNs, ΣANs and HNO_3 all thermally dissociate to NO_2 and a companion radical at a characteristic temperature. The ambient channel measures NO_2 alone, the second channel (180°C) measures NO_2 produced from the dissociation of ΣPNs in addition to ambient NO_2 so the observed signal is NO_2 + ΣPNs, the third channel (380°C) measures NO_2+ΣPNs+ΣANs and the last channel (580°C) measures NO_2 + ΣPNs+ΣANs+HNO_3. Concentrations of each class of compound correspond to the difference in NO_2 signal between two channels set at adjacent temperatures. The difference in NO_2 signal between the 180°C and the 380°C channel, for example, is the ΣANs mixing ratio. To minimize the

impact of secondary chemistry following thermal decomposition, the quartz tubes are maintained at reduced pressure (∼300 Torr).

NO_2 was observed by laser-induced fluorescence as described in detail by Thornton et al. (2000). Briefly, a tunable dye laser is pumped at 7 kHz by a Q-switched, frequency doubled Nd^{+3}YAG laser. The dye laser (Pyrromethene 597 in isopropanol) is tuned to a specific rovibronic feature of NO_2 around 585 nm. The frequency is held for 20 s at the peak of the feature and then for 5 s at an offline position in the continuum absorption and the NO_2 number density is proportional to the difference between the online and offline signals. The laser light is focused through two multipass (White) cells in series and the red-shifted fluorescence is detected using a red-sensitive photomultiplier tube (Hamamatsu). Fluorescence counts are collected at 5 Hz, scattered light at wavelengths less than 700 nm is rejected by bandpass filters and time-gated detection is used to eliminate prompt noise. Calibrations were performed at least once every two hours using a 4.7 ppmv NO_2 reference gas with a stated uncertainty of ± 5% which is regularly compared (∼6 months) to a library of tanks at UC Berkeley to confirm its stability.

The instrument used in these experiments had two detection cells. Cell 1 sampled either the ambient or the 380°C channel while cell 2 sampled either the 180°C or the 580°C channel. The direction of flow into the cell was controlled using a three-way valve and a bypass pump was used to maintain flow in the non-sampled channel. Cell 1 sampled the unheated NO_2 channel 25% of the time and the 380°C channel (ΣANs) 75% of the time. Cell 2 sampled the 180°C 75% of the time and the 580°C channels 25% of the time. Thus for every ∼2 min duty cycle there was 20 s of NO_2 data, 20s of ΣPNs data, 40 s of ΣANs data and 20 s of HNO_3 data. Here we have averaged to a 1 min time resolution.

A proton-transfer-reaction mass spectrometer (PTRMS-FDT-s, Ionicon Analytik GmbH, Innsbruck, Austria) was also used for trace gas analysis. This instrument detects gaseous molecules that have a higher proton affinity than H_2O which includes the large majority of polyatomic volatile organics and also a few inorganic molecules (e.g. HNO_2, HNO_3 and N_2O_5). The PTR-MS technique has been described in detail elsewhere (see reviews by Hansel et al., 1999; de Gouw and Warneke, 2007). The results presented here build on previous smog chamber work including product studies (Wisthaler et al., 2001; D'Anna et al., 2005; Wegener et al., 2007) and intercomparison exercises (Apel et al., 2008; Wisthaler et al., 2008).

Isoprene was calibrated using a dynamically diluted multicomponent VOC standard (Apel-Riemer Environmental Inc., Broomfield, CO, USA) containing ∼1.2 ppmv of isoprene. The specified accuracy of the gas mixture for isoprene was ±3% and a volumetrically calibrated isoprene standard prepared at Purdue University agreed to within 6%. The multicomponent VOC standard also contained ∼1 ppmv of acetone and methyl ethyl ketone (MEK), respectively, with a specified uncertainty of ±5%. Both ketones produced an identical instrumental response factor which was used as a proxy for determining the sum of the isomeric species MVK and MACR. Results from an intercomparison exercise (Apel et al., 2008; Wisthaler et al., 2008) have shown that the sum of MVK and MACR can be accurately (±5%) determined with this calibration approach. Volumetrically calibrated MVK and MACR standards prepared at Purdue University agreed to within 3% and 6%, respectively.

PTR-MS formaldehyde measurements are described by Wisthaler et al. (2008). PTR-MS response factors for formaldehyde were obtained by three independent methods: i) by calculation using simple pseudo first-order ion molecule reaction kinetics (Hansel et al., 1998; Wisthaler et al., 2008) ii) by using a permeation-tube-based gas standard generator (Dassau et al., 2002), and references therein) and iii) by using a molybdenum catalyst to quantitatively convert a calibrated amount of methanol into formaldehyde (Chu et al., 1997). Based on the uncertainties associated with the various calibration methods we estimate the accuracy of the formaldehyde values reported herein to be within -5% and +50%.

The detection of alkyl nitrates by PTR-MS is outlined in D'Anna et al. (2005) and Aoki et al. (2007). Both studies consistently show that the dominant chemical ionization pathway for alkyl nitrates is HNO_3 loss after protonation [MH^+-HNO_3], resulting in the formation of the bare alkyl ions. The protonated parent ions [MH^+] are only present in trace amounts (<2%) but both studies also indicate that, at standard PTR-MS operating conditions (E/N ∼ 120 Td; 1 Td=10^{-17} cm^2 V $molecule^{-1}$), significant amounts of the NO_2^+ fragment are produced from alkyl nitrates. To reduce this fragmentation, we lowered the E/N value to ∼75 Td where we expect the alkyl ions to dominate the mass spectrum (with minor contributions from hydrated alkyl ions [MH^+-HNO_3+H_2O] and alkoxy ions [MH^+-HNO_2]). The product studies described herein were performed in dry air and the primary PTR-MS reagent ions were H_3O^+ and $H_3O^+(H_2O)$ ions in an apparent 60:40 ratio. During a preliminary experiment the PTR-MS instrument was run in the full scan mode (scan range: m/z 20–241; dwell time: 0.1 s per m/z) to identify the m/z-signals of interest. In the experiment presented here the instrument was run in the selected ion monitoring (SIM) mode with a single ion dwell time of 0.5 s and a total SIM cycle time of 35 s.

Calibration factors for nitrates (INs) were obtained by assuming that nitroxy compounds have a ∼20% lower sensitivity than simple oxygenated compounds (D'Anna et al., 2005) and by taking into account typical alkyl nitrate fragmentation patterns (D'Anna et al., 2005; Aoki et al., 2007). We performed an intercomparison measurement with the TD-LIF instrument in which we sampled dry zero air passed over a home-made isopropyl nitrate permeation source and, based on this calibration approach, isopropyl nitrate data from both instruments agreed to within 12%. We estimate the PTR-MS accuracy for alkyl nitrates to be within −20% and +30%.

D'Anna et al. (2005) suggest that the variability of PTR-MS calibration factors for mono- and multi-functional VOCs is less than ±30% so it is reasonable to assume that even unidentified m/z-signals can be quantified with a similar accuracy.

Davidson et al. (1978) and Böhringer et al. (1983) have shown that both H_3O^+ and $H_3O^+(H_2O)$ ions react with N_2O_5 to produce NO_2^+, $NO_2^+(H_2O)$ and $NO_2^+(HNO_3)$ ions. The latter two are weakly bound ionic clusters which dissociate in the PTR-MS drift field to give an NO_2^+ signal at m/z=46. N_2O_5 is thus exclusively detected as NO_2^+; possible interferences at m/z=46 may arise from alkyl nitrates and HNO_3 (Wisthaler et. al, 2006). At low E/N the interference from alkyl nitrates is expected to be negligible and the HNO_3 contribution to the m/z=46 signal can be determined by thermally decomposing N_2O_5in the inlet as described below.

The commercial PTR-MS instrument used for this study was equipped with a ∼50 cm (ID: 0.01 in.) long passivated stainless steel capillary (Restek Corp., Bellefonte, PA, USA). The inlet flow was ∼50 sccm. A switchable 5-channel inlet system was set-up between PTR-MS instrument and the environmental chamber. Channel 1, in which chamber air was directly fed to the PTR-MS instrument, was active during most of the experiment. At the end of the experiment chamber air was sequentially directed to the instrument via inlet channels 2 through 4, which were kept at 150, 250, and 350°C, respectively, and via channel 5, which included a basic scrubber (Na_2CO_3 impregnated nylon wool). All channels were connected to the PTR-MS instrument via 3-way Teflon solenoid valves (Teqcom Industries, Inc. Santa Ana, California, USA). Depending on valve position the flow was either fed to the PTR-MS instrument or discarded into a pump. Channels 2–4 were used for thermal decomposition studies similar to the approach used in the TD-LIF instrument (Day et al., 2002). In contrast to the TD-LIF where the increase in NO_2 with temperature is monitored, in the PTR-MS instrument the signal decrease with increased inlet temperature can be used to identify thermolabile species such as PAN-type compounds (Hansel et al., 1999), alkyl nitrates (Aoki et al., 2007) or N_2O_5. The basic scrubber was used to aid identification of acidic compounds. The instrumental background was determined using zero air from a zero air generator (Parker-Balston, Haverhill, MA, USA). All inlet lines were temperature-controlled at 35°C. The drift tube was kept at 60°C.

3 Results

The environmental chamber was flushed overnight with dry ultrapure zero air. O_3 and NO_2 were sequentially injected and reached steady-state levels of 10 ppbv and 230 ppbv respectively, prior to injection of isoprene. The TD-LIF instrument sampled from the chamber approximately once per hour and observed increases in both $\sum$PNs (including N_2O_5) and HNO_3 which has been seen to be produced from conversion of N_2O_5 to HNO_3 in previous smog chamber studies (Tuazon et al., 1983). NO_y was lost to the walls at an average rate of ∼4% per hour for the 4 h prior to injection, corresponding to a wall loss rate of $5{\cdot}10^{-6}$ s^{-1} for N_2O_5 or $2.5{\times}10^{-6}s^{-1}$ for HNO_3 although it should be noted that the overall loss rate of N_2O_5 may be faster than the wall loss rate alone.

The PTR-MS instrument sampled from the chamber continuously and observed increases of greater than 1 ppbv in ion signals at m/z=31, 45, 46, 47, 59, 61 and 64. The ion signals at m/z 31, 45 and 59 arise from formaldehyde, acetaldehyde and acetone/propanal. The m/z 47 and m/z 61 signals are assigned to formic acid and acetic acid/hydroxyacetaldehyde, respectively. These carbonyls and carboxylic acids are believed to be formed during the O_3 generation/injection process and/or due to heterogeneous reactions with organic impurities on the chamber walls. As they are less reactive with NO_3 than isoprene (Wayne et al., 1991), their presence at low concentrations does not affect the experimental results presented here. In the case of formaldehyde a background concentration of 1.5 ppbv present in the chamber prior to isoprene injection was subtracted to calculate product yields of the isoprene-NO_3 reaction.

The m/z 46 and m/z 64 signals are produced from both HNO_3 ([MH^+-H_2O], [MH^+]) and N_2O_5 ([MH^+-HNO_3], [MH^+-HNO_3+H_2O]). Thermal decomposition of N_2O_5 in the 150 ° C PTR-MS inlet channel 2 made it possible to quantify the relative contributions of N_2O_5 and HNO_3 to the observed signal and the HNO_3 signal observed at the end of the experiment was subtracted from the total to calculate N_2O_5. A calibration factor calculated purely from ion-molecule reaction kinetics was scaled by −15% to bring the TD-LIF and PTR-MS measurements of HNO_3 at the end of the experiment into agreement. This allowed us to take advantage of the fast time resolution and continuous coverage provided by the PTR-MS measurement. Approximately half an hour prior to the isoprene injection, the TD-LIF observed ∼42 ppbv HNO_3 and ∼90 ppbv $\sum$PNs (including N_2O_5) and just prior to injection the PTR-MS observed ∼82 ppbv N_2O_5. NO_3 was calculated to be ∼540 pptv just prior to injection.

A nominal 134 ppbv of isoprene (38L nitrogen containing 19.5 ppmv isoprene was diluted into a volume of 5500L) was injected into the chamber over 6 minutes, during which time the isoprene was partially consumed by reaction with NO_3. The PTR-MS instrument detected a ∼100 ppbv increase in the m/z=69 ion signal, assigned to isoprene, and a simultaneous increase in a series of ion signals from the products of the isoprene-NO_3 reaction. Both instruments observed a rapid consumption of N_2O_5. N_2O_5 measured by PTR-MS decreased to ∼5 ppbv after half an hour and $\sum$PNs decreased to ∼8 ppbv. Since the $\sum$PNs measurement would detect not only N_2O_5 but also any other peroxy- or peroxy-acyl nitrates present in the chamber, it is not surprising that it is slightly

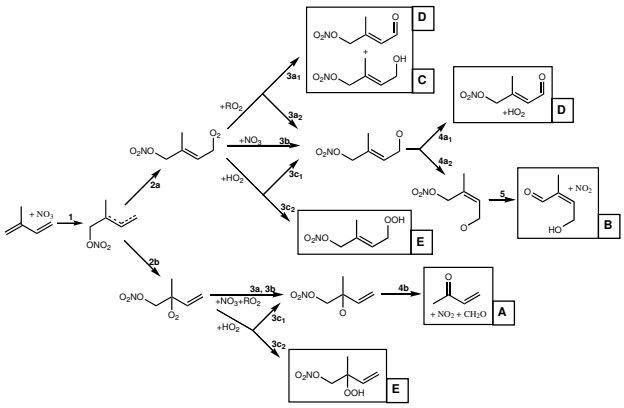

Fig. 1. Partial oxidation scheme for NO_3+isoprene showing products resulting from initial addition of NO_3 at the C_1 position. Capital letters indicate the type of product molecule shown as follows: C_4-carbonyls **(A)**, C_5-hydroxycarbonyls **(B)**, hydroxy-nitrates **(C)**, nitrooxy-aldehydes **(D)** and nitrooxy-hydroperoxides **(E)**.

higher than the N_2O_5 measured by PTR-MS. It should be noted that both instruments will respond to HO_2NO_2 in the same signal as N_2O_5 but HO_2NO_2 concentrations are not expected to exceed 5 ppbv.

4 Product identification

Major product ion signals were observed at m/z=31, 43, 71, 83, 85, 87, 99 and 101 with minor product signals detected at m/z=(89), (103), (105), (117), (119), 130, 132, 146, 148, 162, 164. Signals written in parentheses are believed to be hydrated ions [MH^++H_2O] of the major signals given above and will not be discussed further. In PTR mass spectra even-numbered signals are produced from compounds containing one nitrogen atom so the even-numbered high molecular weight signals are indicative of the formation of nitrooxy compounds. Experiments involving isoprene addition without NO_3 present showed that the non-isoprene signals were not due to impurities in the isoprene standard.

The observed PTR mass spectrum of the products of the isoprene-NO_3 reaction is in excellent agreement with a previously reported API mass spectrum (Fig. 2 in Kwok et al., 1996). PTR-MS and $H^+(H_2O)_n$-based API-MS are closely related techniques and similar mass spectra are expected. In general, our results are consistent with the associated compound assignments. The main differences between the two mass spectra are as follows: i) Kwok et al. (1996) do not report ion signals below m/z 69; ii) Kwok et al. (1996) report the formation of protonated dimers while such dimers are not observed in the PTR-MS instrument at the concentration levels present in our experiments.

Based on MS/MS analyses and isoprene d_8-studies Kwok et al. (1996) identified product ions, in ascending order of mass, as follows: m/z 71 [MH^+] as the sum of MVK and MACR (A), m/z 101 [MH^+] as C_5 hydroxycarbonyls (B), m/z 130 [MH^+-H_2O] and m/z 148 [MH^+] as hydroxy-nitrates (C), m/z 83 [MH^+-HNO_3] and m/z 146 [MH^+] as nitrooxy-aldehydes (D) and m/z 164 [MH^+] as nitrooxy-hydroperoxides (E). Capital letters in parentheses indicate the respective compounds in the reaction scheme shown in Fig. 1. Note that neither API-MS nor PTR-MS resolve isomers that arise from NO_3 addition at different positions on the isoprene molecule.

We sampled chamber air through three heated inlets (150°C, 250°C and 350°C) and one inlet equipped with a basic scrubber. We use these observations to aid in compound assignment and identification of thermally labile or acidic compounds. Confounding results may occur however if multiple species are detected on the same m/z signal in that one compound may be destroyed upon heating while another, detected at the same m/z, is formed upon heating. The absolute and relative changes of the main product signals are reported in Table 1. Low intensity signals are not included in the table but all even numbered high molecular weight signals disappeared at 350°C as expected for nitrooxy-compounds. Notably, all of these nitrooxy-compounds were completely removed by the basic scrubber indicating that a similar uptake may occur on basic surfaces in nature.

The ion signal at m/z 71 was partially scrubbed by the basic filter indicating either that some species other than MVK and MACR may also produce that ion signal or that MVK and/or MACR are partially removed by the basic scrubber. We therefore recommend reported MACR+MVK yields to be taken as an upper limit. Also, we should note that when air was sampled through the 350°C PTR-MS inlet, the m/z 69 signal decreased by ∼4 ppbv which leads us to deduce either a minor (<5%) interference from a thermolabile species detected at m/z 69 or a partial decomposition of isoprene in the 350°C inlet. The impacts of both the basic scrubber and thermal decomposition on observed isoprene and (MACR+MVK) concentrations were assessed during a separate experiment and no losses were observed for either m/z. It is therefore likely that the interferences reported here result from the presence of additional compounds at the same m/z as isoprene and (MACR+MVK). Due to the small size of the potential interference, however, we do not consider this effect in further analysis.

The ion signal at m/z 101, indicative of C_5-hydroxycarbonyls with possible minor contributions from hydroxy-nitrates [MH^+-HNO_2], nitrooxy-carbonyls [MH^+-HNO_3+H_2O] and nitrooxy-hydroperoxides [MH^+-HNO_3], was observed to decrease somewhat with increasing temperature and to decrease strongly when sampling through the basic scrubber. C_5-hydroxycarbonyls are expected to show such behavior although we would expect full decomposition at 350°C. As pointed out above, the thermal decay may be obscured by formation of a different species also detected at m/z 101.

Table 1. Changes in observed m/z signals,reported as both absolute changes in concentration and as percentage changes, following thermal decomposition at 150°C (columns 1 and 2), 250°C (columns 3 and 4) and 350°C (columns 5 and 6) and following passage through a basic scrubber (columns 7 and 8).

m/z	150°C		250°C		350°C		basic scrubber	
	Δppbv	Δ%	Δppbv	Δ%	Δppbv	Δ%	Δppbv	Δ%
31	+0.6	+10%	+5.9	+108%	+12.9	+234%	−0.7	−13%
43	±0	±0%	±0	±0%	−1.0	−26%	−2.0	−53%
71	±0	±0%	+2.1	+40%	+6.0	+112%	−1.9	−35%
83	−5.2	− 8%	−17.7	−62%	−24.8	−87%	−27.1	−94%
85	+1.7	+85%	+2.4	+1 17%	+2.7	+131%	−1.7	−85%
87	+0.4	+17%	+0.9	+36%	+0.8	+30%	−0.3	−13%
99	+5.0	+197%	+10.8	+424%	+9.4	+367%	+14.5	+568%
101	−0.3	−8%	−1.0	−27%	−1.4	−39%	−3.1	−86%

The ion signal at m/z 83 shows a ∼90% decrease at both 350°C and when sampling through the basic scrubber. Nitrooxy-carbonyls have been seen to be a major product of the isoprene-NO_3 reaction (Barnes et al., 1990; Skov et al., 1992; Kwok et al., 1996; Berndt and Boge, 1997). We expect their main appearance at this ion mass [MH^+-HNO_3]. m/z 83 may also be generated from the C_5-hydroxy-carbonyls [MH^+-H_2O] but previous work (Kwok et al., 1995; Zhao et al., 2004) indicates that detection of C_5-hydroxycarbonyls at m/z 101 dominates over that at m/z 83 and we therefore conclude that the m/z = 83 signal is dominated by nitrooxy-carbonyls. We attribute the ion signal at m/z 146 to nitrooxy-carbonyls but note that it may also be produced from dinitrates [MH^+-HNO_2], nitrooxy-peroxy-nitrates [MH^+-HNO_3] and nitrooxy-hydroperoxides [MH^+-H_2O]. m/z 164 may arise from the nitrooxy-hydroperoxides [MH^+] or nitrooxy-peroxy-nitrates [MH^+-HNO_3+H_2O]or it may simply be the hydrated m/z 146 ion [MH^++H_2O].

In addition to the ion signals reported by Kwok et al. (1996), we also observed signals at m/z 31, 43, 85, 87, 132 and 162. The signal at m/z 31 is assigned to formaldehyde [MH^+]. The signal at m/z 43 is a CH_3CO^+ fragment ion that cannot be assigned to a specific parent molecule but MS/MS spectra from hydroxy-nitrates show an intense fragment at m/z 43 (Kwok et al., 1996). The signal at m/z 85 may be an additional hydroxy-nitrate signal [MH^+-HNO_3] although the epoxide (C_5H_8O), which has been observed in low-pressure studies but is not thought likely at atmospheric pressure (Skov et al., 1994) would also be detected at that mass. Nitrooxy-carbonyls may give rise to a m/z 99 signal [MH^+-HNO_2] in addition to the signal at m/z 146 and the ion signal at m/z 162 seems to be specific for the nitrooxy-peroxy-nitrates [MH^+-HNO_2]. The signals detected at m/z 87 and 132 remain unassigned.

5 Product quantification and yields

Clearly compound identification in PTR-MS and API-MS is non-trivial as the ion formed upon loss of functional groups (-ONO_2, -NO_2, -OH) after protonation is not necessarily specific to a single compound. Although we are unable to identify all detected compounds with certainty, we take advantage of the inherent similarity of PTR-MS calibration factors for oxygenated species to convert product ion signals at m/z=31, 43, 71, 83, 85, 87, 99 and 101 into volume mixing ratios. PTR ionization occurs under well-defined conditions (temperature, pressure, reaction time) and strictly follows pseudo-first-order kinetics. As proton transfer reaction rate coefficients are similar to within ±30% for all oxygenated species, calibration factors for oxygenates including multifunctional compounds containing carbonyl, hydroxy and nitrooxy groups can be determined to within ±30% (D'Anna et al., 2005).

As described above, the m/z=31 signal was calibrated using several different formaldehyde standards with an estimated accuracy of -5 to +50%. For the remaining signals we used a calibration factor typical of C_3 and C_4 carbonyls and using this quantification, we observe mass balance in the carbon-containing products to within 10%. We assume that all observed signals except that for formaldehyde arise from C_5 compounds. MVK and MACR (m/z=71) are C_4 compounds, but the simultaneously formed C_1 fragment (formaldehyde) was observed in approximately the same amounts as MVK and MACR so if formaldehyde is excluded from the mass balance, m/z 71 can be treated as a C_5 compound. The signal at m/z=43 is assumed to be an ionic fragment of a C_5 compound. The sum of isoprene and all major products is 134±16 ppbv at the beginning of the experiment and 144±17 ppbv at the end of the experiment (solid blue line in Fig. 2a). The observed 7% increase may be explained by small differences in PTR-MS calibration factors for different species or by incomplete chamber mixing. The initially observed sum of isoprene and

all major products of 134±16 ppbv is in excellent agreement with the calculated injected isoprene mixing ratio of 134±7 ppbv, shown in Fig. 2a as a shaded gray region. We can also assess the carbon balance by comparing the total concentration of products formed to the isoprene consumed ($\text{isoprene}_{\text{injected}}-\text{isoprene}_{\text{measured}}$). The isoprene consumed increases from 38±8.5 ppbv to 42±8.5 ppbv from t=8 min to t=18 min while the total products measured increases from 40 +13/−10 ppbv to 46 +13/−10 ppbv over the same interval. The agreement between the calculated isoprene consumed and the observed products is slightly better at the beginning of the experiment than at the end although the two quantities agree to within the experimental error for the entire interval.

Figure 2b shows the time evolution of the main product ion signal observed at m/z=83 (nitrooxy-carbonyls) together with the $\sum$(organic nitrates) signal determined by the TD-LIF instrument. The two measurements agree well and, as expected, the nitrooxy-carbonyls account for almost all (> 95%) of the $\sum$(organic nitrates) produced from the isoprene-NO_3 reaction. The uncertainty in the PTR-MS data is estimated to be −20% to +30% and, as discussed above, we have seen evidence of additional nitrooxy compounds at m/z ratios other than 83. If all signals except the portion of the m/z 71 signal which is not scrubbed by the basic scrubber (corresponding to the sum of MVK + MACR) are assumed to arise from organic nitrates this would increase reported nitrooxy-carbonyl concentrations by 30%. This is an upper limit for total nitrates which is in reasonable agreement with the upper margin (+15%) in the TD-LIF data.

Figure 2c shows the time evolution of the other observed product ion signals. It is interesting to note that they do not all have the same temporal behavior. Signals at m/z=99 and m/z=101, for example, continue to increase after most other concentrations have reached steady state and the signal at m/z=101 continues to increase even after m/z=99 has plateaued.

The fact that the sum ($\text{isoprene}_{\text{measured}}+\text{products}_{\text{measured}}$) matches ($\text{isoprene}_{\text{injected}}$) implies that we are likely not missing any major products and that the calibration factors for the unidentified products are reasonably accurate. The fractional yield of any one product can therefore be calculated simply as the concentration of that product divided by the sum of all products. Figure 3a shows the observed correlation between the signal at m/z 71 and the sum of all products seen by PTR-MS. MVK and MACR are formed with an 10% yield (upper limit); considering a potential ∼35% signal interference (as indicated by the signal drop when the basic filter is switched in) this could be as low as 7%. This value is in excellent agreement with the GC-derived MACR and MVK molar yields of 3.5% each (Kwok et al., 1996). Figure 1 shows MVK production. MACR production arises from the analogous NO_3 addition at the C_4 position. Formaldehyde was observed in 11(+5/−1)% yield, slightly higher than expected from simultaneous production with MVK and MACR. This value is, however, in excellent agreement with the 11% yield reported by Barnes et al. (1990). Skov et al. (1992) report a formaldehyde yield <5%. Figure 3b displays the correlation between the LIF $\sum$ANs measurement and the sum of all products and between the PTR-MS m/z=83 measurement and the sum of all products. These correlations imply a nitrooxy-carbonyl formation ratio of between 63% (based on PTRMS) and 67% (based on LIF) from NO_3+isoprene.

We can also calculate fractional yields as the concentration of a given product divided by the difference ($\text{isoprene}_{\text{injected}}-\text{isoprene}_{\text{measured}}$). This has the advantage of depending solely on the injected amount and the PTR-MS measurement of isoprene which has been rigorously tested and compared with other measurement techniques rather than on the quantification of unidentified products. This calculation gives slightly but not significantly different product yields as implied by the agreement between ($\text{isoprene}_{\text{measured}}+\text{products}_{\text{measured}}$) and ($\text{isoprene}_{\text{injected}}$).

Upper limits for total nitrates are ∼82% (PTR-MS derived) and 81% (TD-LIF derived) as determined by the uncertainties in the PTR-MS m/z 83 calibration (−20%/+30%), the uncertainty associated with the TD-LIF $\sum$ANs measurement (10%) and the combined uncertainties in the sum of the measured products (roughly −20%/+30%, similar to that for the m/z 83 signal). Taking instrumental errors and the 95% confidence interval for the linear fits into account, the range of nitrate formations based on the present, carbon-based calculation are 63±18% (PTR-MS) and 67±15% (LIF) to give an overall value of 65±12%. Barnes et al. (1990) and Berndt and Böge (1997) report values of 80% (a rough estimate) and 90–95% total nitrate yields, respectively. We note that the "yields" are not necessarily fixed fundamental quantities, as they depend on the relative concentrations of NO_3 and RO_2/HO_2 radicals (see Fig. 1), and thus potentially on the reaction conditions.

The molar yields for the other signals are: m/z 43 (7.5%), m/z 85: (2%), m/z 87 (5.5%), m/z 99 (5%) m/z 101 (7%). It should be noted that part of the m/z 99 and m/z 101 signals may also represent additional nitrooxy-carbonyl compounds as it is difficult to assign these signals to specific compounds. If we assume that m/z 43 derives from the hydroxy-nitrates and consider that m/z 130 (which would result from dehydration of the quasi-molecular hydroxy-nitrate ion at m/z 148) is the second most abundant of the minor, even-numbered product ion signals (m/z 146, nitrooxy-carbonyls, being the most abundant), we can speculate that the hydroxy-nitrates are the second most abundant of the nitrooxy species, but we are unable to quantify the yield.

The suite of observations of the various reactive nitrogen species offers a second, independent lens through which to assess the fractional yield of INs in the NO_3+isoprene reaction. The TD-LIF observed a decrease in total NO_y between half an hour prior to and just after isoprene injection. A similar effect had been observed previously and we believe this was due to particle or droplet formation or some other process which removed N_2O_5 from the gas phase precipitated

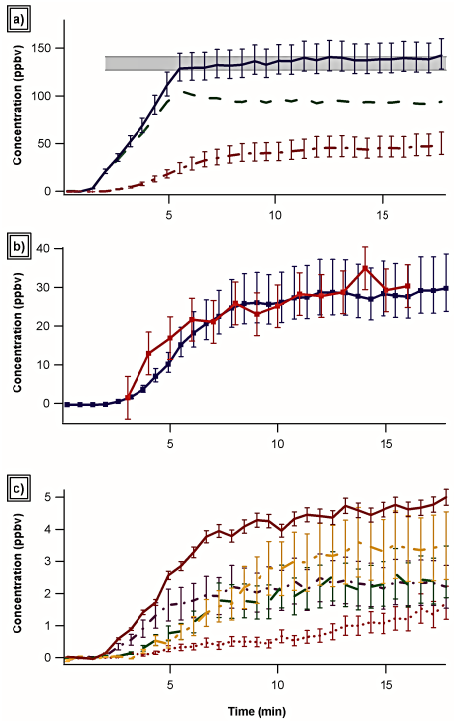

Fig. 2. a) Time evolution of isoprene (green dashed), the sum of all products (pink dash-dot) and the sum of isoprene and all products (blue solid) as compared to injected isoprene (shaded gray) **b)** Time evolution of the nitrogen-containing products as measured by both LIF (total nitrates in red) and PTR-MS (nitrooxy carbonyls in blue) and c) Time evolution of the following non-nitrate carbonyl products as measured by PTR-MS: MACR+MVK (solid red), m/z 101 (yellow dot-dot-dash), m/z 99 (green dash), m/z 87 (blue dot-dash) and m/z 85 (pink dotted).

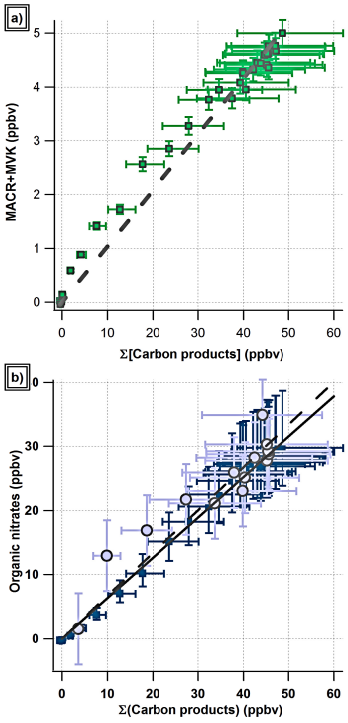

Fig. 3. Top panel a): (MACR+MVK) formed vs. total products formed (green squares) with the best fit line which has a slope of 0.103±0.001 (R^2=0.992). Bottom panel b): Dark blue squares are m/z 83 (PTR-MS nitrooxy carbonyls) vs. total products formed, slope=0.63±0.003 (R^2=0.998). Light blue circles are $\sum$ANs (LIF nitrates) vs. total products formed, slope=0.67±0.023 (R^2=0.944).

by the presence of extremely high localized concentrations of isoprene. Once the isoprene injection was complete, nitrogen closure for the subsequent 20 min was better than 95%. For the portion of the experiment where total NO_y is constant, we extract information about the nitrate yield from the relationships between the NO_y reservoirs which are interconverting. Using a rate constant of $3.03{*}10^{-12} * e^{-440/T}$ for NO_3+isoprene (Dlugokencky and Howard, 1989), the lifetime of NO_3 against reaction with 100 ppbv of isoprene is less than 1 s but NO_3 will be regenerated from N_2O_5, which has a thermal lifetime of about 20s, until NO_3 and N_2O_5 reach a stationary state with the NO_2, O_3 and isoprene in the chamber. Thus, the amount of NO_3 that will react rapidly with isoprene is equal to the initial sum (NO_3+N_2O_5) which is converted into either NO_2 or INs via the interaction between isoprene and NO_3. If the NO_3+isoprene reaction is the only process converting one NO_y reservoir into another, then we would expect $\sum$ANs and N_2O_5 to be related as follows, where $\alpha$is the nitrate formation branching ratio:

$$\Delta\Sigma[\mathrm{ANs}] = \alpha\Delta[\mathrm{N_2O_5}] \quad (3)$$

Figure 4 shows the correlations observed between both the TD-LIF measurements of N_2O_5 and $\sum$ANs (circles) and the PTR-MS measurements of N_2O_5 and m/z 83 (squares). The slopes of these correlations are −0.56 (R^2=0.95) and −0.57 (R^2=0.973) respectively corresponding to an IN yield of 57±11% accounting for the 95% confidence interval for the linear fits and instrumental uncertainties. As noted above, the TD-LIF $\sum$PNs measurement was ∼3 ppbv higher than the PTR-MS measurement of HO_2NO_2+N_2O_5, possibly due to the presence of other peroxy-nitrate compounds. These issues should not, in fact, impact the slope of the correlation but simply change the intercept of the best-fit line and the absolute agreement of the two N_2O_5 observations.

6 Discussion

The discrepancy between the carbon- (65%±12%) and nitrogen- (57%±11%) based calculations of nitrate yield for NO_3+isoprene is small but significant. As discussed above, the carbon-based calculation could be an overestimate if there are appreciable unmeasured products. Similarly, the nitrogen-based calculation could be an underestimate if there is a significant reaction that converts NO_3 directly into NO_2

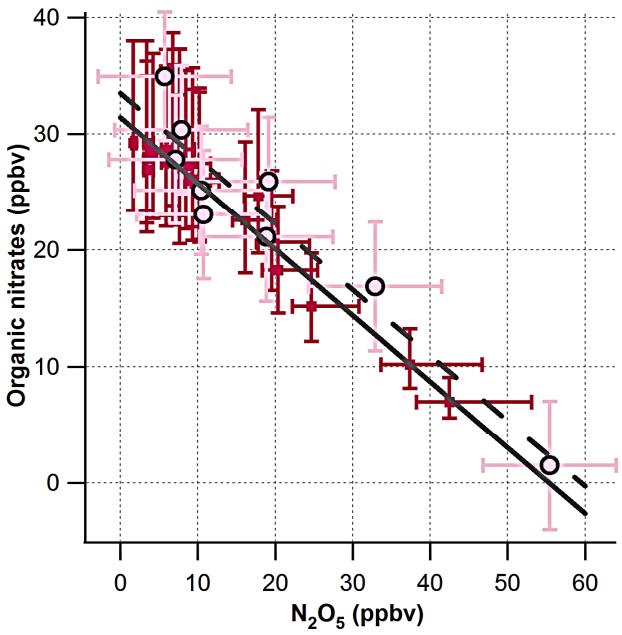

Fig. 4. Red squares and the solid line show the correlation between N_2O_5 and m/z 83 as observed by PTR-MS, slope=−0.57±0.029 (R^2=0.973). Light pink circles with black outline and the dashed line show the correlation between N_2O_5 and $\sum$ANs as observed by the LIF, slope=−0.56±0.069 (R^2=0.95).

other than the NO_3+isoprene reaction. Since the two measurements of the nitrate products agree well, the discrepancy between the two yields is driven entirely by our different proxies for the extent to which reaction has occurred.

For the carbon budget calculation we used the sum of all measured products to infer the amount of isoprene that had reacted and for the nitrogen budget we used ΔN_2O_5 to infer the amount of NO_3 consumed by reaction with isoprene. The first method assumes that we have measured all of the possible products, an assumption supported by the fact that the calculated "initial" isoprene and the observed sum of isoprene+ products agree to within 10%. The second method assumes that NO_3 and N_2O_5 interact with only isoprene and do not deposit to or react with the walls of the chamber or any other chemical species. NO_3 is likely lost both to the walls of the chamber and to reaction with RO_2 and HO_2 and products such as MVK, MACR, and HCHO, making the calculation for the nitrate branching ratio based on nitrogen a lower limit. The yield based on measured carbon products is likely more accurate of the two and we take our best estimate of the nitrate formation ratio to be 65±12% given all of the results and the instrumental uncertainties. We note, however, that much of the uncertainty in this result is driven by the instrumental uncertainty in the PTR-MS isoprene nitrate calibration (stated as −20%/+30%). The uncertainty in the LIF detection of isoprene nitrates (∼10%) is much smaller and the fact that the two detection methods agree to within 10% indicates that the accuracy of the PTR-MS calibration is likely better than the stated uncertainty. The real uncertainty in the nitrate yield presented here is therefore likely smaller than the stated uncertainty of 12%.

The nitrate yield of 65±12% for the NO_3+isoprene reaction given here is slightly lower than the previously reported value of 80% by Barnes et al. (1990). The Barnes et al. measurement depends on an estimated IR cross section for the nitrate functional group rather than on a product mass balance. Both of the techniques used in this study are more direct measurements of the nitrate product. The observation of closure in both the nitrogen and carbon budgets lends strong support for the reaction proceeding as outlined above and the uncertainty in the nitrate yield is smaller than that previously reported (±20%). This measured yield implies that a significant amount of NO_2 is regenerated via reactions similar to pathways 4b and 5 shown in Fig. 1.

The majority of isoprene oxidation occurs during the daytime and via reaction with OH but the much higher nitrate formation branching ratio for the NO_3 oxidation pathway means that uncertainties in the nitrate yield of this pathway will have a large impact on overall ΣAN concentrations. Atmospheric concentrations of INs derived from NO_3+isoprene, and thus their effectiveness as a NO_x reservoir and their availability for incorporation into SOA, however, are determined not only by formation processes but also by their atmospheric lifetime to deposition and further oxidation. We note that these nitrates, which retain a double bond, will be rapidly oxidized in the atmosphere. Highly oxidized products of isoprene oxidation have been seen to be an important component of SOA formation (Kroll et al., 2005, 2006; Surratt et al., 2006; Ng et al., 2007) and this could be especially important in the relatively humid and cool nighttime boundary layer environment.

As discussed above, previous studies (Barnes et al., 1990; Skov et al., 1992; Kwok et al., 1996; Berndt and Boge, 1997) have indicated that the major products will be hydroxy and carbonyl nitrates with the non-nitrate functional group δ to the nitrate. Rollins et al. (2009) observed a rate constant of 7×10^{-14} cm^3/sfor oxidation of isoprene nitrates by NO_3 at room temperature (about an order of magnitude slower than the reaction of NO_3 with isoprene) and the results presented here agree with this finding. If the product nitrates are more reactive than isoprene itself, we would expect to see appreciable dinitrate formation which would make the PTR-MS and LIF nitrate measurements diverge significantly. In general the presence of an OH group is expected to enhance the reactivity of a double bond to addition by OH or NO_3 while the presence of a carbonyl or nitrate functional group is expected to diminish it. By analogy, the reactivity of the double bond in MVK is 20 times less reactive than that in the non-oxidized C_4 analogue 1-butene. Although isoprene nitrates produced from NO_3+isoprene are less reactive to NO_3 than is isoprene itself importantly, they will be rapidly consumed by OH and O_3, with daytime lifetimes on the order of a few

hours. Thus a significant fraction of the ΣAN in isoprene-impacted boundary layers is likely highly oxidized.

The permanence of INs as a NO_x reservoir is also uncertain. This has to do partly with their oxidative lifetimes but also with the products formed from further oxidation of INs. If INs maintain their nitrate functionality through an additional oxidation step, the resulting compounds would be small keto- and hydroxy-nitrates and di-nitrates which could allow for transport of oxidized nitrogen on local, regional and global scales. However these highly polar, multifunctional product nitrates may also be likely to deposit via wet or dry deposition (Shepson et al., 1996). If, on the other hand, subsequent oxidation leads to the release of NO_2, then INs would constitute only a temporary NO_x reservoir. Earlier work has shown a high (75–90%) recycling efficiency for nitrate products (i.e. a low probability of NO_x regeneration) resulting from the OH-initiated oxidation of isoprene (Paulot et al., 2009; Perring et al., 2009) but the structural isomers likely differ widely from each other on an individual basis and the nighttime chemistry is sufficiently different that the same conclusions may not apply.

7 Conclusions

The initial step in the oxidation of isoprene by NO_3 was studied in a 5500L smog chamber using PTR-MS and TD-LIF. The combination of these measurements allows us to close both the nitrogen and carbon budgets over the course of the experiment. The organic nitrate yield for the NO_3+isoprene reaction was calculated from both the carbon and nitrogen perspective and found to be 65±12%. This is a downward revision and a significant reduction in uncertainty as compared to the previously reported 80% yields. Other products from this reaction include, MACR and MVK which were produced in a combined 10% yield, in rough agreement with previous studies. Small (<10%) yields of hydrocarbon products at masses 85, 87, 99 and 101 were also observed. The lower IN yield we report will have significant effects on predictions of local and global concentrations of alkyl and multifunctional nitrates or ΣANs and on NO_x. However, while these carbonyl nitrates are produced in substantial yields from NO_3 reaction with isoprene, they are likely quite short lived (a few hours) in the atmosphere. How changes to nocturnal isoprene chemistry affect predictions will thus depend in detail on treatment of the second generation oxidation step in the chemical mechanism. The reaction kinetics and mechanisms for OH, O_3, and NO_3 reaction with these olefinic carbonyl nitrates are poorly known and require further study.

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