

Supplemental Information for:

The nitrate radical ( $\text{NO}_3$ ) oxidation of  $\alpha$ -pinene is a significant source of secondary organic aerosol and organic nitrogen under simulated ambient nighttime conditions

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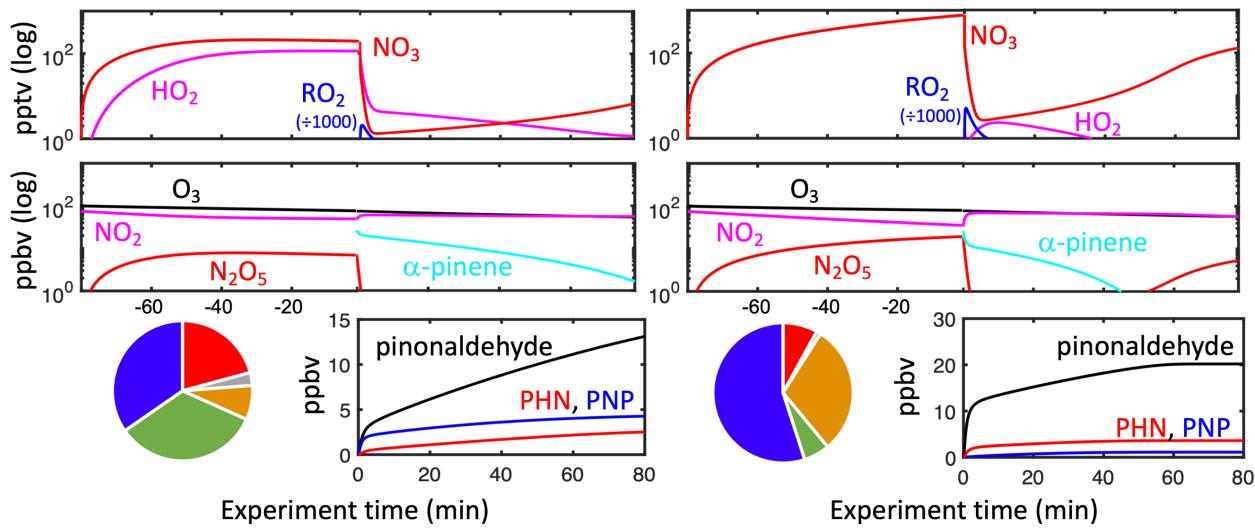
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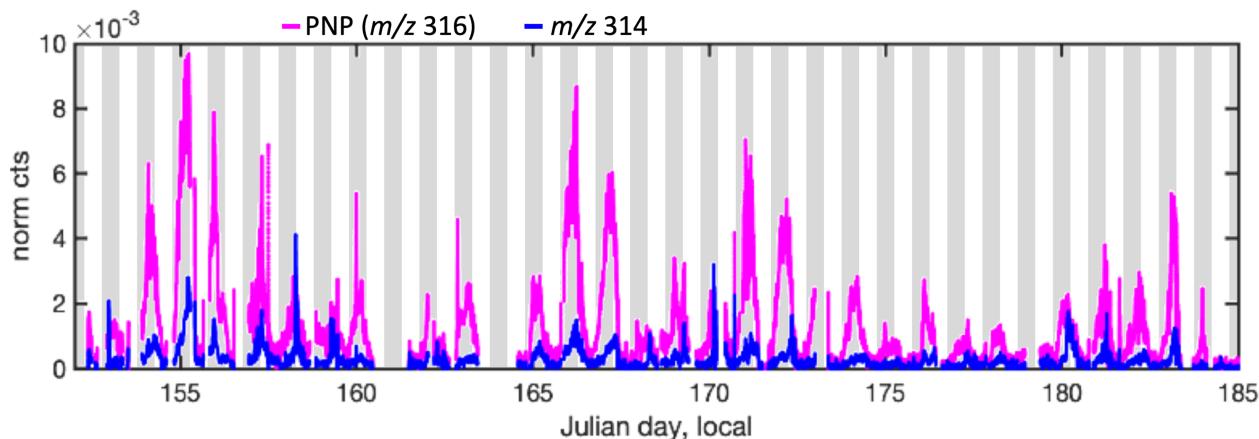
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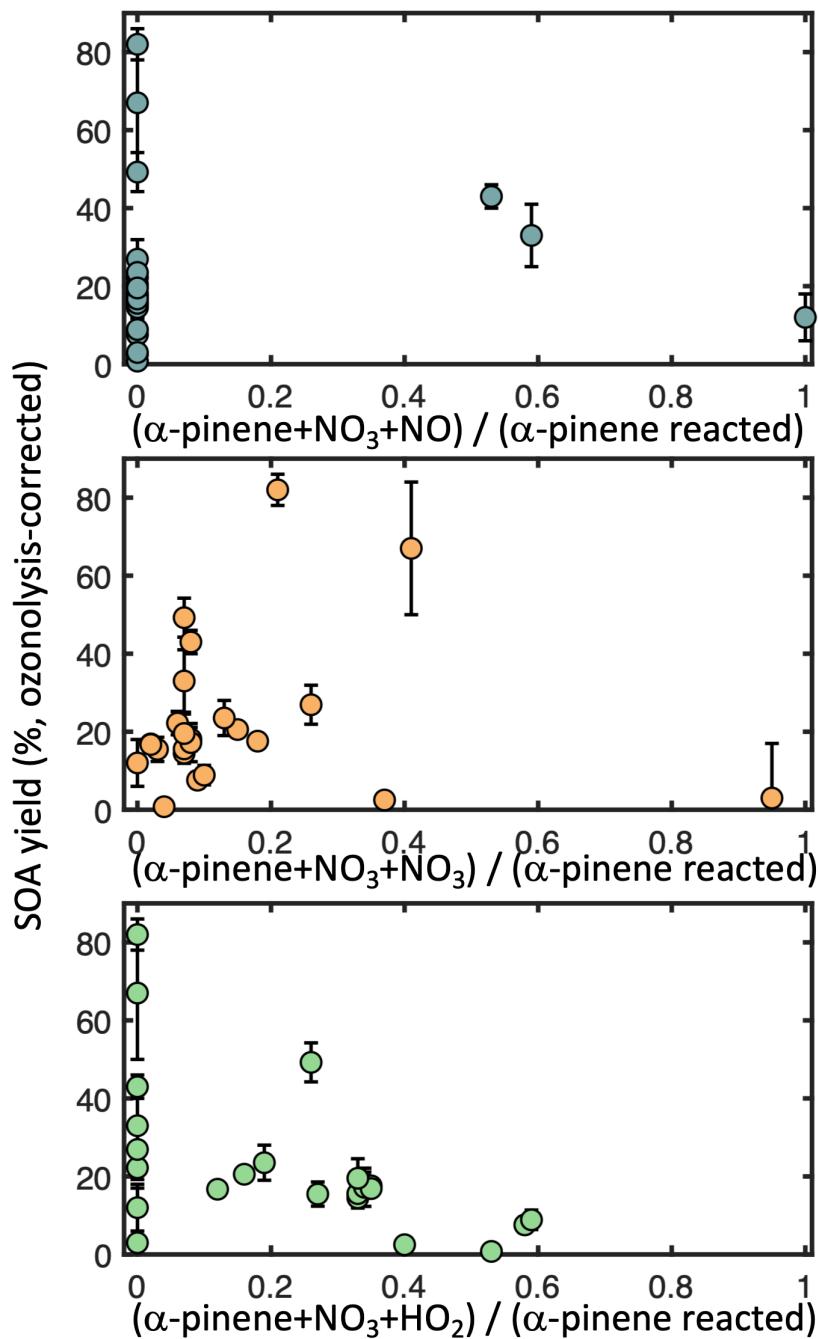
References



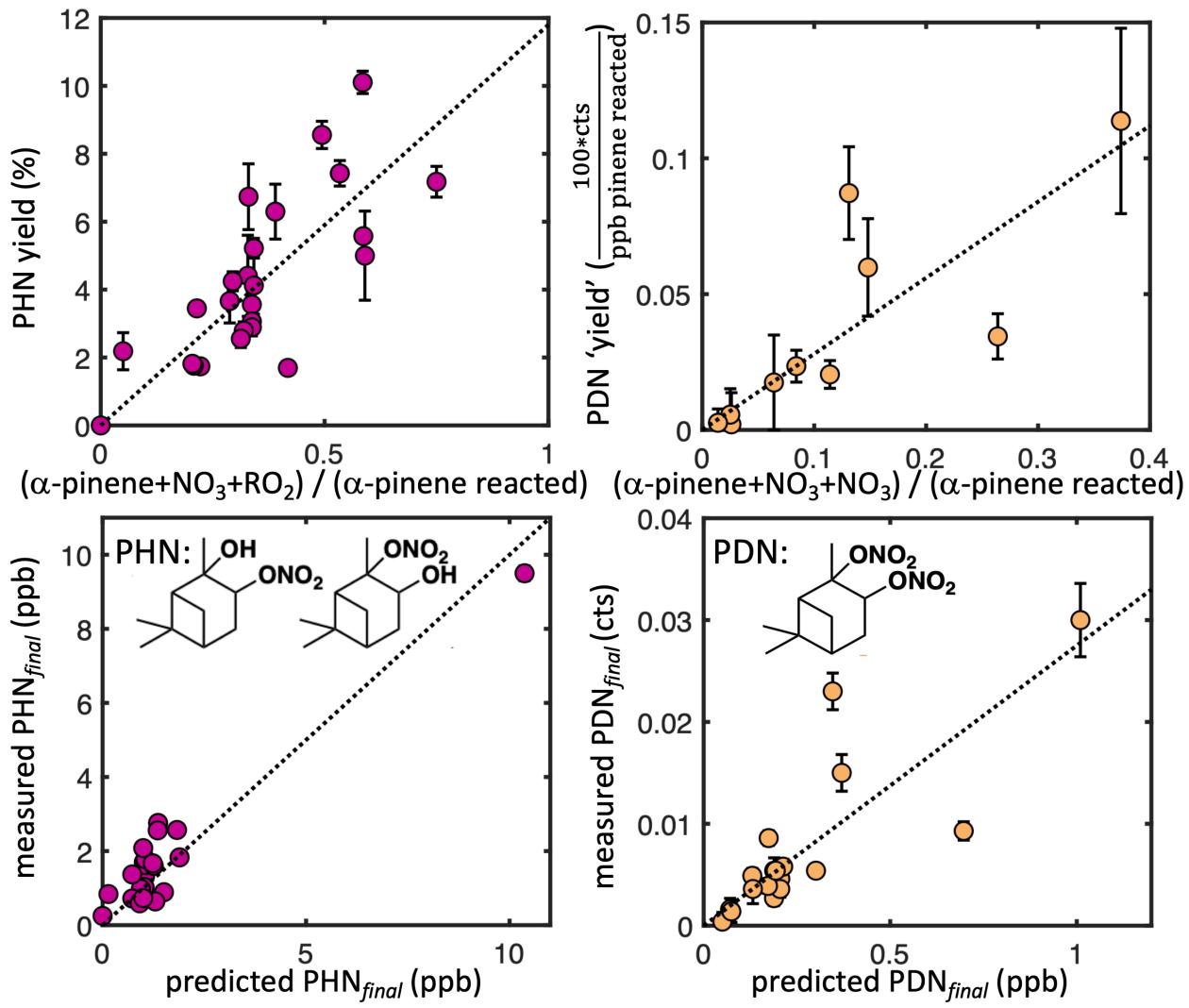
**Figure S1.** Modeled concentrations of key reactive species (top) and contributions of reactive pathways (bottom) in an example ‘simulated nighttime’ experiment with (left) and without (right) inclusion of the  $\text{NO}_3 + \text{H}_2\text{O}_2$  reaction to produce HO<sub>2</sub>. Experiment time of 0 corresponds to the  $\alpha$ -pinene injection and beginning of its oxidation. Pie charts show the percent contribution of each  $\alpha$ -pinene oxidative pathway ( $\alpha$ -pinene+O<sub>3</sub> in red,  $\alpha$ -pinene+OH in grey and  $\alpha$ -pinene+NO<sub>3</sub> speciated by subsequent RO<sub>2</sub> reaction partner: orange for NO<sub>3</sub>, blue for RO<sub>2</sub>, green for HO<sub>2</sub>). Without the  $\text{NO}_3 + \text{H}_2\text{O}_2$  reaction, the  $n\text{RO}_2 + \text{HO}_2$  pathway only contributes 6% of the total  $\alpha$ -pinene fate, which is incompatible with our high (~22%) measured yields of PNP. In our kinetic model, we use a rate constant of  $k_{\text{NO}_3+\text{H}_2\text{O}_2} = 1.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , estimated from  $(k_{\text{NO}_3+\text{CH}_2\text{O}} / k_{\text{OH}+\text{CH}_2\text{O}}) \times k_{\text{OH}+\text{H}_2\text{O}_2}$ . This is well below the upper limit of  $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  estimated by Burrows, Tyndall, & Moortgat.<sup>1</sup>



**Figure S2.** Select gas-phase organonitrates observed by  $\text{CF}_3\text{O}^-$  CIMS during the Southern Oxidant and Aerosol Study (SOAS), including PNP (*m/z* 316) and an unknown compound at *m/z* 314. Both compounds had similar diurnal cycles at SOAS (peaking at night), and were also observed during ‘simulated nighttime’ experiments in this work (Fig. 3)



**Figure S3.** Measured SOA yields from chamber experiments plotted against modeled contributions of the  $n\text{RO}_2 + \text{NO}$ ,  $n\text{RO}_2 + \text{NO}_3$ , and  $n\text{RO}_2 + \text{HO}_2$  pathways.



**Figure S4.** Measured yields of  $\alpha$ -pinene hydroxynitrate (PHN, left, a product of  $\text{RO}_2 + \text{RO}_2$  chemistry) and  $\alpha$ -pinene dinitrate (PDN, right, a product of  $\text{RO}_2 + \text{NO}$  and/or  $\text{RO}_2 + \text{NO}_3$  chemistry) as a function of the modeled contribution of their formation pathway (top) and plotted against the yields predicted by the simple kinetic model. For PDN, the CIMS cannot be properly calibrated due to a lack of standards or calibrant analogs, so the measurement values are reported as normalized CIMS counts. Dotted lines denote ordinary least squares regressions, constrained to pass through the origin, with  $R^2$  of (clockwise from top left) 0.58, 0.66, 0.67, and 0.91.

**Table S1.** Masses of proposed  $\alpha$ -pinene RO<sub>2</sub> dimers as observed in HRMS analysis of SOA from filters collected during experiments 26 ( $n\text{RO}_2 + n\text{RO}_2$ ) and 27 (simulated nighttime).<sup>a</sup>

Positive <sup>b</sup>		$n\text{RO}_2 \alpha$ C <sub>10</sub> H <sub>16</sub> NO <sub>5</sub>	$n\text{RO}_2 \beta$ C <sub>10</sub> H <sub>16</sub> NO <sub>6</sub>	$n\text{RO}_2 \gamma$ C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub>	$n\text{RO}_2 \delta$ C <sub>7</sub> H <sub>10</sub> NO <sub>7</sub>	$n\text{RO}_2 \varepsilon$ C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>10</sub>	$o\text{n}\text{RO}_2 1$ C <sub>10</sub> H <sub>17</sub> O <sub>5</sub>	$o\text{H}\text{RO}_2 2$ C <sub>10</sub> H <sub>17</sub> O <sub>7</sub>	$o_3\text{RO}_2 \text{i}$ C <sub>10</sub> H <sub>15</sub> O <sub>4</sub>	$o_3\text{RO}_2 \text{ii}$ C <sub>10</sub> H <sub>15</sub> O <sub>6</sub>	$o_3\text{RO}_2 \text{iii}$ C <sub>10</sub> H <sub>15</sub> O <sub>8</sub>
$n\text{RO}_2 \alpha$	C <sub>10</sub> H <sub>16</sub> NO <sub>5</sub>	*357.204 <sup>c</sup>	*467.200	*483.195	*441.148	*544.175	438.210	*470.200	420.199	452.189	484.179
$n\text{RO}_2 \beta$	C <sub>10</sub> H <sub>16</sub> NO <sub>6</sub>	*467.200	*483.195	*499.190	*457.143	*560.170	*454.205	*486.195	436.194	*468.184	*500.174
$n\text{RO}_2 \gamma$	C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub>	*483.195	*499.190	*515.185	473.138	576.165	*470.200	502.190	452.189	484.179	516.169
$n\text{RO}_2 \delta$	C <sub>7</sub> H <sub>10</sub> NO <sub>7</sub>	*441.148	*457.143	473.138	431.091	534.118	428.153	460.143	410.142	442.132	474.122
$n\text{RO}_2 \varepsilon$	C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>10</sub>	*544.175	*560.170	576.165	534.118	637.145	531.180	563.170	513.169	545.159	577.149
Negative <sup>d</sup>		$n\text{RO}_2 \alpha$ C <sub>10</sub> H <sub>16</sub> NO <sub>5</sub>	$n\text{RO}_2 \beta$ C <sub>10</sub> H <sub>16</sub> NO <sub>6</sub>	$n\text{RO}_2 \gamma$ C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub>	$n\text{RO}_2 \delta$ C <sub>7</sub> H <sub>10</sub> NO <sub>7</sub>	$n\text{RO}_2 \varepsilon$ C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>10</sub>	$o\text{H}\text{RO}_2 1x$ <sup>e</sup> C <sub>10</sub> H <sub>18</sub> NO <sub>9</sub>				
$n\text{RO}_2 \alpha$	C <sub>10</sub> H <sub>16</sub> NO <sub>5</sub>	*490.204	*506.199	*522.194	*480.147	*583.174	*556.200				
$n\text{RO}_2 \beta$	C <sub>10</sub> H <sub>16</sub> NO <sub>6</sub>	*506.199	*522.194	*538.189	496.142	*599.169	572.195				
$n\text{RO}_2 \gamma$	C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub>	*522.194	*538.189	554.184	512.137	615.164	588.190				
$n\text{RO}_2 \delta$	C <sub>7</sub> H <sub>10</sub> NO <sub>7</sub>	*480.147	496.142	512.137	470.090	573.117	546.143				
$n\text{RO}_2 \varepsilon$	C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>10</sub>	*583.174	*599.169	615.164	573.117	676.144	649.170				

<sup>a</sup>As in Figure 8, dimers in pink are observed only in the ‘simulated nighttime’ experiment, and those marked with a \* have moderate-to-high signal (40>S/N). Dimers in blue are observed in both the ‘simulated nighttime’ and  $n\text{RO}_2 + n\text{RO}_2$  experiments, while dimers in black are not observed. <sup>b</sup>Positive mode ions are generally sodium clusters (M+Na<sup>+</sup>). <sup>c</sup>This mass corresponds to the parent compound -2HNO<sub>2</sub>, presumably lost during ionization; the sodiated parent mass (451.205) was also observed but with low signal due to a lack of carbonyl groups on this dimer. <sup>d</sup>Negative mode ions are generally nitrate clusters (M+NO<sub>3</sub><sup>-</sup>). <sup>e</sup> $o\text{H}\text{RO}_2$  (1x) is an oxidation product of  $o\text{H}\text{RO}_2$  (1) in Figure 8.

## Mechanism S1.

Here we provide the list of new species and reactions added to the kinetic model in this work. The mechanism accurately simulates measured decay of  $\alpha$ -pinene (Figure 1), production of  $\alpha$ -pinene nitrooxy-hydroperoxide (PNP, Figure 4), production of  $\alpha$ -pinene hydroxy-nitrate (PHN, Figure S2), and concentrations of inorganic species (Figure 1) under the range of experimental conditions, but is not meant to simulate SOA formation or later-generation chemistry. While dimer formation from RO<sub>2</sub> + RO<sub>2</sub> reactions is included to approximate the levels observed in SOA, a complete representation of dimer formation would require more detailed treatment of peroxy radical isomerization as shown in Schemes 2-3. Additional reactions of inorganic species relevant to radical dynamics in the chamber are taken from the JPL Chemical Kinetics and Photochemical Data Evaluation,<sup>2</sup> and the reaction of NO<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> (producing HO<sub>2</sub> and HNO<sub>3</sub>) was added (see Fig. S1). In reaction rates, T denotes temperature (K).

### {Species}

APIN =  $\alpha$ -pinene;

APINNO2a = tertiary (major) peroxy radical from APIN + NO<sub>3</sub> + O<sub>2</sub>;

APINNO2b = secondary (minor) peroxy radical from APIN + NO<sub>3</sub> + O<sub>2</sub>;

PNP = pinene nitrooxy-hydroperoxide;

PHN = pinene hydroxy-nitrate;

PDN = pinene dinitrate;

PINAL = pinonaldehyde;

DIMER = dimers from RO<sub>2</sub> + RO<sub>2</sub> reactions;

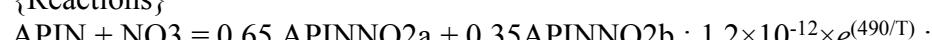
APINO2a = tertiary (major) peroxy radical from APIN + OH + O<sub>2</sub>;

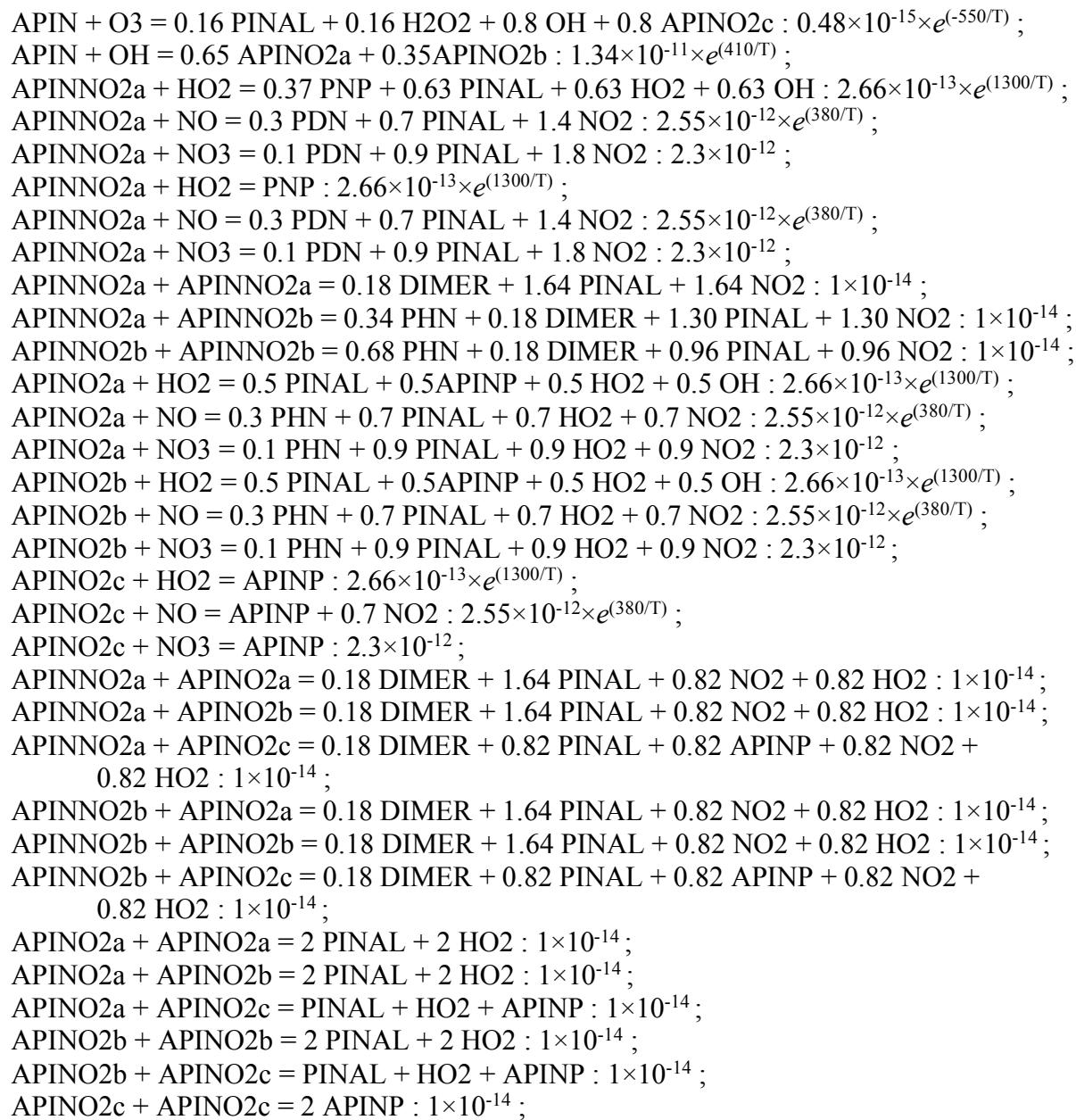
APINO2b = secondary (minor) peroxy radical from APIN + OH + O<sub>2</sub>;

APINO2c = peroxy radical from APIN + O<sub>3</sub>;

APINP = generic product of APINO2 reactions;

### {Reactions}





## References:

1. J. P. Burrows, G. S. Tyndall, and G. K. Moortgat: Absorption spectrum of  $\text{NO}_3$  and kinetics of the reactions of  $\text{NO}_3$  with  $\text{NO}_2$ ,  $\text{Cl}$ , and several stable atmospheric species at 298 K. *J. Phys. Chem.*, 89 (22), 4848-4856, DOI: 10.1021/j100268a038, 1985.
2. J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, C. Cappa, J. D. Crounse, T. S. Dibble, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, C. J. Percival, D. M. Wilmouth, and P. H. Wine "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19," JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019  
<http://jpldataeval.jpl.nasa.gov>