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*Supplement of*

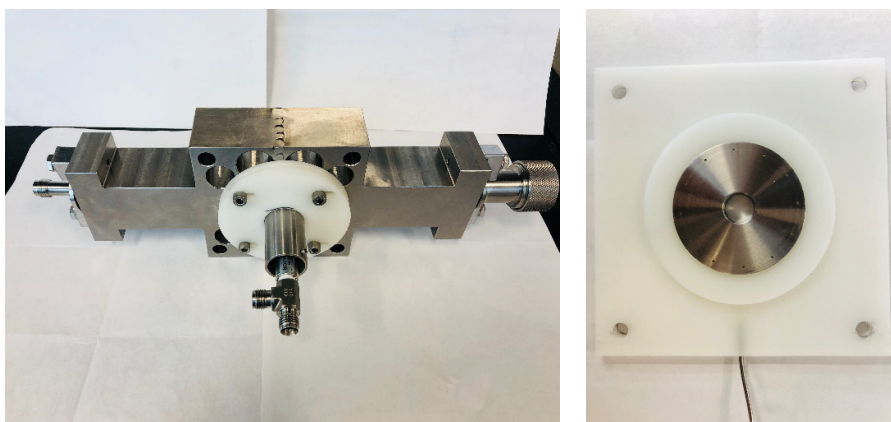
## **Relative humidity effect on the formation of highly oxidized molecules and new particles during monoterpene oxidation**

**Xiaoxiao Li et al.**

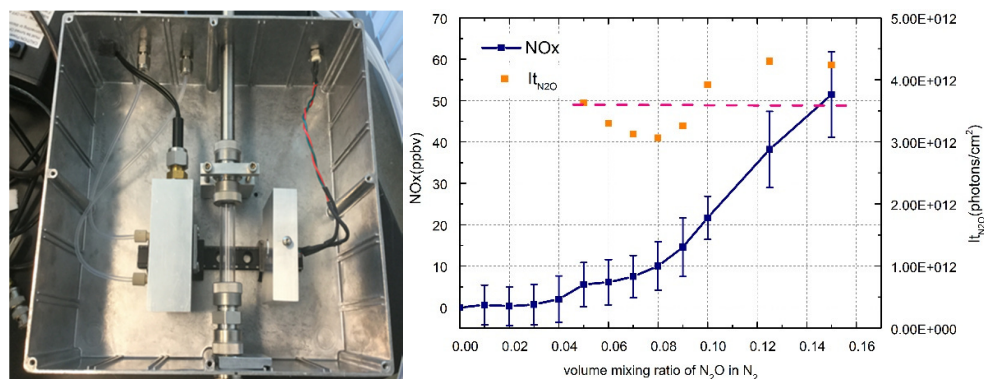
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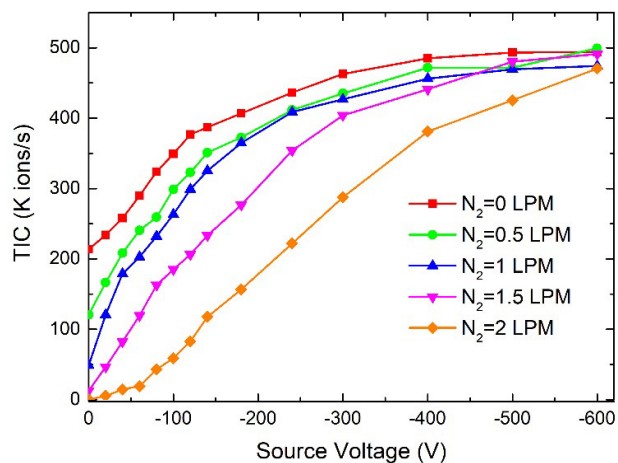
Supplemental Information: Relative Humidity Effect on the Formation of Highly Oxidized Molecules and New Particles during Monoterpene Oxidation



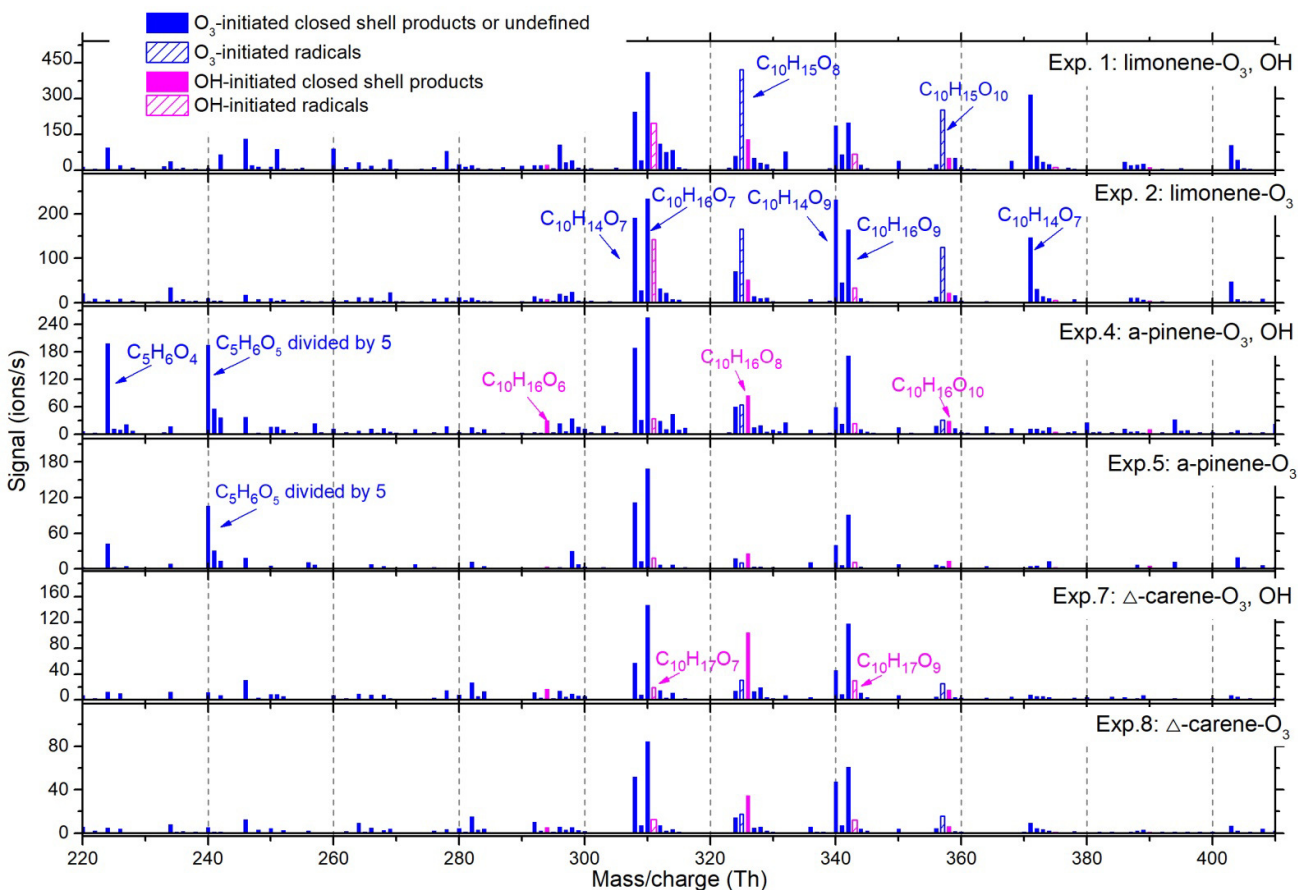
**Figure S1.** Photographs of the Transverse Ionization inlet (left) and the N<sub>2</sub> curtain gas plate (right).



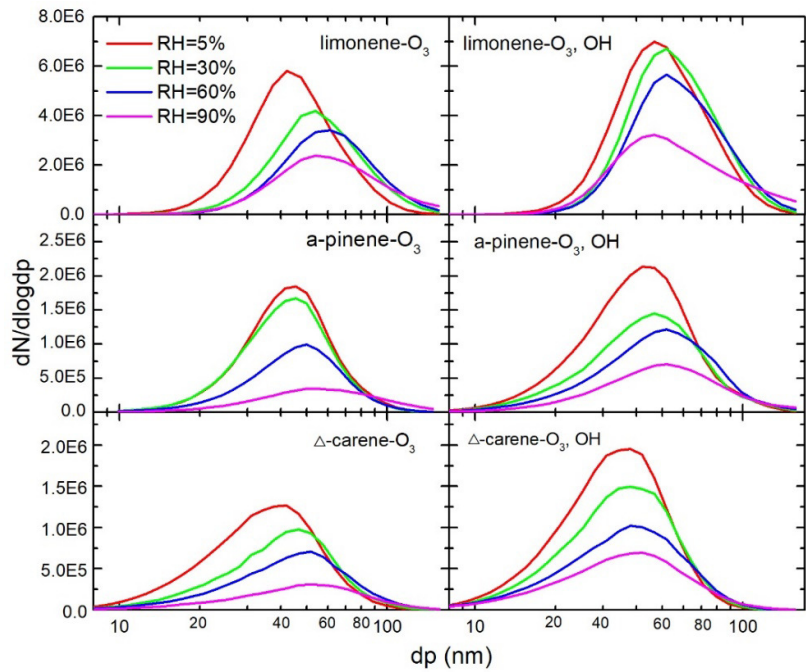
**Figure S2.** (Left) H<sub>2</sub>SO<sub>4</sub> calibration system based on the design of Kurten et al. (Kurten et al., 2012). H<sub>2</sub>SO<sub>4</sub> is generated by exposing known concentrations of gaseous SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O to 185nm UV radiation produced by a mercury lamp (model 90-0012-01, Pen Ray) and a 185 nm bandpass filter (model XB32, 185BP20, Omega). Varying [H<sub>2</sub>SO<sub>4</sub>] was achieved under conditions of constant [SO<sub>2</sub>] by varying [OH] in the system. OH is generated from the photolysis of water vapor. The water vapor concentration is calculated from the measured relative humidity (RH) and temperature. The [OH] in the system depends on both [H<sub>2</sub>O] and the light strength, represented by *It* (amount of photons per cm<sup>2</sup>), which is the product of the photon intensity *I* (amount of photons per second per cm<sup>2</sup>) and the illumination time *t<sub>r</sub>* (s). (Right) Calibration of photodiode from the N<sub>2</sub>O experiment. *It* was determined through chemical actinometry (N<sub>2</sub>O to NO<sub>x</sub> conversion). The light strength was kept constant between photodiode calibration and H<sub>2</sub>SO<sub>4</sub> calibration experiments, this was assured by measurements from a photodiode (model R5764, Hamamatsu) followed by an electrometer (model 485, Keithley). It<sub>N<sub>2</sub>O</sub> was determined to be 3.85×10<sup>12</sup> photons cm<sup>-2</sup> when the photodiode current was 62nA. In the H<sub>2</sub>SO<sub>4</sub> calibration experiment, all generated OH was transformed to H<sub>2</sub>SO<sub>4</sub> within several milliseconds, 10% of [H<sub>2</sub>SO<sub>4</sub>] diffusion loss was applied to the 15 cm connection tube between the illumination area and the LTOF inlet. The generated [H<sub>2</sub>SO<sub>4</sub>] was constrained to above ~3×10<sup>8</sup> cm<sup>-3</sup> because of the low detection limit of the RH sensor and the incomplete conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> under low [OH]. (Kurten et al., 2012).



**Figure S3.** Total ion counts from the TI-CIMS as a function of ion source voltage at different curtain gas flow rates. As the ion source voltage increased, the voltage applied to the reaction chamber changed accordingly and always kept at half of the ion source voltage. A 1 LPM curtain gas flow rate and a -100V source voltage were used in our experiments.



**Figure S4.** Averaged monomer and RO<sub>2</sub> radical mass spectra in six of the particle generation experiments. OH- and O<sub>3</sub>-derived species were identified from previous studies (Jokinen et al., 2014). No significant differences were seen between experiments with and without OH scavengers. Peak labels are the identified neutral molecule, but the mass spectra show these compounds clustered with NO<sub>3</sub><sup>-</sup> or HNO<sub>3</sub>NO<sub>3</sub><sup>-</sup> reagent ions.



**Figure S5.** Averaged size distributions as a function of RH in each experiment.

**Table S1.** The Volatility of the major products were predicted with SIMPOL.1 (Pankow and Asher, 2008) and Molecular Corridor (298K) methods (Li et al., 2016).

	molecular	$\overline{OS}_c$	non-aromatic ring <sup>1</sup> , b <sub>4</sub>	-OH, b <sub>7</sub>	-CH=O, b <sub>8</sub>	-C=O-, b <sub>9</sub>	-O-O-, b <sub>26</sub>	-OOH, b <sub>27</sub>	SIMPOL lgC* <sup>2</sup>	M-corridor lgC*	Peak area
O <sub>3</sub> -ROH	C <sub>10</sub> H <sub>16</sub> O <sub>7</sub>	-0.4	1	1	1	1	0	2	-2.49	0.5	412
	C <sub>10</sub> H <sub>16</sub> O <sub>9</sub>	-0.1	1	1	1	1	0	3	-4.88	-1.85	199
O <sub>3</sub> -ROOH	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>	-0.6	1	0	1	1	0	2	-0.34	1.58	22
	C <sub>10</sub> H <sub>16</sub> O <sub>8</sub>	-0.3	1	0	1	1	0	3	-2.72	-0.65	129
	C <sub>10</sub> H <sub>16</sub> O <sub>10</sub>	0	1	0	1	1	0	4	-5.11	-3.10	51
O <sub>3</sub> -carbonyl	C <sub>10</sub> H <sub>14</sub> O <sub>7</sub>	-0.2	1	0	1	2	0	2	-1.25	0.50	245
	C <sub>10</sub> H <sub>14</sub> O <sub>9</sub>	0.1	1	0	1	2	0	3	-3.64	-1.85	187
O <sub>3</sub> -dimer	C <sub>20</sub> H <sub>30</sub> O <sub>10</sub>	-0.65	2	0	2	2	1	2	-2.74	-4.98	65
	C <sub>20</sub> H <sub>30</sub> O <sub>12</sub>	-0.5	2	0	2	2	1	3	-5.15	-7.00	111
	C <sub>20</sub> H <sub>30</sub> O <sub>14</sub>	-0.35	2	0	2	2	1	4	-7.56	-9.16	64
OH-carbonyl	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>	-0.6	2	1	0	1	0	2	-1.22	1.58	22
	C <sub>10</sub> H <sub>16</sub> O <sub>8</sub>	-0.3	2	1	0	1	0	3	-3.60	-0.65	129
	C <sub>10</sub> H <sub>16</sub> O <sub>10</sub>	0	2	1	0	1	0	4	-5.99	-3.1	51
OH&O <sub>3</sub> -dimer	C <sub>20</sub> H <sub>32</sub> O <sub>7</sub>	-1	3	1	1	1	1	1	-0.29	-2.32	18
	C <sub>20</sub> H <sub>32</sub> O <sub>9</sub>	-0.85	3	1	1	1	1	2	-2.70	-4.04	91
	C <sub>20</sub> H <sub>32</sub> O <sub>11</sub>	-0.7	3	1	1	1	1	3	-5.11	-5.97	84
OH-dimer	C <sub>20</sub> H <sub>32</sub> O <sub>13</sub>	-0.55	3	1	1	1	1	4	-7.52	-8.06	60
	C <sub>20</sub> H <sub>34</sub> O <sub>8</sub>	-1.05	4	2	0	0	1	2	-2.66	-3.15	--
	C <sub>20</sub> H <sub>34</sub> O <sub>10</sub>	-0.9	4	2	0	0	1	3	-5.07	-4.98	--
	C <sub>20</sub> H <sub>34</sub> O <sub>12</sub>	-0.75	4	2	0	0	1	4	-7.47	-7.00	--

<sup>1</sup>The functional groups used here were directly predicted from the proposed formation pathways in Figure 9 and did not include the intramolecular isomerization, like ring closure of unsaturated RO<sub>2</sub> (Berndt et al., 2016).

<sup>2</sup>At T=298K, the parameters in SIMPOL.1 were b<sub>0</sub> = 1.842, b<sub>4</sub> = -0.021, b<sub>7</sub> = -2.183, b<sub>8</sub> = -1.320, b<sub>9</sub> = -0.937, b<sub>26</sub> = -0.392, and b<sub>27</sub> = -2.440. The equation used for volatility calculation is  $\log_{10}P_{L,i}^0(T) = \sum_k v_{k,i} b_k(T)$ , where  $P_{L,i}^0(T)$  is the liquid vapor pressure of the compound.  $v_{k,i}$  is the number of groups of type k, and  $b_k(T)$  is the contribution by each group of type k. (Pankow and Asher, 2008).

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