Supplemental material

Model mechanism tests

The base photochemical box model uses the Regional Atmospheric Chemistry Mechanism, Version 2 (RACM2) mechanism (Henderson et al., 2011). The “RACM2 + IEPOX” scheme was modified by replacing isoprene oxidation in RACM2 with the isoprene nitrate chemistry described in Paulot et al. (2009a) and the isoprene epoxide chemistry in Paulot et al. (2009b). The “RACM2 + IEPOX + Isomerization” scheme was modified based on “RACM2 + IEPOX”, by adding the unimolecular isomerization mechanism described by Peeters et al. (Peeters et al., 2009) and Peeters and Müller (2010). The “RACM2 + IEPOX + Reduced Isomerization” was modified based on “RACM2 + IEPOX + Isomerization”, by using the reduced rate of isomerization for isoprene hydroxylperoxy radicals suggested by Crounse et al. (Crounse et al., 2011). The MBO oxidation was explicitly treated in “RACM2 + IEPOX”, “RACM2 + IEPOX + Isomerization” and “RACM2 + IEPOX + Reduced Isomerization”, following Carrasco et al. (2007), Steiner et al. (2007), and Chan et al. (2009). Photooxidation of monoterpenes and sesquiterpenes was based on Wolfe and Thornton (2011). Photolysis rates were calculated by the Tropospheric Ultraviolet and Visible (TUV) radiation model and then scaled based on the Photosynthetically Active Radiation (PAR) measurements.

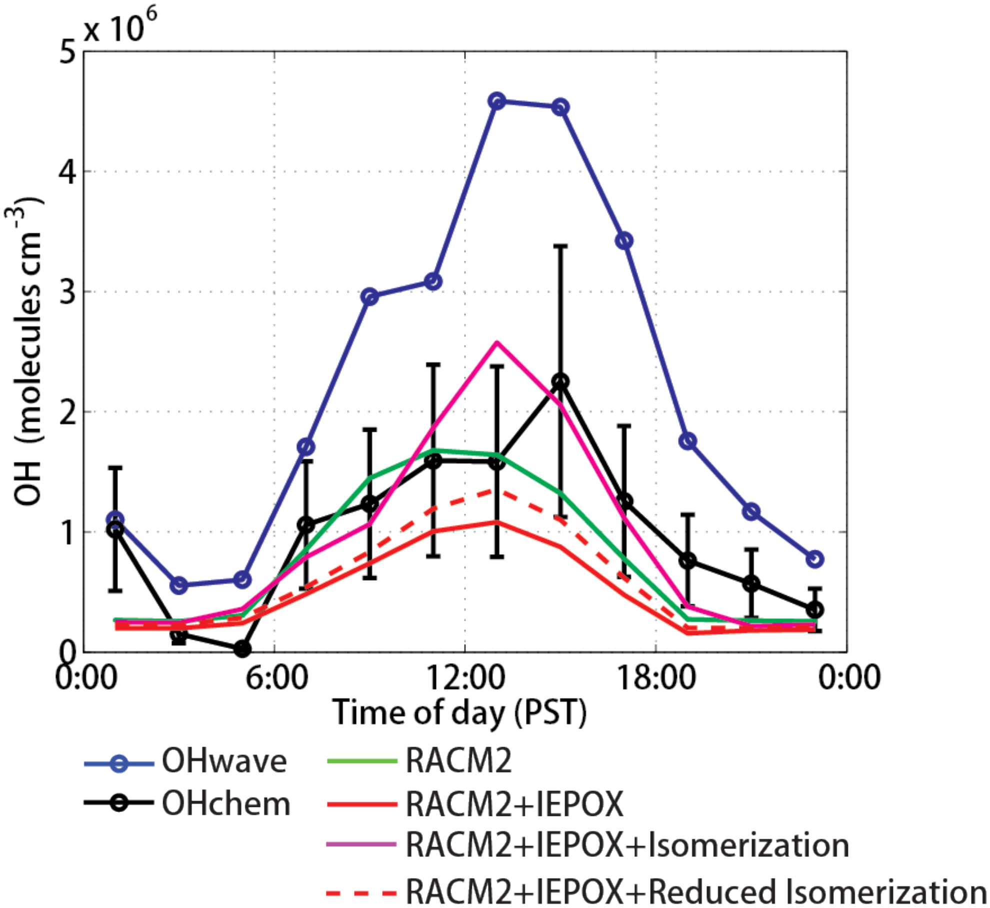

Figure S1. Diurnal cycle of measured and modeled OH between 20 June and 30 July 2009 near the Blodgett Forest Research Station (BFRS). "OHwave" is represented by blue open circles and "OHchem" by black open circles. The vertical bars indicate OHchem's absolute uncertainty of ±50% (2σ confidence), which comes from combining the uncertainty from the internally generated OH is removed by the C_3F_6 addition used to measure OHchem (±30%) and the absolute uncertainty of the OH measurements (±40% at 2σ confidence). Model results are shown as the base RACM2 model (green solid lines), the "RACM2 + IEPOX" scheme (red solid lines), the "RACM2 + IEPOX + Isomerization" scheme (magenta solid lines), and the "RACM2 + IEPOX + Reduced Isomerization" scheme (red dashed lines) (see text for details). Note that the "RACM2 + IEPOX + Reduced Isomerization" scheme is identical to the simulation used in the main text.

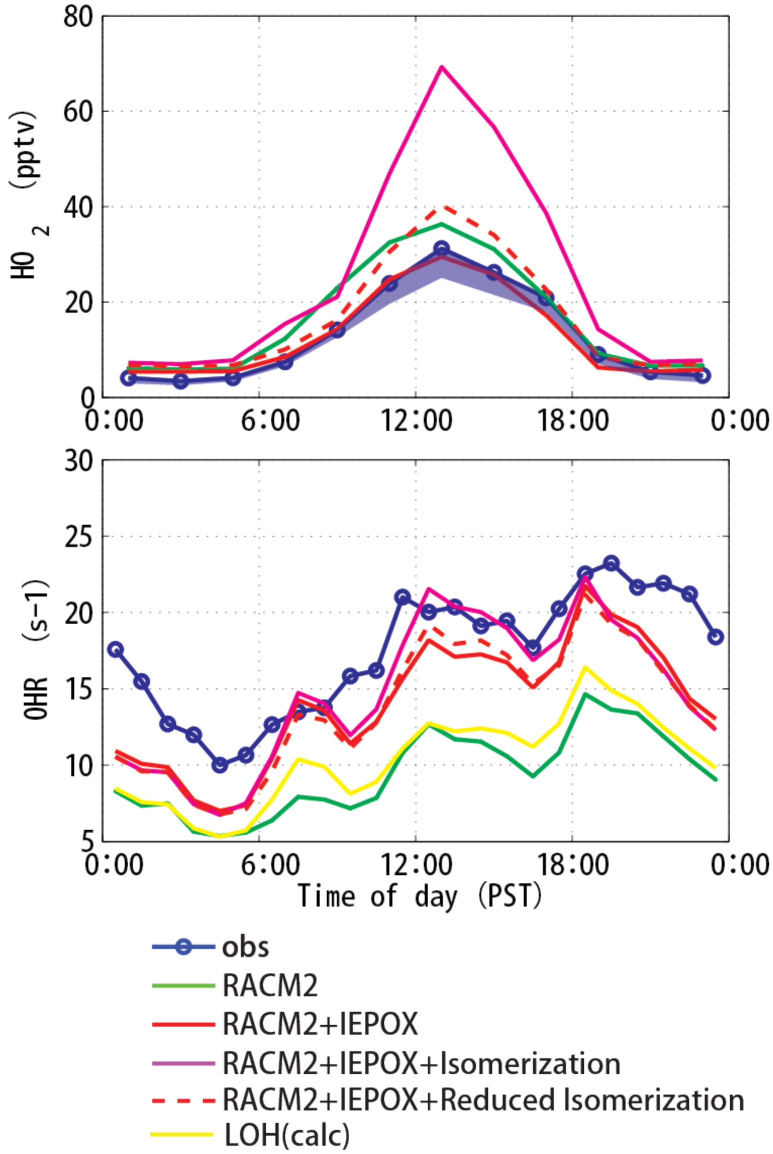

Figure S2. Diurnal cycle of HO_2 (top panel) and OH reactivity (bottom panel) between 20 June and 30 July 2009 near the Blodgett Forest Research Station (BFRS). In the top panel, the shaded area below measured HO_2 (blue open circles) indicates the contribution to measured HO_2 from an RO_2 interference from isoprene, MVK and MACR (Fuchs et al., 2011). In the bottom panel, the calculated OH reactivity from available measurements (LOH) is represented by a yellow line. Model results are shown as the base RACM2 model (green solid lines), the "RACM2 + IEPOX" scheme (red solid lines), the "RACM2 + IEPOX + Isomerization" scheme (magenta solid lines), and the "RACM2 + IEPOX + Reduced Isomerization" scheme (red dashed lines) (see text for details). Note that the "RACM2 + IEPOX + Reduced Isomerization" scheme is identical to the simulation used in the main text. The discrepancy between LOH and RACM2 is mainly due to the species lumping.

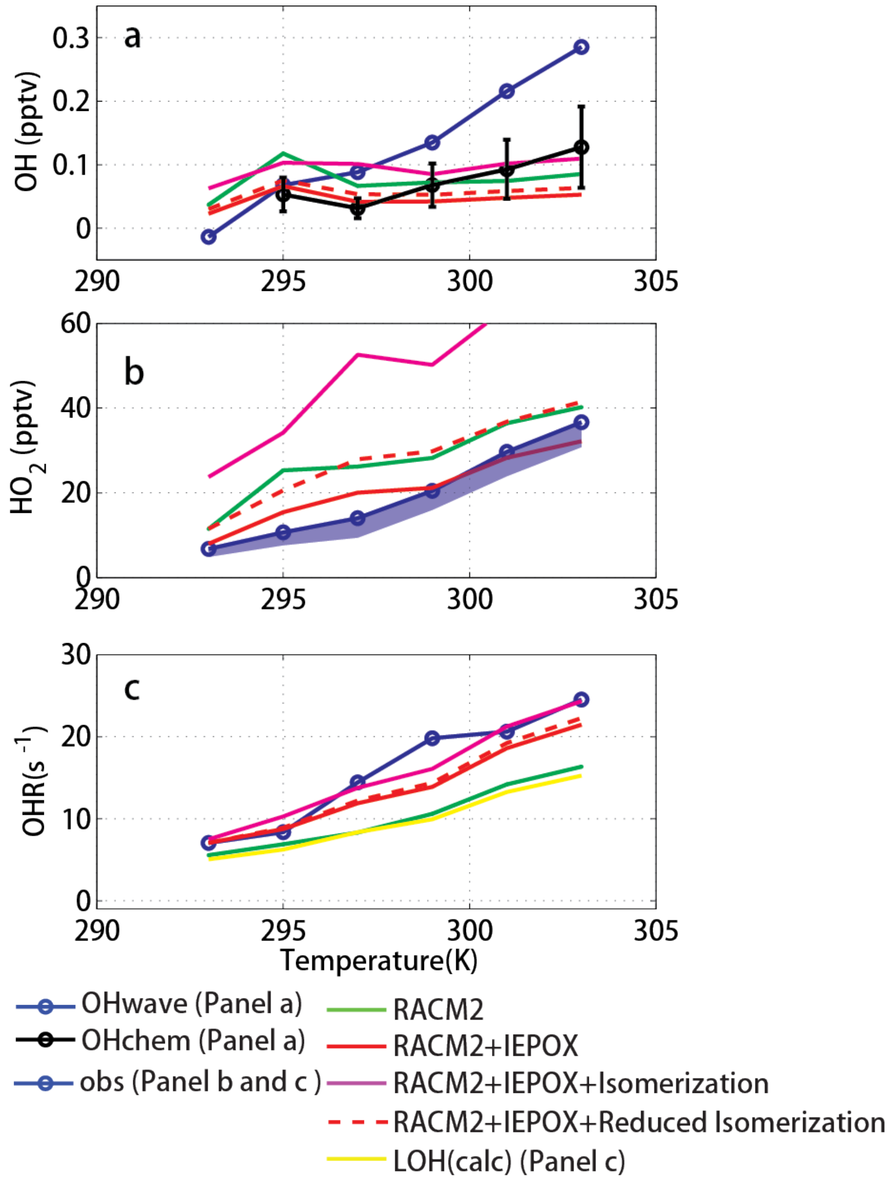

Figure S3 Temperature dependence of (a) daytime measured and modeled OH, (b) daytime measured and modeled HO_2, and (c) OH reactivity between 9:00 and 15:00 PST during BEARPEX09. In panel (a), "OHwave" is represented by blue open circles and "OHchem" by black open circles. The vertical bars indicate a combined uncertainty from the internally generated OH is removed by the C_3F_6 addition used to measure OHchem (30%), and the absolute uncertainty of the OH measurements (±40% at 2σ confidence). In panel (b), the shaded area below measured HO_2 (blue open circles) indicates the contribution to measured HO_2 from a RO_2 interference from isoprene, MVK and MACR (Fuchs et al., 2011). In panel (c), the calculated OH reactivity from available measurements is represented by a yellow line. Model results are shown as the base RACM2 model (green solid lines), the "RACM2 + IEPOX" scheme (red solid lines), the "RACM2 + IEPOX + Isomerization" scheme (magenta solid lines), and the "RACM2 +

IEPOX + Reduced Isomerization” scheme (red dashed lines) (see text for details). Note that the “RACM2 + IEPOX + Reduced Isomerization” scheme is identical to the simulation used in the main text.

Table S1 Other measured species and their averaged concentrations (Unit: pptv) [a]

Species	Daytime Conc (9am-3pm)	24h average	Measured by	Height
Glyoxal	64 ± 33	65 ± 36	Laser-Induced Phosphorescence	2m, 3m, 9m ,18m
HCHO	4300 ± 2200	4600 ± 2300	Laser-Induced Fluorescence	2m, 3m, 9m ,18m
Glycolaldehyde	1110 ± 694	1108 ± 673	CIMS	18m
H_2O_2	1105 ± 348	822 ± 396	CIMS	18m
Hydroxyacetone	697 ± 460	760 ± 460	CIMS	18m
Acetone	3300 ± 1300	3600 ± 1300	GC-FID/PTR-MS	2, 6, 10, 14, 18m
Acetonitrile	150 ± 50	160 ± 50	PTR-MS	2, 6, 10, 14, 18m
Acetaldehyde	1500 ± 800	1900 ± 1000	PTR-MS	2, 6, 10, 14, 18m
α-Pinene	100 ± 60	210 ± 160	GC-FID	18m
β-Pinene	70 ± 40	130 ± 90	GC-FID	18m
Butane	160 ± 180	170 ± 190	GC-FID	18m
Butanol	3100 ± 800	3700 ± 1300	GC-FID	18m
Camphene	9.4 ± 6.7	13 ± 9.6	GC-FID	18m
Isobutylalcohol	120 ± 60	130 ± 50	GC-FID	18m
Isoprene	1700 ± 800	1.4 ± 0.7) × 10^3	GC-FID	18m
MVK	570 ± 400	540 ± 390	GC-FID/PTR-MS	18m
MACR	220 ± 160	230 ± 160	GC-FID/PTR-MS	18m
MBO	3000 ± 1600	2200 ± 1900	GC-FID/PTR-MS	2, 6, 10, 14, 18m
Sum of Sesquiterpenes	62 ± 44	83 ± 68	PTR-MS	2, 6, 10, 14, 18m
MethylChavicol	62 ± 40	98 ± 90	PTR-MS	2, 6, 10, 14, 18m
Methanol	13700 ± 5400	16300 ± 8100	PTR-MS	2, 6, 10, 14, 18m
Ethanol	1700 ± 700	800 ± 700	GC-FID	18m
Benzene	48 ± 31	62 ± 40	PTR-MS	2, 6, 10, 14, 18m
Toluene	195 ± 129	253 ± 185	GC-FID	18m
HNO_3	330 ± 20	320 ± 60	TD-LIF	18m
MPAN	29 ± 15	19 ± 15	CIMS	1,2 ,6, 10, 14, 18m
PAN	275 ± 199	248 ± 171	CIMS	1,2 ,6, 10, 14, 18m
PPN	15 ± 16	13 ± 16	CIMS	1,2 ,6, 10, 14, 18m

NO_2[b]	200 ± 200	800 ± 3300	TD-LIF	1, 4, 9, 18 m
NO [b]	74 ± 240	300 ± 4300	Chemiluminescence	1, 4, 9, 18 m
HONO	15 ± 10	33 ± 31	Wet chemistry	14 m
CO	$(130 \pm 28) \times 10^3$	$(137 \pm 29) \times 10^3$	TECO 48C	12.5 m
O_3	$(54 \pm 8) \times 10^3$	$(53 \pm 11) \times 10^3$	Dasibi 1008-PC Ozone Analyzers	2, 6, 10, 14, 18m

[a] Total alkyl nitrates are not included due to the lack of detailed speciation.

[b] NO and NO_2 were influenced by generator plumes at night.

Table S2 OH yield from ozonolysis of terpenes

Species	Yield	Reference
β-caryophyllene (C15H24)	0.16 ± 0.4	Winterhalter et al. (2009)
Camphene	<0.18	Atkinson et al. (1992)
2-Carene	0.81 ± 0.11	Aschmann et al. (2002)
3-Carene	0.86 ± 0.11	Aschmann et al. (2002)
Limonene	0.67 ± 0.10	Aschmann et al. (2002)
Myrcene	0.63 ± 0.09	Aschmann et al. (2002)
β-Phellandrene	0.14	Atkinson et al. (1992)
α-Pinene	0.77 ± 0.10	Aschmann et al. (2002)
β-Pinene	0.35	Atkinson et al. (1992)
Ocimene	0.55 ± 0.09	Atkinson et al. (1992)
Sabinene	0.33 ± 0.05	Atkinson et al. (1992)
α-Terpinene	0.38 ± 0.05	Aschmann et al. (2002)
γ-Terpinene	0.81 ± 0.11	Aschmann et al. (2002)
Terpinolene	0.74 ± 0.10	Atkinson et al. (1992)
Linalool	0.66 ± 0.10	Atkinson et al. (1995)
α -Phellandrene	0.34 ± 0.08	Herrmann et al. (2010)

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