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lifetime of isoprene
nitrates**

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Interactive Discussion

Airborne observations of total RONO$_2$: new constraints on the yield and lifetime of isoprene nitrates

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Abstract

Formation of isoprene nitrates (INs) is an important free radical chain termination step ending production of ozone and possibly affecting formation of secondary organic aerosol. Isoprene nitrates also represent a large, unmeasured contribution to OH reactivity and are a major pathway for the removal of nitrogen oxides from the atmosphere. Current assessments indicate that formation rates of isoprene nitrates are uncertain to a factor of 2–3 and the subsequent fate of isoprene nitrates remains largely unconstrained by laboratory, field or modeling studies. Measurements of total alkyl and multifunction nitrates (ΣANs), NO_2, total peroxy nitrates (ΣPNs), HNO_3, H_2CO, isoprene and other VOC were obtained from the NASA DC-8 aircraft during summer 2004 over the continental US during the INTEX-NA campaign. These observations represent the first characterization of ΣANs over a wide range of land surface types and in the free troposphere. ΣANs were a significant, 12–20%, fraction of NO_y throughout the experimental domain and ΣANs were more abundant when isoprene was high. We use the observed VOC to calculate the relative contributions of ΣAN precursors to their production. These calculations indicate that isoprene represents at least 76% of the ΣAN source in the summertime continental boundary layer of the US. An observed correlation between ΣANs and CH_2O is used to place constraints on nitrate yields from isoprene oxidation, atmospheric lifetimes of the resulting nitrates and recycling efficiencies of nitrates during subsequent oxidation. We recommend sets of production rates, lifetimes and recycling efficiencies of INs as follows [4.4%, 5 h, 92%], [8%, 2.5 h, 84%] and [12%, 90 min, 74%]. The analysis indicates that the lifetime of ΣANs as a pool of compounds is considerably longer than the lifetime of the individual isoprene nitrates to reaction with OH, implying that the organic nitrate functionality is at least partially maintained through a second oxidation cycle.

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1 Introduction

Global isoprene emissions are estimated at 400–500 Tg/yr, more than the estimated sum of all anthropogenic non-methane organic compounds (130 Tg/yr) (Piccot et al., 1992; Guenther et al., 1995; Bey et al., 2001). Isoprene emissions and subsequent chemistry are thus major influences on tropospheric chemistry with notable effects on O_3, secondary organic aerosol, OH concentrations and on the NO_y budget (NO_y=NO+NO_2+HNO_3+peroxy nitrates (ΣPNs)+alkyl and mulitfuctional nitrates (ΣANs)+other minor species) (Atkinson et al., 1983; Houweling et al., 1998; Fiore et al., 2005; Wu et al., 2007; Ito et al., 2007). Recent experiments and calculations show that there is still much to be learned about the chemistry of isoprene and its oxidation products. For example, chamber experiments now show that isoprene photooxidation can be an important source of SOA (Kroll et al., 2005; Boge et al., 2006; Lee et al., 2006) consistent with the implications of field observations of tetrols with an isoprene backbone (Claeys et al., 2004).

Uncertainties in the gas phase chemistry remain as well. Analyses of field measurements imply that the reaction of isoprene hydoxyperoxy radicals with HO_2 is not an effective HO_x chain termination step (Thornton et al., 2002) and there are several observations indicating that there is higher OH than predicted by models in the presence of isoprene. (Tan et al., 2001; Ren et al., 2003; Kuhn et al., 2007; Lelieveld et al., 2008). In particular, we note that there are no laboratory experiments in which a complete carbon balance for the oxidation of isoprene by OH, O_3 or NO_3 have been reported. We focus here primarily on the OH-initiated pathway and Table 1 summarizes the findings of past product studies.

Photooxidation of isoprene is initiated by the addition of OH (R_1), and then O_2 (R_2), resulting in the formation of six chemically distinct unsaturated hydroxyperoxy radicals.

$$C_5H_8 + OH \rightarrow C_5H_8(OH) \tag{R1}$$

$$C_5H_8(OH) + O_2 \rightarrow C_5H_8(OH)O_2 \tag{R2}$$

The reactions of these peroxy radicals with NO have two product channels. The dominant channel, R_{3a}, propagates the HO_x and NO_x catalytic cycles with production of NO_2 and an alkoxy radical which rapidly undergoes subsequent reactions while the minor channel, R_{3b}, results in production of a stable unsaturated hydroxynitrate.

$$C_5H_8(OH)O_2 + NO \rightarrow C_5H_8(OH)O + NO_2 \qquad\qquad (R3a)$$
$$C_5H_8(OH)O_2 + NO \rightarrow C_5H_8(OH)ONO_2 \qquad\qquad (R3b)$$

Examples of each class of the observed products from Table 1 are shown in Fig. 1. The more recent studies have found higher combined yields of methacrolein (MACR) and methyl vinyl ketone (MVK) than previously reported, (Sprengnether et al., 2002; Karl et al., 2006) and appreciable yields of C5 carbonyls and hydroxy-carbonyls have been observed. (Zhao et al., 2004; Baker et al., 2005) A number of studies have reported small (<5%) yields of 3-methylfuran (Atkinson et al., 1989; Tuazon and Atkinson, 1990a; Sprengnether et al., 2002; Lee et al., 2005) but there is some controversy over whether this is a primary oxidation product or a secondary reaction product of the C5 hydroxycarbonyls (Zhao et al., 2004; Francisco-Marquez et al., 2005). Taken in combination, these experiments approach carbon balance and indicate that the nitrate yield is likely not more than 12%.

Uncertainties regarding the products of the reaction of isoprene hydroxyperoxy radicals with NO are important because of their effects on the NO_y budget. The resulting uncertainties in the NO_y budget propagate to uncertainty in spatial patterns of O_3 and OH concentration as well as the spatial patterns of nitrogen deposition. These uncertainties also affect predictions of the response of O_3 and presumably SOA to changes in isoprene emissions (as will likely occur in a warmer climate). For example, Wu et al. (2007) show that increasing the production rate of isoprene nitrates (INs) in a global model by a factor of three (within the currently established range of uncertainty) decreases the source of global tropospheric ozone by 10%.

IN production is important to the extent that the fate of NO_2 radical sequestered in

the organic nitrate is different than that of free NO_2. Possible fates that have been discussed include (1) reaction of IN with O_3, OH, or NO_3 to produce (a) a more complex organic nitrate or (b) NO_2, (Paulson and Seinfeld, 1992; Grossenbacher et al., 2001; Giacopelli et al., 2005) (2) removal from the atmosphere by dry or wet deposition

5   (Shepson et al., 1996; Treves and Rudich, 2003; von Kuhlmann et al., 2004; Horii et al., 2004; Rosen et al., 2004; Giacopelli et al., 2005;) or (3) incorporation into aerosol (Kroll et al., 2005; Ng et al., 2007; Ervens et al., 2008) with subsequent liquid phase chemistry.

Shepson and colleagues are the only group that has reported field measurements

10 of specific IN isomers. They use GC to isolate the specific compounds and thermal dissociation followed by luminol detection of NO_2 to observe them (Grossenbacher et al., 2001, 2004; Giacopelli et al., 2005). INs were ~10 ppt at a site in Michigan and ~115 ppt at a site in Tenessee. First-generation INs were observed to be ~5% of NO_y at both sites. These results and the differences between the two sites have been

15 interpreted to show that INs are important in reactive nitrogen cycling but that their abundance is strongly impacted by both NO_x abundance and photochemical age. Giacopelli et al. (2005) conclude that, due to short lifetimes of first-generation INs to further oxidation and/or deposition, more highly oxidized derivatives of INs are likely also important and that further understanding of secondary chemistry and loss processes is

20 needed.

In this paper, we describe observations of ΣANs from the NASA DC-8 aircraft over the Eastern U.S during the INTEX-NA campaign in summer of 2004. In this study, ΣANs were measured by thermal decomposition followed by detection of NO_2 with laser-induced fluorescence, described in detail below, which detects all compounds

25 of the form $RONO_2$ (where R represents a hydrocarbon) regardless of the identity of R. With respect to detection of INs, this non-specificity means that the technique is equally sensitive to all six first-generation isomers as well as any subsequent oxidation products that retain the nitrate functional group and that the measurement represents the sum of all of these compounds as well as any other alkyl or multifunctional nitrates

that may be present. These are the most spatially extensive measurements of ΣANs to date and constitute the first observations of ΣANs in the free troposphere. In a first manuscript describing these observations, Horowitz et al. (2007) compared the measurements to output from the MOZART chemical transport model, showing that the
5 best agreement of observations and the model within the continental boundary layer were achieved when the branching ratio for IN production was at the low end of the reported range (4%), conversion to non-nitrate species following reaction with O_3 or OH was low (40%) and when deposition was fast. Here we extend this analysis, isolating measurements where isoprene oxidation by OH is unambiguously the dominant source
10 of ΣANs, investigating factors controlling the production and the removal of molecules from the total nitrate pool and examining correlations of ΣANs with other products of isoprene oxidation.

2   Methods

NO_2, total peroxy nitrates (ΣPNs) and total alkyl and multifunctional nitrates (ΣANs)
15 were measured using the Berkeley thermal dissociation-laser induced fluorescence technique. (Thornton et al., 2000; Day et al., 2002). Briefly, gas is pulled simultane- ously through four channels, one for each compound above and one used to evaluate inlet transmission of HNO_3. Each channel consists of a section of heated quartz tube followed by detection of NO_2 using laser-induced fluorescence. Due to differing X-
20 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 dissocia- tion 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
25 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

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ΣANs mixing ratio. The instrument deployed for INTEX-NA had one inlet with a heated tip and immediate introduction to the heated quartz tubes for detection of ΣPNs, ΣANs and HNO_3 and one unheated inlet at ambient temperature for detection of NO_2.

Ambient NO_2 and NO_2 produced by thermal dissociation 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 incoming gas is cooled through the use of a supersonic expansion (Cleary et al., 2002) and the dye laser, utilizing Pyrromethene 597 in isopropanol, is tuned to an isolated rovibronic feature of jet-cooled NO_2 at 585 nm. The dye laser frequency is held for 20 s at the peak of this strong resonant feature and then for 5 s at an offline position in the continuum absorption. The ratio of the peak to background fluorescence of the chosen feature is 10 to 1 at 1 atm and the difference between the two signals is directly proportional to the NO_2 mixing ratio. 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. We observe a strong dependence of NO_2 fluorescence on the external pressure. We calibrate at a variety of altitudes and apply an empirical normalized pressure correction determined by flowing constant NO_2 during a test-flight descent to interpolate between them. Calibrations were performed at least once every two hours during a level flight leg using a 4.7 ppm NO_2 reference gas with a stated certainty of +/− 5%. The reference gas was compared to a library of standards in lab both before and after the campaign. The library of standards are intercompared on a regular basis (about every 6 months) to ensure stability and highlight when a given tank has degraded. These standards have been observed to remain stable for up to 5 years and to be accurate at atmospherically relevant mixing ratios to within 1%. (Bertram et al., 2005)

The instrument deployed for INTEX-NA 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. 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 75% and the 380°C channel (ΣANs) 25% of the time. Cell 2 sampled the 180°C and the 580°C channels 50% of the time each. Thus for every ~2 min duty cycle there were three measurements of NO_2, two direct measurements of ΣPNs, one direct measurement of HNO_3 and one measurement of ΣANs using interpolated ΣPNs values. ΣANs were not reported above 4 km.

HNO_3 was measured by the University of New Hampshire with a mist chamber followed by ion chromatography (Dibb et al., 1994) and by Caltech using Chemical Ionization Mass Spectrometry (CIMS). (Huey et al., 1996, 2004; Crounse et al., 2006) Hydrocarbons were measured by UC Irvine using gas chromatography of whole air samples (Colman et al., 2001). NO (Penn State) and O_3 (NASA Langley) were measured through chemiluminesence.

The INTEX-NA campaign has been described in detail (Singh et al., 2006). It consisted of 18 flights over the continental US east of 40° W and between 30 and 50° N during July and August of 2004 with extensive vertical profiling. The data used in this analysis are a subset of points taken over the continental US and are from a 1-min merged data set, available as described at www-air.larc.nasa.gov

3 Results and discussion

3.1 ΣAN and NO_y vertical profiles

Figure 2 shows vertical profiles of ΣANs, NO_y and ΣANs/NO_y. As shown in panel 2c, ΣANs were ~12% of NO_y at the surface over the continental U.S. For regions of high isoprene impact the median ΣANs component of NO_y at the surface was 18%. For the sake of the present discussion, "high isoprene" observations are those where the boundary layer isoprene concentration exceeds 500 ppt. Approximately 14% of the data over the continental U.S. below 2 km falls into the high isoprene category. ΣANs

are a larger fraction of NO_y when isoprene is high than in the bulk data because of both a higher concentration of ΣANs (250 ppt vs. 200 ppt) and a reduced overall NO_y concentration (1500 ppt vs. 2000 ppt). The lower boundary layer NO_y concentration when isoprene is high is due to both lower NO_2 (380 ppt vs. 600 pt) and lower HNO_3 (820 ppt vs. 1050 ppt) and indicates that the regions of highest biogenic activity were generally removed from anthropogenic NO_x sources.

3.2 ΣANs v CH$_2$O correlations

As indicated in Fig. 1, both ΣANs and CH_2O are first generation stable reaction products of isoprene oxidation. If isoprene were the only or if it were the primary source of these two then we would expect a strong correlation between them in ambient samples. Calculations using the observed VOC confirm (Fig. 4) that isoprene is indeed the primary source of ΣANs and Fig. 3 shows that ΣANs and H_2CO are correlated with a fit to the observations giving ΣANs $=0.098 \times H_2CO$, $R^2=0.47$. If we ignore loss processes and atmospheric mixing, the slope of the ΣANs/CH_2O correlation observed during INTEXA (0.098 ΣANs per CH_2O) implies a nitrate branching ratio of ~6.8% :

$$\left[\frac{\sum ANs}{CH_2O} \right] \times [CH_2O \text{ formation ratio}] \times [INs \text{ formation ratio}]$$

We use the known formaldehyde yield as a transfer standard to determine the nitrate formation yield. In what follows, we test some of the assumptions that are implicit in Eq. (1), including the assumption that isoprene is the sole source of H_2CO and ΣANs, and the assumption that mixing and removal processes are not important to the IN concentration.

3.3 Investigation of ΣAN and H$_2$CO sources

Recently, satellite measurements of H_2CO have been used to infer isoprene emissions (Millet et al., 2006; Palmer et al., 2007; Holzinger et al., 2007). Palmer et al. (2007)

find that isoprene is responsible for 32% of the H_2CO production potential and that it drives the H_2CO variability almost entirely as the other main precursors (methane and methanol) are significantly longer lived and well mixed and thus simply raise the formaldehyde background. Also, since we are focusing specifically on the lower tropo-
5 sphere where isoprene originates we would expect the contribution from isoprene to be even higher than when averaged over the entire tropospheric column.

Measured OH combined with OH production and loss rates calculated from measured species indicate that we are likely missing only 10–30% of the total reactivity and that the suite of measured VOC's is reasonably complete. The ΣANs contribution
10 to OH reactivity can be estimated at an average of $0.45\,s^{-1}$ or roughly 18% of the total OH loss rate assuming a rate constant typical of addition to a double bond as would be the case for an isoprene derived nitrate. This is likely an upper limit to the actual reactivity for ΣANs as any more highly oxidized compounds that lack a double bond would be significantly less reactive. The relative contributions to OH loss at the lowest
15 altitude (0–0.5 km) are shown graphically in the left panel of Fig. 4a. For the entire data set, 24% of the reactivity at the surface is due to isoprene (comparable to the reactivity due to either CO or OVOC) while that due to the sum of all other non-methane hydrocarbons is only 4%. For the high isoprene data 53% of the reactivity at the surface is due to isoprene and that due to other NMHC is approximately 4%. The second most
20 important category for the high isoprene case is OVOC.

The relative reactivities of measured hydrocarbons were weighted by their nitrate branching ratios to calculate a fractional contribution to the ΣANs signal resulting from each precursor. Nitrate branching ratios for non-isoprene alkanes were taken from (O'Brien et al., 1998; Atkinson et al., 1982), for alkenes from (O'Brien et al., 1998) and
25 that for isoprene was assumed to be 4.4% (Chen et al., 1998; Horowitz et al., 2007). Nitrates derived from MAC and MVK, VOC precursors which were not measured, are not included in the calculation, however their nitrate branching ratios are expected to be small (Tuazon and Atkinson, 1990b). The results of this calculation are shown graphically in the right panel of Fig. 4b. On average, 76% of ΣANs are predicted to be

isoprene derived and, in the specifically high isoprene points, the calculated contribution increases to 82%. If, instead, we use a 12% branching ratio the isoprene source of ΣANs exceed 90% in the average and 93% in the high isoprene case.

In summary, the first key assumption underlying our association of the slope of the ΣANs/ H_2CO correlation with the IN yield holds true: isoprene is the primary source of ΣANs and of H_2CO for the suite of measurements used in this analysis, collected over the summertime continental U.S.

3.4 Atmospheric processing of isoprene nitrates

The second assumption requires that chemical conversion of nitrates to other forms of NO_y and that atmospheric mixing and deposition have little effect on the slope of the correlation between ΣANs and H_2CO. Taking the mixing question first, we observe that the free tropospheric (above 2 km) levels of ΣANs and CH_2O lay along the line of the same ΣANs-H_2CO correlation line as observed from 0–1 km in the boundary layer (shown in Fig. 3). Although higher precision observations would likely be able to resolve some effects of mixing, overall the observations indicate that there is not a pool within the regional atmosphere that has concentrations that can alter the ΣANs/H_2CO ratio by mixing.

The remaining factors to assess are chemistry and deposition. The H_2CO lifetime to the sum of photolysis and OH oxidation was approximately 3 h in the planetary boundary layer during INTEX-NA. Deposition is not expected to significantly shorten its lifetime. Estimation of the ΣAN lifetime requires consideration of the composition of ΣANs and speciation among different INs, Fig. 5 shows the six possible IN isomers and their relative percentage yields as calculated by (Giacopelli et al., 2005). These six isomers are each predicted to have different rate constants for reaction with OH, O_3 and NO_3. To arrive at an overall estimate we calculate effective rate constants for the suite of INs using a weighted average of those for the individual isomers and derive 6.92×10^{-11} cm^3/molecs/s for OH+IN, and 2.18×10^{-16} cm^3/molecs/s for O_3+IN, neglecting the effects of daytime NO_3. Using observed average 0–1 km concentrations

of OH (3.9×10^6 molecs/cm^3) and O$_3$ (49 ppb), the lifetime of INs to OH is about 60 min and to O$_3$ is about 65 min, giving a combined oxidative lifetime of about 32 min. If the deposition velocity (v_d) of INs were equal to that of HNO$_3$ (4 cm/s Seinfeld and Pandis), the lifetime to deposition in a 1 km boundary layer would be given by:

$$\left[\frac{B.L.\ Ht\ \text{(km)}}{v_d} \right] = \left[\frac{1\ \text{km}}{\left(4\frac{\text{cm}}{\text{s}} \times 3600\frac{\text{s}}{\text{h}} \times 10^{-5}\frac{\text{km}}{\text{cm}}\right)} \right] = 7\ \text{h}$$

Thus the overall lifetime is determined by the instantaneous lifetime to oxidation.

Although these reactions unambiguously result in production of new chemicals, it is not clear from previous laboratory experiments whether the products of IN oxidation are still ΣANs or whether they release the nitrogen in the form of HNO$_3$ or NO$_2$.

Figure 6 shows a possible mechanism and products resulting from the OH oxidation of one of the six possible IN isomers (for a complete reaction scheme for the production of INs see Sprengnether et al., 2002). Pathway 1 proceeds via H-abstraction by OH and regenerates NO$_2$ from the nitrate. Pathway 2 proceeds via addition of OH to the double bond to produce a peroxy radical that reacts subsequently. For simplicity, we show here the more likely of two possible peroxy radical intermediates and products only of its reaction with NO. The scheme is representative but not comprehensive and products from the other radical isomer or from reactions of the radical with something other than NO would be different. Pathway 2a shows an alkoxy radical decomposition that produces NO$_2$ from the nitrate. Pathway 2b shows decomposition resulting in a stable mononitrate and formaldehyde. Pathway 2c produces a dinitrate and is expected to be a minor pathway but is interesting in that it results in sequestration of additional NO$_x$. Pathway 3 proceeds via OH addition to the nitrate group to produce HNO$_3$. Ozonolysis of INs could produce a similarly complex mixture of multifunctional nitrates, aldehydes and ketones (Giacopelli et al., 2005). The products of these reactions, however, are unknown and model treatment of them varies widely. Oxidation constitutes a loss process for ΣANs only if INs are converted into something that is no longer a nitrate such as HNO$_3$ or NO$_2$ (via pathways 1, 2a or 3 in Fig. 6 for example). If OH+IN

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reactions result simply in more functionalized nitrates, then the reaction represents a renaming but not a loss from the pool of ΣAN compounds (pathway 2b in Fig. 6). If, for example, 10% of reactions with OH lead to NO_2 production while the other 90% retain the nitrate functional group but change the identity of the parent molecule, then the effective lifetime to loss by reaction with OH would be an order of magnitude longer (10 h) than the lifetime of an individual IN. Pathway 2c is expected to be minor as the nitrate branching ratio for the intermediate peroxy radical should be no higher than for isoprene itself. We would expect less than 5% of ΣANs to be di-nitrates.

Figure 7 shows calculations of the ΣANs/CH_2O correlation for a range of ΣANs lifetimes (45 min to 20 h) assuming an initial IN yield of 4.4%. We also show a calculation for a lifetime of 90 min and a 12% IN branching ratio. It should be noted here that the ΣAN lifetimes shown have been calculated relative to that for CH_2O so that we would expect deviations of OH or O_3 from the average values to result in scatter but not in a change in the overall slope expected for a given lifetime. The observed correlation between ΣANs and CH_2O is inconsistent with ΣAN lifetimes shorter than 1 hour (or less than 1/3 that of CH_2O). Unless the estimate of the OH and O_3 rate constants (6.92×10^{-11} molecs$\times$cm^{-3}s^{-1} and 2.18×10^{-16} molecs$\times$cm$^{-3}\times$s^{-1}) are in gross error, this indicates that some significant fraction of IN oxidation reactions transform one nitrate into another and possibly supports an IN branching ratio on the high end of the published range. If the initial nitrate production ratio is 4.4%, then a lifetime of ∼5 hours provides a reasonable fit of the data. Such a lifetime indicates about a 92% rate of nitrate recycling for IN oxidation reactions. Note that this is not a unique solution. We can fit the data equally well if the initial nitrate production ratio from isoprene oxidation is 12% and the IN lifetime is ∼1.5 hours (an implied recycling of 74%) or if the branching ratio is 8% and the lifetime is ∼2.5 hours (an implied recycling of 84%). The observed correlation between ΣANs and O_3 is most consistent, however, with a nitrate branching ratio that is on the low end of the 4.4–12% range (see Horowitz et al., 2007 for a graphical depiction).

Formation of HNO_3 is commonly thought to be the primary mechanism for removal

of reactive nitrogen from the atmosphere. Hydroxy nitrates, of which INs are a subset, have high Henry's law coefficients ($\sim6\times10^3$ M/atm (Shepson et al., 1996) as compared to 2.1×10^5 M/atm for HNO_3 Lelieveld and Crutzen, 1991) and may therefore represent a similarly permanent NO_x termination event and be a removal pathway for nitrogen that competes with that of HNO_3 (Munger et al., 1998; Shepson et al., 1996; Farmer and Cohen, 2008). ΣANs were $\sim$23% of HNO_3 on average and more than 35% of HNO_3 for the high isoprene points. Thus if INs deposit as rapidly as HNO_3, then 1/5 to 1/4 of total N deposition (defined here as HNO_3+IN deposition) is via isoprene nitrates.

4 Conclusions

Extensive measurements of ΣANs were made over the summertime continental US and they were observed to comprise an important (12–20%) part of the NO_y budget. The ΣANs fraction of NO_y was highest when boundary layer isoprene was >500 ppt both because NO_y was lower and ΣANs were higher in those regions. Evidence was presented to indicate that the measured hydrocarbon suite was reasonably comprehensive and calculations based on the observed hydrocarbons indicate that isoprene was the main precursor to organic nitrates not only when isoprene was especially high but on average as well. A strong correlation was observed between ΣANs and CH_2O, a high-yield product of isoprene oxidation, and this was used to constrain uncertainties in both the nitrate yield from OH-initiated isoprene oxidation and in the loss processes governing the resulting hydroxy nitrates. The data presented here constrain combinations of branching ratios and lifetimes and show that the extent to which the nitrate functionality is maintained through the second generation of isoprene oxidation products is at least 75%. Observations of ΣANs, O_3, hydrocarbons and speciated nitrates are in best agreement when isoprene nitrate branching ratios are at the lower end of the published range of values (4.4–12%). We recommend sets of production rates, lifetimes and recycling efficiencies of INs as follows [4.4%, 5 h, 92%], [8%, 2.5 h, 84%] and [12%, 90 min, 74%]. None of the models commonly used to describe ozone in re-

gions where isoprene is important represent this chemistry in sufficient detail to capture the effects of these mechanistic relationships on O_3 or aerosol production. Improving the mechanisms in these models as well as through laboratory observations will lead to more realistic assessments of the combine effects of isoprene and NO_x on O_3 and SOA production.

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Table 1. Percentage yields of products observed in OH-initiated isoprene oxidation studies.

Reference	1	2	3	4	5	6	7	8
Product								
MVK	29 (7)	36 (4)	32 (5)		44 (6)	55 (6)		41(3)
MAC	21 (5)	25 (3)	22 (2)		28 (4)	(MAC+MVK)		27 (3)
Organic Nitrates	8–14			4.4	8–12			
C5 hydroxy-carbonyls					19 (6.1)	15		
C5 hydroxy-carbonyls					3.3 (1.6)			
C5 carbonyls					8.4 (2.4)			
Carbon accounted for	58–66	61	55	4.4	80–84	86	15	68

1=Tuazon et al., 1990
2=Paulson and Seinfeld, 1992
3=Myoshi et al., 1994
4=Chen et al., 2002
5=Sprengnether et al., 2002
6=Zhao et al., 2004
7=Baker et al., 2005
8=Karl et al., 2006
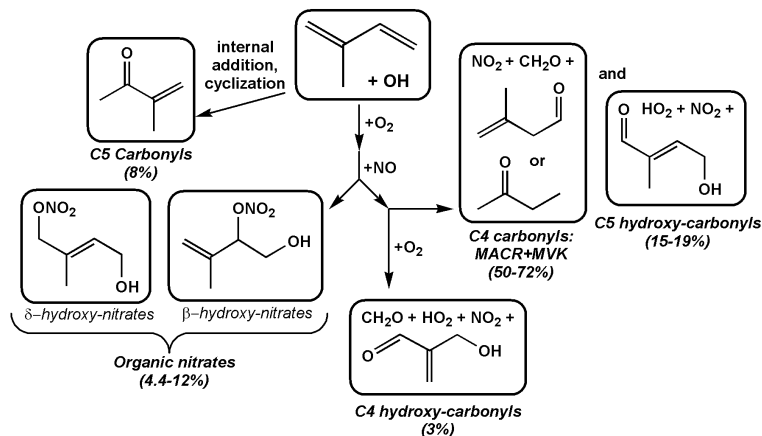
Fig. 1. Examples of each class of OH-initiated isoprene oxidation products observed (in the presence of NO_x) and the ranges of observed yields.
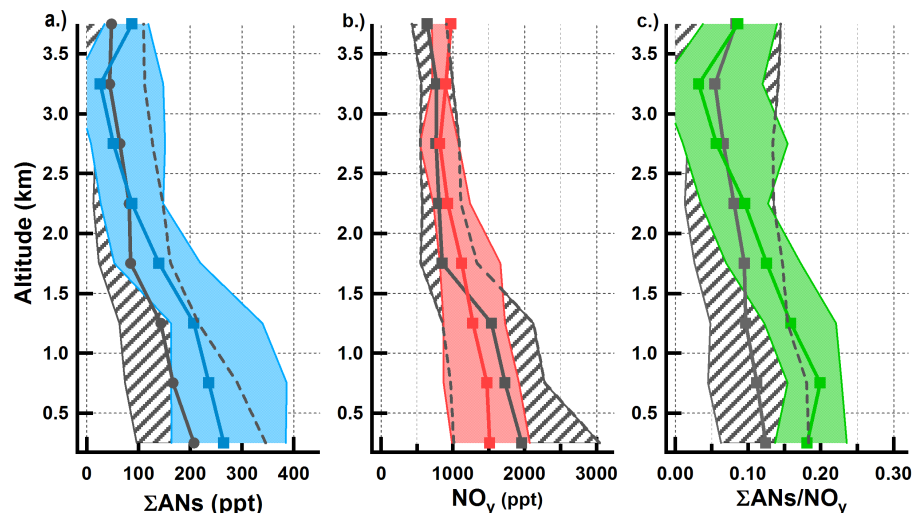
Fig. 2. Medians and interquartile ranges of **(a)** ΣANs, **(b)** NO_y (NO_y=NO+NO_2 + ΣPNs+ΣANs+HNO_3), and **(c)** ΣANs/NO_y. The colored points and shading are regions where isoprene exceeded 500 ppt in the planetary boundary layer below the measurement. The gray lines represent all continental data.
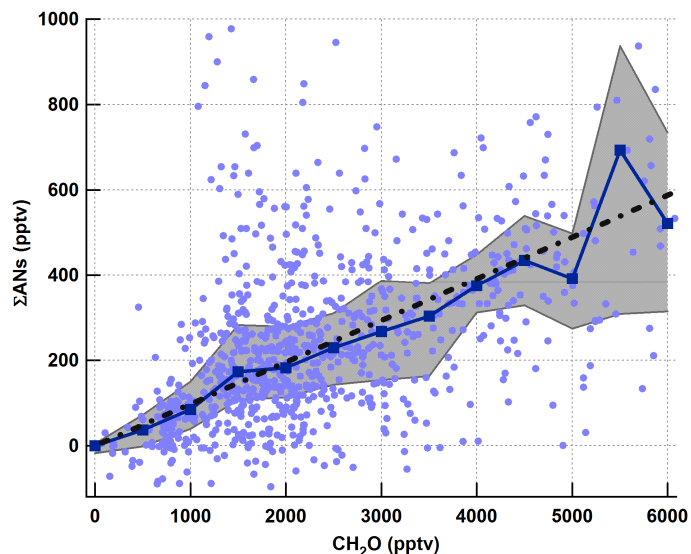
Fig. 3. Observed correlation between ΣANs and CH_2O; light blue circles represent all continental points below 1 km, dark blue squares are the mean ΣAN concentrations in 500 ppt CH_2O bins and the shaded grey area is the interquartile range of the data. The black line is the best fit of the data points (slope=0.098, intercept fixed at 0, r^2=0.47).
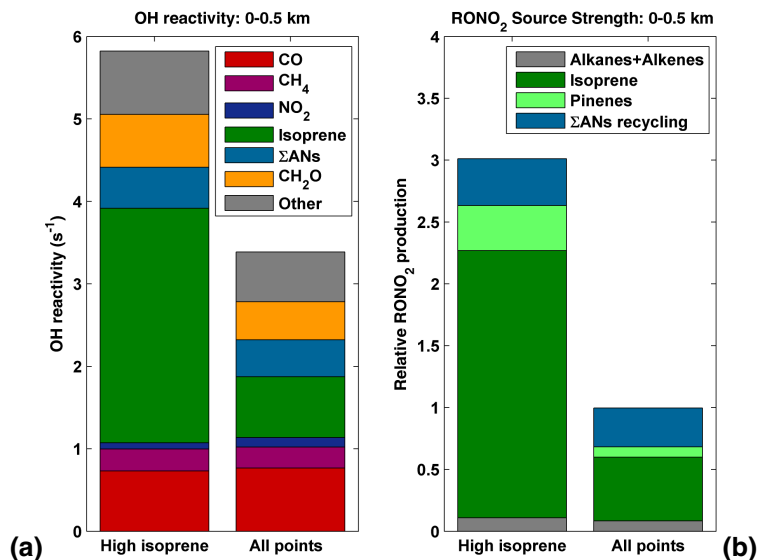
Fig. 4. (a) Calculated contributions to OH reactivity when isoprene is high and in the bulk data. "Other" includes all measured non-methane hydrocarbons as well as HNO_3, peroxides and HO_x self-reactions. **(b)** Calculated contribution to the ΣANs signal for high isoprene points and the bulk data normalized to the bulk data ΣANs production, using an isoprene branching ratio of 4.4% and a recycling efficiency of 80%.
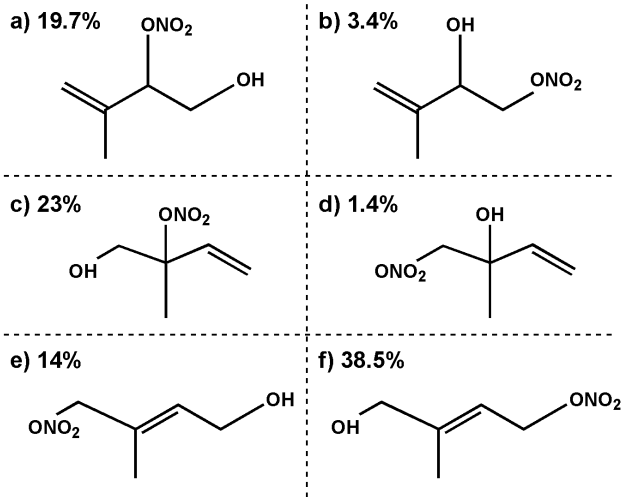
Fig. 5. Relative abundances of the six possible first-generation INs as calculated based on formation pathway branching ratios presented in Giacopelli et al. (2005).
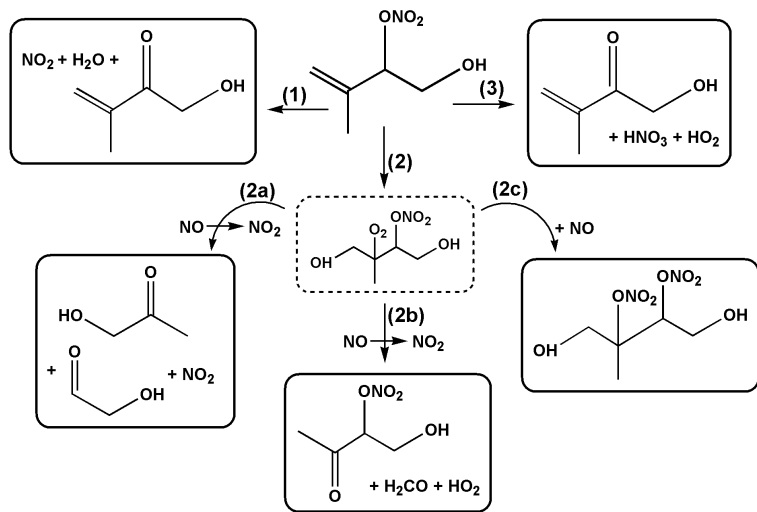
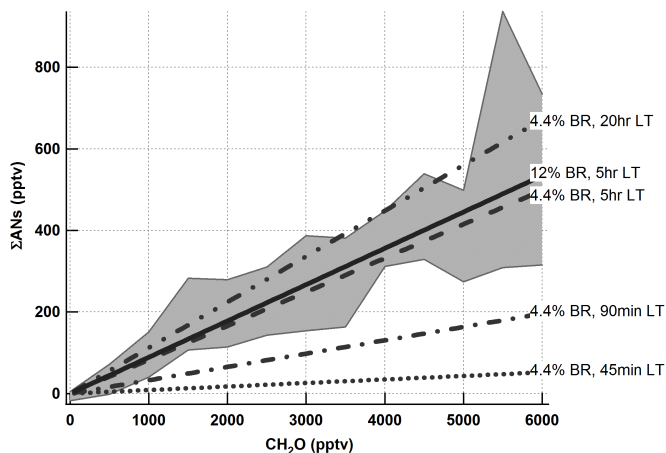**Fig. 6.** Possible OH oxidation products for one of the IN isomers.

Fig. 7. As in Fig. 2, the shaded area is the interquartile range of all continental data below 1 km. Lines represent the expected correlation after 2 h of aging for various nitrate branching ratios and ΣAN lifetime combinations. From the bottom up: a 4.4% branching ratio and 45 min lifetime (dotted), a 4.4% branching ratio and 90 min lifetime (dash-dot-dash), a 4.4% branching ratio and 5 h lifetime (dashed), a 12% branching ratio and 90 min lifetime (solid) and a 4.4% branching ratio and 20 h lifetime (dor-dot-dash).