

## Supporting Information

### Observational Constraints on the Oxidation of NO<sub>x</sub> in the Upper Troposphere

Benjamin. A. Nault,<sup>1</sup> Charity Garland,<sup>2</sup> Paul J. Wooldridge,<sup>2</sup> William H. Brune,<sup>3</sup> Pedro Campuzano-Jost,<sup>4</sup> John D. Crouse,<sup>5</sup> Douglas A. Day,<sup>4</sup> Jack Dibb,<sup>6</sup> Samuel R. Hall,<sup>7</sup> L. Gregory Huey,<sup>8</sup> José L. Jimenez,<sup>4</sup> Xiaoxi Liu,<sup>8</sup> Jingqiu Mao,<sup>9</sup> Tomas Mikoviny,<sup>10</sup> Jeff Peischl,<sup>11</sup> Ilana B. Pollack,<sup>11,12</sup> Xinrong Ren,<sup>13</sup> Thomas B. Ryerson,<sup>11</sup> Eric Scheuer,<sup>6</sup> Kirk Ullmann,<sup>7</sup> Paul O. Wennberg,<sup>14</sup> Armin Wisthaler,<sup>15</sup> Li Zhang,<sup>3</sup> Ronald C. Cohen<sup>1,2,\*</sup>

<sup>1</sup>Department of Earth and Planetary Science, University of California, Berkeley, California 94709, United States

<sup>2</sup>Department of Chemistry, University of California, Berkeley, California 94709, United States

<sup>3</sup>Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania 16802, United States

<sup>4</sup>Cooperative Institute for Research in the Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States

<sup>5</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

<sup>6</sup>Earth Systems Research Center, Institute for the Study of Earth Oceans and Space, University of New Hampshire, Durham, New Hampshire 03824, United States

<sup>7</sup>Atmospheric Chemistry Division, National Center for Atmospheric Research (NCAR), Boulder, Colorado 80307, United States

<sup>8</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

<sup>9</sup>National Oceanic and Atmospheric Administration Geophysical Fluid Dynamics Laboratory, Princeton, New Jersey 08540, United States

<sup>10</sup>Oak Ridge Associated Universities, Oak Ridge, Tennessee 37831, United States

<sup>11</sup>Chemical Sciences Division, Earth System Research Lab, National Oceanic and Atmospheric Administration, Boulder, Colorado 80305, United States

<sup>12</sup>Now at: Atmospheric Science Department, Colorado State University, Fort Collins, Colorado 80523, United States

<sup>13</sup>Air Resources Laboratory, National Oceanic and Atmospheric Administration, College Park, Maryland 20740, United States

<sup>14</sup>Division of Engineering and Applied Science and Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, United States

<sup>15</sup>Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria

### **Corresponding Author**

\*Phone: (510)-642-2735. E-mail: rccohen@berkeley.edu

<b>Measurements Intercomparison</b>	S3
<b>Calculation of Alkyl and Multifunctional Nitrate</b>	S4
<b>Calculation of Alkyl and Multifunctional Nitrate in Aerosol-Phase</b>	S4–S5
<b>Description of GEOS-Chem Model</b>	S5
<b>Figure S1</b>	S6
<b>Figure S2</b>	S7
<b>Figure S3</b>	S8
<b>Figure S4</b>	S9
<b>Figure S5</b>	S10
<b>Table S1</b>	S11
<b>Table S2</b>	S11
<b>Table S3</b>	S12
<b>Table S4</b>	S13
<b>Table S5</b>	S15

## Measurement Intercomparisons

During DC3, the NASA DC-8 payload included measurements of speciated ( $\text{CH}_3\text{O}_2\text{NO}_2$ ,  $\text{HO}_2\text{NO}_2$ , PAN, and PPN) and total peroxy nitrates, gas-phase, and gas- and particle-phase  $\text{HNO}_3$ , allowing for intercomparisons of the total peroxy nitrates and  $\text{HNO}_{3(\text{g+p})}$  for the entire mission. Also, the NSF National Center for Atmospheric Research GV and DC-8 conducted 5 wing tip-to-wing tip intercomparisons, allowing comparison of two  $\text{HO}_2\text{NO}_2$  measurements. The results are shown in Figure S1. Finally, the DC-8 payload included measurements of temperature, pressure,  $\text{NO}_2$  photolysis rate,  $\text{HO}_2$ , and  $\text{O}_3$  (Table 1). These measurements are used to calculate photostationary steady state (PSS)  $\text{NO}_2$  (Eq. 1) to compare against measured  $\text{NO}_2$  (Fig. S2). The PSS  $\text{NO}_2$  is calculated for observations where  $\text{NO}_x/\text{NO}_y < 0.4$  (removes emissions), solar zenith angle  $< 80^\circ$  (removes nighttime observations),  $\text{O}_3/\text{CO} < 1.25$  (removes stratospheric intrusion), and at all temperatures due to the lack of observations meeting these criteria in the upper troposphere. We assumed that  $[\text{RO}_2] \approx [\text{HO}_2]$ . The rate constants are from Sander et al.<sup>1</sup>

$$[\text{NO}_{2,\text{PSS}}] = \frac{k_{\text{NO}+\text{O}_3}[\text{O}_3][\text{NO}] + 2 \cdot k_{\text{NO}+\text{HO}_2}[\text{HO}_2][\text{NO}]}{j_{\text{NO}_2}} \quad (1)$$

The difference between the two  $\text{HO}_2\text{NO}_2$  measurements is 35%. We scale the DC-8 observations to the average of the two measurements. For the peroxy nitrates, the difference between the speciated sum and total peroxy nitrates is 4%. There is a 10% difference between the two  $\text{HNO}_{3(\text{g+p})}$  measurements. We take the average of the two measurements as the  $\text{HNO}_{3(\text{g+p})}$ .

## Calculation of Alkyl and Multifunctional Nitrate

To calculate the speciated  $\Sigma$ ANs production, we use 15 minute averaged observations of the hydrocarbons. The hydrocarbons, OH rate constants, and  $\alpha$  are listed in Table S4. We also include the fraction of time the peroxy radical reacts with NO versus other species (~80%) in the calculation of the speciated  $\Sigma$ ANs production. The  $\alpha$  also includes any contribution from secondary organic nitrate formation after radical isomerization (e.g., Lee et al.<sup>2</sup>). For hydrocarbons at or near the limit of detection (indicated in Table S4), we take the median mixing ratio observed during Leg 2 and calculate what the concentration should be in Leg 3, using the median OH concentration during Leg 2 ( $2.5 \times 10^6$  molecules/cm<sup>3</sup>) and the time between sampling Leg 2 and Leg 3 (~ 4000 s). Then, we use that calculated mixing ratio as the initial mixing ratio for the rest of the flight. For the hydrocarbons that do not have a temperature dependent rate constant reported (i.e., methylhexane), we use a temperature dependent rate constant that has a similar value at 298 K. Finally, for isoprene nitrate, we use the branching ratios for the different peroxy radicals from Paulot et al.,<sup>3</sup> and we use the recommended rate constants and mechanism from Lee et al.<sup>4</sup> to produce other isoprene nitrate species (i.e., isoprene dinitrate, ethanal nitrate, etc.) from the first generation isoprene nitrates.

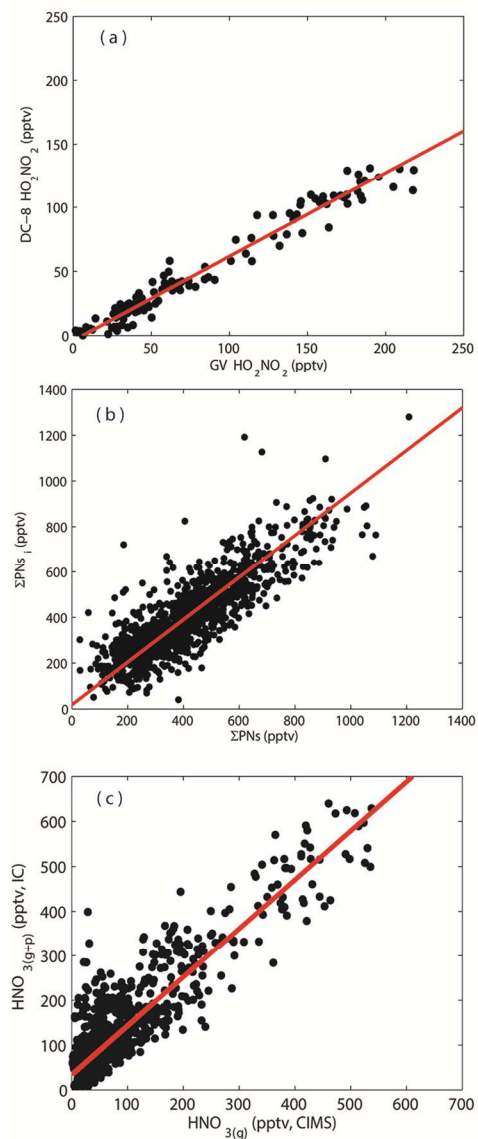
## Calculation of Alkyl and Multifunctional Nitrate in Aerosol-Phase

Here are the following definitions for the values used in Eq. 4 – 5 to calculate the partitioning into aerosol.  $R$  is the gas constant ( $8.206 \times 10^{-5}$  atm m<sup>3</sup> K<sup>-1</sup> mol<sup>-1</sup>),  $T$  is temperature (225 K),  $f_{\text{om}}$  is the weight fraction of organic material in the total aerosol (0.8 for this experiment),  $MW_{\text{om}}$  is the molecular weight of the absorbing organic material (assumed to be 180 g/mol),  $\zeta$  is the activity coefficient of the compound of interest in the condensed phase

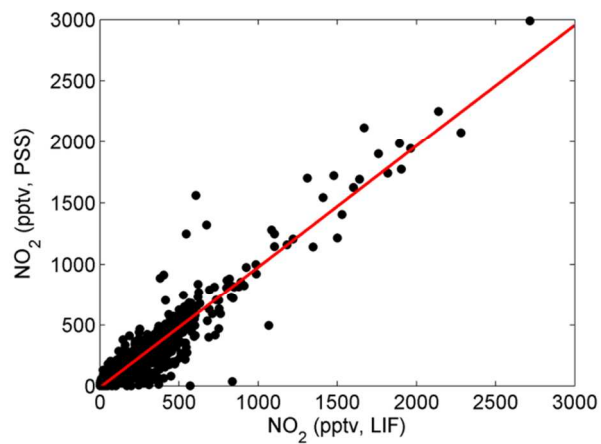
(assumed to be 1 for this experiment),  $p_{\text{vap}}$  is the subcooled vapor pressure of interest (atm),  $10^6$  ( $\mu\text{g/g}$ ) is a conversion factor,  $m_{\text{om}}$  is the mass of the background organic aerosol (ranged from  $0.015 - 0.030 \mu\text{g/m}^3$  at ambient T and P), and  $m_{AN_{i,g}}$  and  $m_{AN_{i,p}}$  are the masses of the speciated alkyl and multifunctional nitrates in the gas- and particle-phase, respectively. The units of  $K_p$  are  $\text{m}^3 \mu\text{g}^{-1}$ .

### **Description of GEOS-Chem Model**

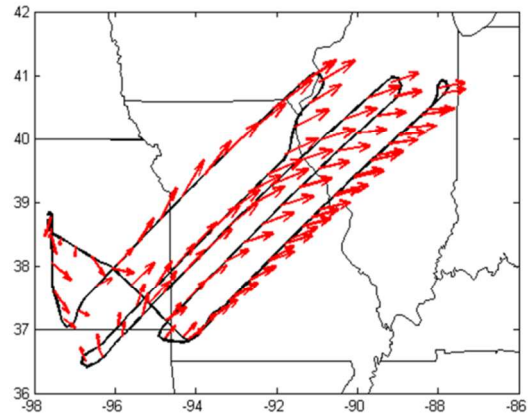
GEOS-Chem version 09-02b<sup>5</sup> (<http://geos-chem.org>) is used at  $2 \times 2.5$  degree resolution. The standard chemistry is described by Mao et al.<sup>6</sup> and includes  $\text{CH}_3\text{O}_2\text{NO}_2$  chemistry as recommended by Browne et al.<sup>7</sup> Two separate runs were conducted: one with current recommendations<sup>1,6</sup> (Base Case) and one with the slower recommendations<sup>8,9</sup> (Updated Chemistry Case) for the  $\text{HNO}_3$  and  $\text{HO}_2\text{NO}_2$  production rate constant. Both models were run from January 2011 to December 2012, and only results from January – December 2012 are analyzed to minimize memory from the initialization of the model. We use the output between 200 – 400 hPa (upper troposphere) and remove output defined as being above the meteorological tropopause.



**Figure S1.** Intercomparison of **(a)** DC-8 versus GV HO<sub>2</sub>NO<sub>2</sub>, **(b)** ΣPNs<sub>i</sub> (ΣPNs<sub>i</sub> = CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> + HO<sub>2</sub>NO<sub>2</sub> + PAN + PPN) versus ΣPNs, and **(c)** IC HNO<sub>3(g+p)</sub> versus CIMS HNO<sub>3(g)</sub>. The slopes ( $\pm 1\sigma$ ), intercepts ( $\pm 1\sigma$ ), and R<sup>2</sup> values are **(a)** 0.66( $\pm 0.01$ ), -3( $\pm 1$ ), and 0.96, **(b)** 0.96( $\pm 0.02$ ), 7( $\pm 9$ ), and 0.68, and **(c)** 1.09( $\pm 0.02$ ), 34( $\pm 2$ ), and 0.81.

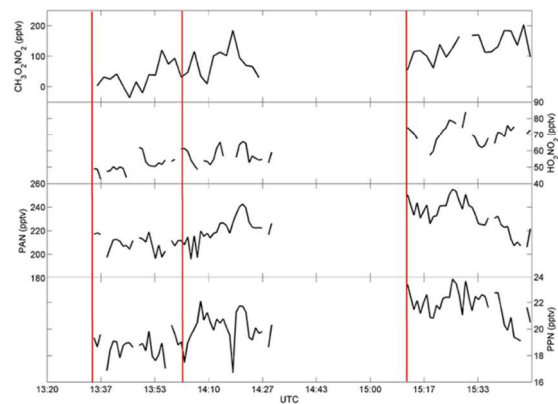


**Figure S2.** Intercomparison of photostationary steady state (PSS) NO<sub>2</sub> versus measured NO<sub>2</sub>. The slope ( $\pm 1\sigma$ ), intercept ( $\pm 1\sigma$ ), and  $R^2$  is  $0.99(\pm 0.01)$ ,  $-12(\pm 2)$ , and 0.89.

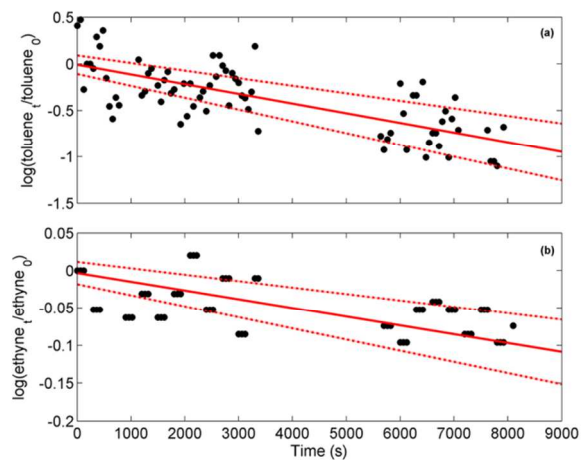


**Figure S3.** The full flight path of the NASA DC-8 is shown in black for the entire 21 June 2012 experiment. Wind direction and relative speed observed on the DC-8 is shown by the red arrows.





**Figure S4.** Time series of **(a)**  $\text{CH}_3\text{O}_2\text{NO}_2$ , **(b)**  $\text{HO}_2\text{NO}_2$ , **(c)** PAN, and **(d)** PPN. The red vertical lines indicate the start of Legs 1, 2, and 3, respectively, in Fig. 2. The  $\text{CH}_3\text{O}_2\text{NO}_2$  observations are three minute averages and the values.



**Figure S5.** First order loss rate of **(a)** toluene and **(b)** ethyne. The solid red line is the slope ( $-1.01 \times 10^{-4}$  and  $-5.9 \times 10^{-6} \text{ s}^{-1}$  for toluene and ethyne, respectively) and the dashed-dot red line is the  $2\sigma$  uncertainty ( $\pm 2.3 \times 10^{-5}$  and  $\pm 2.6 \times 10^{-6} \text{ s}^{-1}$  for toluene and ethyne, respectively).

**Table S1.** Reactions and rate constants at T = 225 K and P = 230 hPa used to calculate PAN production rate and CH<sub>3</sub>C(O)O<sub>2</sub> concentrations.

Reaction	Rate Constant (cm <sup>3</sup> /molecules/s)
CH <sub>3</sub> C(O)OOH + OH → CH <sub>3</sub> C(O)O <sub>2</sub> + H <sub>2</sub> O	9.2×10 <sup>-12a</sup>
CH <sub>3</sub> C(O)H + OH + O <sub>2</sub> → CH <sub>3</sub> C(O)O <sub>2</sub> + H <sub>2</sub> O	2.2×10 <sup>-11b</sup>
CH <sub>3</sub> C(O)O <sub>2</sub> + HO <sub>2</sub> → Products	4.4×10 <sup>-11b</sup>
CH <sub>3</sub> C(O)CH <sub>3</sub> + hv + O <sub>2</sub> → CH <sub>3</sub> C(O)O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	Measured
CH <sub>3</sub> C(O)CH <sub>3</sub> + OH $\xrightarrow{80\%}$ CH <sub>3</sub> C(O)O <sub>2</sub> + products	1.4×10 <sup>-13a</sup>
CH <sub>2</sub> CHC(O)CH <sub>3</sub> + hv → CH <sub>3</sub> C(O)O <sub>2</sub> + products	Assumed same as methyl vinyl ketone photolysis <sup>c</sup>
CH <sub>2</sub> CHC(O)CH <sub>3</sub> + OH $\xrightarrow{60\%}$ CH <sub>3</sub> C(O)O <sub>2</sub> + products	3.9×10 <sup>-11b,c,d</sup>
CH <sub>2</sub> C(CH <sub>2</sub> )C(O)H + hv $\xrightarrow{35\%}$ CH <sub>3</sub> C(O)O <sub>2</sub> + products	Assumed same as butanal photolysis <sup>c,d</sup>
CH <sub>2</sub> C(CH <sub>2</sub> )C(O)H + hv $\xrightarrow{30\%}$ CH <sub>3</sub> C(O)O <sub>2</sub> + products	Assumed same as butanal photolysis <sup>c,d</sup>
CH <sub>2</sub> C(CH <sub>2</sub> )C(O)H + OH $\xrightarrow{15\%}$ CH <sub>3</sub> C(O)O <sub>2</sub> + products	4.3×10 <sup>-11b,c,d</sup>
CH <sub>3</sub> C(O)CH <sub>2</sub> OH + hv → CH <sub>3</sub> C(O)O <sub>2</sub> + products	Assumed same as acetone photolysis <sup>c</sup>
CH <sub>3</sub> C(O)O <sub>2</sub> + NO → CH <sub>3</sub> O <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub>	2.7×10 <sup>-11a</sup>
C <sub>2</sub> H <sub>5</sub> C(O)CH <sub>3</sub> + hv → CH <sub>3</sub> C(O)O <sub>2</sub> + products	Measured

<sup>a</sup>Ref 1.

<sup>b</sup>Ref 10.

<sup>c</sup>We assumed that 40% of MACR+MVK measurements from the PTR-MS is MACR and 60% is MVK.

<sup>d</sup>The percent over the arrow includes the branching between reacting with NO, HO<sub>2</sub>, and NO<sub>2</sub>.

**Table S2.** Reactions and rate constants used to calculate PPN production rate and C<sub>2</sub>H<sub>5</sub>C(O)O<sub>2</sub> concentrations.

Reaction	Rate Constant (cm <sup>3</sup> /molecules/s)
C <sub>2</sub> H <sub>5</sub> CHO + OH + O <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> C(O)O <sub>2</sub> + H <sub>2</sub> O	3.0×10 <sup>-11a</sup>
C <sub>2</sub> H <sub>5</sub> C(O)O <sub>2</sub> + HO <sub>2</sub> → Products	4.4×10 <sup>-11b</sup>
C <sub>2</sub> H <sub>5</sub> C(O)O <sub>2</sub> + NO → CH <sub>3</sub> O <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub>	2.7×10 <sup>-11b</sup>

<sup>a</sup>Ref 10.

<sup>b</sup>Ref 1.

**Table S3.** Reactions and rate constants used to calculate CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> production rate and CH<sub>3</sub>O<sub>2</sub> concentrations.

Reaction	Rate Constant (cm <sup>3</sup> /molecules/s)
CH <sub>4</sub> + OH + O <sub>2</sub> → CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	9.2×10 <sup>-16a</sup>
CH <sub>3</sub> C(O)O <sub>2</sub> + NO → CH <sub>3</sub> O <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub>	2.7×10 <sup>-11a</sup>
CH <sub>3</sub> C(O)CH <sub>3</sub> + hν + O <sub>2</sub> → CH <sub>3</sub> C(O)O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	Measured
CH <sub>3</sub> OOH + OH <sup>70%</sup> → CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	9.2×10 <sup>-12a</sup>
CH <sub>3</sub> C(O)OH + hν + O <sub>2</sub> → CH <sub>3</sub> O <sub>2</sub> + HCO	Measured
CH <sub>3</sub> O <sub>2</sub> + NO → CH <sub>3</sub> O + NO <sub>2</sub>	1.1×10 <sup>-11a</sup>
CH <sub>3</sub> O <sub>2</sub> + HO <sub>2</sub> → Products	1.1×10 <sup>-11a</sup>
CH <sub>3</sub> C(O)OOH + hν → CH <sub>3</sub> O <sub>2</sub> + product	Assumed same as methyl hydrogen peroxide
CH <sub>3</sub> C(O)O <sub>2</sub> + HO <sub>2</sub> <sup>45%</sup> → CH <sub>3</sub> O <sub>2</sub> + OH + product	4.4×10 <sup>-11a</sup>

<sup>a</sup>Ref 1.

**Table S4.** Species, rate constants, average  $\alpha$ , and classification used to calculate alkyl nitrate production (eq. 1 and Fig. 8b) at T = 225 K and P = 230 hPa.

Parent Compound	Rate constant (cm <sup>3</sup> /molecules/s)	Initial Concentration (pptv)	$\alpha$	Classification in Fig. 8b
<i>Alkanes</i>				
Methane	$9.2 \times 10^{-16d}$	$1.85 \times 10^6$	0.0014	$\Sigma$ ANs < C6
Ethane	$8.1 \times 10^{-14e}$	1880	0.0036	$\Sigma$ ANs < C6
Propane	$5.7 \times 10^{-13e}$	880	0.0189	$\Sigma$ ANs < C6
i-Butane	$1.6 \times 10^{-12e}$	136	0.0479	$\Sigma$ ANs < C6
n-Butane	$1.5 \times 10^{-12e}$	308	0.0426	$\Sigma$ ANs < C6
i-Pentane	$2.6 \times 10^{-12f}$	85	0.0535	$\Sigma$ ANs < C6
n-Pentane	$2.8 \times 10^{-12g}$	71	0.1436	$\Sigma$ ANs < C6
Cyclopentane	$3.6 \times 10^{-12g}$	6	0.1030	$\Sigma$ ANs < C6
2-Methylpentane	$4.9 \times 10^{-12h}$	10	0.1821	$\Sigma$ ANs $\geq$ C6
3-Methylpentane	$4.9 \times 10^{-12h}$	9	0.1354	$\Sigma$ ANs $\geq$ C6
n-Hexane	$4.9 \times 10^{-12g}$	8	0.4486	$\Sigma$ ANs $\geq$ C6
Methyl Cyclopentane <sup>a</sup>	$6.9 \times 10^{-12i}$	9	0.1937	$\Sigma$ ANs $\geq$ C6
Cyclohexane <sup>a</sup>	$5.3 \times 10^{-12g}$	12	0.2096	$\Sigma$ ANs $\geq$ C6
2,3-Dimethylbutane <sup>a</sup>	$5.6 \times 10^{-12g}$	4	0.0735	$\Sigma$ ANs $\geq$ C6
n-Heptane <sup>a</sup>	$6.7 \times 10^{-12g}$	12	0.5052	$\Sigma$ ANs $\geq$ C6
2-Methylhexane <sup>a</sup>	$6.7 \times 10^{-12j}$	7.5	0.3933	$\Sigma$ ANs $\geq$ C6
3-Methylhexane <sup>a</sup>	$6.7 \times 10^{-12j}$	21	0.4003	$\Sigma$ ANs $\geq$ C6
2,4-Dimethylpentane <sup>a</sup>	$2.6 \times 10^{-12k}$	4	0.3134	$\Sigma$ ANs $\geq$ C6
2,3-Dimethylpentane <sup>a</sup>	$2.6 \times 10^{-12k}$	6	0.3134	$\Sigma$ ANs $\geq$ C6
2,2,4-Trimethylpentane <sup>a</sup>	$2.6 \times 10^{-12k}$	11	0.3134	$\Sigma$ ANs $\geq$ C6
<i>Alkenes</i>				
Ethene	$8.9 \times 10^{-12e}$	34	0.0068 <sup>m</sup>	$\Sigma$ ANs < C6
Isoprene <sup>a</sup>	$1.5 \times 10^{-10e}$	15	0.1135	$\Sigma$ ANs Isoprene
$\alpha$ -Pinene <sup>a</sup>	$8.5 \times 10^{-11e}$	10	0.4991	$\Sigma$ ANs Monoterpenes
<i>OVOCs</i>				
Acetone	$1.4 \times 10^{-13d}$	1490	0.0091	$\Sigma$ ANs OVOC
MVK <sup>b</sup>	$3.9 \times 10^{-11l}$	39	0.0184 <sup>n</sup>	$\Sigma$ ANs OVOC
MACR <sup>b,c</sup>	$4.3 \times 10^{-11l}$	26	0.0113	$\Sigma$ ANs OVOC
<i>Aromatics</i>				
Benzene	$9.9 \times 10^{-13l}$	33	0.0063 <sup>o</sup>	$\Sigma$ ANs Aromatic
Toluene	$8.2 \times 10^{-12l}$	21	0.0052 <sup>o</sup>	$\Sigma$ ANs Aromatic
C8 Aromatics	$1.6 \times 10^{-11l}$	8	0.0700 <sup>o</sup>	$\Sigma$ ANs Aromatic

<sup>a</sup>Measurements at or near limit of detection. Calculated the initial concentration using

observations from Leg 2.

<sup>b</sup>We assumed that 40% of MACR+MVK measurements from the PTR-MS is MACR and 60% is MVK.

<sup>c</sup>We assumed the reaction of MACRO<sub>2</sub> with NO is faster than isomerization ( $\sim 0.04$  s<sup>-1</sup> versus 0.005 s<sup>-1</sup>); therefore, it will produce 2 multifunctional nitrates.<sup>11</sup>

<sup>d</sup>Ref 1.

<sup>e</sup>Ref 10.

<sup>f</sup>Ref 12.

<sup>g</sup>Ref 13.

<sup>h</sup>Assumed same as n-hexane

<sup>i</sup>Ref 14.

<sup>j</sup>Assumed same as n-heptane

<sup>k</sup>Assumed same as i-pentane

<sup>l</sup>Ref 15.

<sup>m</sup>Scaled to Ref 16.

<sup>n</sup>Scaled to Ref 17.

<sup>o</sup>Scaled to Ref 18.

**Table S5.** Species, corrected vapor pressure (atm), percent of gas-phase condensing onto the aerosol particle, and percent contribution of each species to the total calculated  $\Sigma\text{ANS}_{(p)}$ . The vapor pressure is calculated using SIMPOL.1<sup>19</sup> and divided by 3.<sup>20-22</sup>

Parent Compound	Corrected Vapor Pressure (atm)	% Gas-Phase Condensing onto Aerosol Particle	% Contribution to Calculated $\Sigma\text{ANS}_{(p)}$
<i>Alkanes</i>			
Methane	$5.2 \times 10^{-4}$	< 1	< 1
Ethane	$9.7 \times 10^{-5}$	< 1	< 1
Propane	$1.8 \times 10^{-5}$	< 1	< 1
i-Butane	$3.3 \times 10^{-6}$	< 1	< 1
n-Butane	$3.3 \times 10^{-6}$	< 1	< 1
i-Pentane 1 <sup>st</sup> Generation	$6.2 \times 10^{-7}$	< 1	< 1
i-Pentane 2 <sup>nd</sup> Generation	$5.1 \times 10^{-10}$	< 1	< 1
n-Pentane 1 <sup>st</sup> Generation	$6.2 \times 10^{-7}$	< 1	< 1
n-Pentane 2 <sup>nd</sup> Generation	$5.1 \times 10^{-10}$	< 1	< 1
Cyclopentane 1 <sup>st</sup> Generation	$1.2 \times 10^{-5}$	< 1	< 1
Cyclopentane 2 <sup>nd</sup> Generation	$7.0 \times 10^{-9}$	< 1	< 1
2-Methylpentane 1 <sup>st</sup> Generation	$1.2 \times 10^{-7}$	< 1	< 1
2-Methylpentane 2 <sup>nd</sup> Generation	$9.4 \times 10^{-11}$	4	< 1
3-Methylpentane 1 <sup>st</sup> Generation	$1.2 \times 10^{-7}$	< 1	< 1
3-Methylpentane 2 <sup>nd</sup> Generation	$9.4 \times 10^{-11}$	4	< 1
n-Hexane 1 <sup>st</sup> Generation	$1.2 \times 10^{-7}$	< 1	< 1
n-Hexane 2 <sup>nd</sup> Generation	$9.4 \times 10^{-11}$	4	3
Methyl Cyclopentane	$4.0 \times 10^{-7}$	< 1	< 1
Cyclohexane 1 <sup>st</sup> Generation	$2.1 \times 10^{-6}$	< 1	< 1
Cyclohexane 2 <sup>nd</sup> Generation	$1.3 \times 10^{-9}$	< 1	< 1
2,3-Dimethylbutane	$1.2 \times 10^{-7}$	< 1	< 1
n-Heptane 1 <sup>st</sup> Generation	$2.2 \times 10^{-8}$	< 1	< 1
n-Heptane 2 <sup>nd</sup> Generation	$1.8 \times 10^{-11}$	24	19
2-Methylhexane 1 <sup>st</sup> Generation	$2.2 \times 10^{-8}$	< 1	< 1
2-Methylhexane 2 <sup>nd</sup> Generation	$1.8 \times 10^{-11}$	24	19
3-Methylhexane 1 <sup>st</sup> Generation	$2.2 \times 10^{-8}$	< 1	< 1
3-Methylhexane 2 <sup>nd</sup> Generation	$1.8 \times 10^{-11}$	24	19
2,4-Dimethylpentane	$2.2 \times 10^{-8}$	< 1	< 1
2,3-Dimethylpentane	$2.2 \times 10^{-8}$	< 1	< 1
2,2,4-Trimethylpentane	$4.0 \times 10^{-9}$	< 1	< 1
<i>Alkenes</i>			
Ethene	$7.8 \times 10^{-8}$	< 1	< 1
Isoprene 1 <sup>st</sup> Generation	$4.4 \times 10^{-10}$	< 1	< 1
Isoprene 2 <sup>nd</sup> Generation	$3.7 \times 10^{-16}$	100	9
$\alpha$ -Pinene 2 Rings	$3.9 \times 10^{-11}$	6	26
$\alpha$ -Pinene 1 Ring	$1.8 \times 10^{-12}$	100	3
<i>OVOcs</i>			
Acetone	$2.2 \times 10^{-6}$	< 1	< 1
MVK	$4.1 \times 10^{-7}$	< 1	< 1
MACR	$4.1 \times 10^{-7}$	< 1	< 1
<i>Aromatics</i>			
Benzene	$2.9 \times 10^{-8}$	< 1	< 1
Toluene	$3.7 \times 10^{-9}$	< 1	< 1
C8 Aromatics	$6.7 \times 10^{-10}$	< 1	< 1

## References

1. Sander, S. P.; Abbatt, J. P. D.; Barker, J. R.; Burkholder, J. B.; Friedl, R. R.; Golden, D. M.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Moortgat, G. K., et al. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation no. 17. *JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011*.
2. Lee, L.; Wooldridge, P. J.; Gilman, J. B.; Warneke, C.; de Gouw, J.; Cohen, R. C. Low Temperatures Enhance Organic Nitrate Formation: Evidence from Observations in the 2012 Uintah Basin Winter Ozone Study. *Atmos. Chem. Phys.* **2014**, *14*, 12441-12454.
3. Paulot, F.; Crouse, J. D.; Kjaergaard, H. G.; Kroll, J. H.; Seinfeld, J. H.; Wennberg, P. O. Isoprene Photooxidation: New Insights into the Production of Acids and Organic Nitrates. *Atmos. Chem. Phys.* **2009**, *9*, 1479-1501.
4. Lee, L.; Teng, A. P.; Wennberg, P. O.; Crouse, J. D.; Cohen, R. C. On Rates and Mechanisms of OH and O<sub>3</sub> Reactions with Isoprene-Derived Hydroxy Nitrates. *J. Phys. Chem. A* **2014**, *118*, 1622-1637.
5. Bey, I.; Jacob, D.; Yantosca, R.; Logan, J.; Field, B.; Fiore, A.; Li, Q.; Liu, H.; Mickley, L.; Schultz, M. Global Modeling of Tropospheric Chemistry with Assimilated Meteorology: Model Description and Evaluation. *J. Geophys. Res.: Atmos.* **2001**, *106*, 23073-23095.
6. Mao, J.; Paulot, F.; Jacob, D. J.; Cohen, R. C.; Crouse, J. D.; Wennberg, P. O.; Keller, C. A.; Hudman, R. C.; Barkley, M. P.; Horowitz, L. W. Ozone and Organic Nitrates over the Eastern United States: Sensitivity to Isoprene Chemistry. *J. Geophys. Res.: Atmos.* **2013**, *118*, 11256-11268.
7. Browne, E. C.; Perring, A. E.; Wooldridge, P. J.; Apel, E.; Hall, S. R.; Huey, L. G.; Mao, J.; Spencer, K. M.; Clair, J. M. S.; Weinheimer, A. J., et al. Global and Regional Effects of the Photochemistry of CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>: Evidence from ARCTAS. *Atmos. Chem. Phys.* **2011**, *11*, 4209-4219.
8. Henderson, B. H.; Pinder, R. W.; Crooks, J.; Cohen, R. C.; Carlton, A. G.; Pye, H. O. T.; Vizuete, W. Combining Bayesian Methods and Aircraft Observations to Constrain the HO<sub>2</sub> + NO<sub>2</sub> Reaction Rate. *Atmos. Chem. Phys.* **2012**, *12*, 653-667.
9. Bacak, A.; Cooke, M. C.; Bardwell, M. W.; McGillen, M. R.; Archibald, A. T.; Huey, L. G.; Tanner, D.; Utembe, S. R.; Jenkin, M. E.; Derwent, R. G., et al. Kinetics of the HO<sub>2</sub> + NO<sub>2</sub> Reaction: On the Impact of New Gas-Phase Kinetic Data for the Formation of HO<sub>2</sub>NO<sub>2</sub> on HO<sub>x</sub>, NO<sub>x</sub> and HO<sub>2</sub>NO<sub>2</sub> Levels in the Troposphere. *Atmos. Environ.* **2011**, *45*, 6414-6422.
10. 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. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Volume II - Gas Phase Reactions of Organic Species. *Atmos. Chem. Phys.* **2006**, *6*, 3625-4055.



11. Crouse, J. D.; Knap, H. C.; Ornsø, K. B.; Jørgensen, S.; Paulot, F.; Kjaergaard, H. G.; Wennberg, P. O. Atmospheric Fate of Methacrolein. 1. Peroxy Radical Isomerization Following Addition of OH and O<sub>2</sub>. *J. Phys. Chem. A* **2012**, *116*, 5756-5762.
12. Wilson, E.; Hamilton, W.; Kennington, H.; Evans, B.; Scott, N.; DeMore, W. Measurement and Estimation of Rate Constants for the Reactions of Hydroxyl Radical with Several Alkanes and Cycloalkanes. *J. Phys. Chem. A* **2006**, *110*, 3593-3604.
13. Atkinson, R. Kinetics of the Gas-Phase Reactions of OH Radicals with Alkanes and Cycloalkanes. *Atmos. Chem. Phys.* **2003**, *3*, 2233-2307.
14. Sprengnether, M. M.; Demerjian, K. L.; Dransfield, T. J.; Clarke, J. S.; Anderson, J. G.; Donahue, N. M. Rate Constants of Nine C<sub>6</sub>-C<sub>9</sub> Alkanes with OH from 230 to 379 K: Chemical Tracers for [OH]. *J. Phys. Chem. A* **2009**, *113*, 5030-5038.
15. Saunders, S.; Jenkin, M.; Derwent, R.; Pilling, M. Protocol for the Development of the Master Chemical Mechanism, MCM V3 (Part A): Tropospheric Degradation of Non-Aromatic Volatile Organic Compounds. *Atmos. Chem. Phys.* **2003**, *3*, 161-180.
16. Teng, A. P.; Crouse, J. D.; Lee, L.; St Clair, J. M.; Cohen, R. C.; Wennberg, P. O. Hydroxy Nitrate Production in the OH-Initiated Oxidation of Alkenes. *Atmos. Chem. Phys.* **2015**, *15*, 4297-4316.
17. Praske, E.; Crouse, J. D.; Bates, K. H.; Kurten, T.; Kjaergaard, H. G.; Wennberg, P. O. Atmospheric Fate of Methyl Vinyl Ketone: Peroxy Radical Reactions with NO and HO<sub>2</sub>. *J. Phys. Chem. A* **2015**, *119*, 4562-4572.
18. Perring, A. E.; Pusede, S. E.; Cohen, R. C. An Observational Perspective on the Atmospheric Impacts of Alkyl and Multifunctional Nitrates on Ozone and Secondary Organic Aerosol. *Chem. Rev.* **2013**, *113*, 5848-5870.
19. Pankow, J. F.; Asher, W. E. SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds. *Atmos. Chem. Phys.* **2008**, *8*, 2773-2796.
20. Fry, J. L.; Kiendler-Scharr, A.; Rollins, A. W.; Wooldridge, P. J.; Brown, S. S.; Fuchs, H.; Dubé, W. P.; Mensah, A.; dal Maso, M.; Tillmann, R., et al. Organic Nitrate and Secondary Organic Aerosol Yield from NO<sub>3</sub> Oxidation of Beta-Pinene Evaluated using a Gas-Phase Kinetics/Aerosol Partitioning Model. *Atmos. Chem. Phys.* **2009**, *9*, 1431-1449.
21. Fry, J. L.; Kiendler-Scharr, A.; Rollins, A. W.; Brauers, T.; Brown, S. S.; Dorn, H. -.; Dubé, W. P.; Fuchs, H.; Mensah, A.; Rohrer, F., et al. SOA from Limonene: Role of NO<sub>3</sub> in Its Generation and Degradation. *Atmos. Chem. Phys.* **2011**, *11*, 3879-3894.

22. Leungsakul, S.; Jaoui, M.; Kamens, R. M. Kinetic Mechanism for Predicting Secondary Organic Aerosol Formation from the Reaction of D-Limonene with Ozone. *Environ. Sci. Technol.* **2005**, *39*, 9583-9594.