Supplementary information

OH, HO$_2$, and RO$_2$ radical chemistry in a rural forest environment: Measurements, model comparisons, and evidence of a missing radical sink

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Text S1: In order to determine the relative accuracy of the LIF and ECHAMP radical measurements, on July 25th the ECHAMP sampled from the IU calibration source. For this comparison, isoprene was added to the humidified air, producing 50% HO$_2$ and 50% isoprene-RO$_2$. Two data points were collected: 1: Calibration source = 335 ppt HO$_2$ + isoprene RO$_2$, RH = 33%, ECHAMP measured 326 ppt, 2. Calibration source = 314 ppt HO$_2$ + isoprene RO$_2$, RH = 31%, ECHAMP measured 309 ppt.
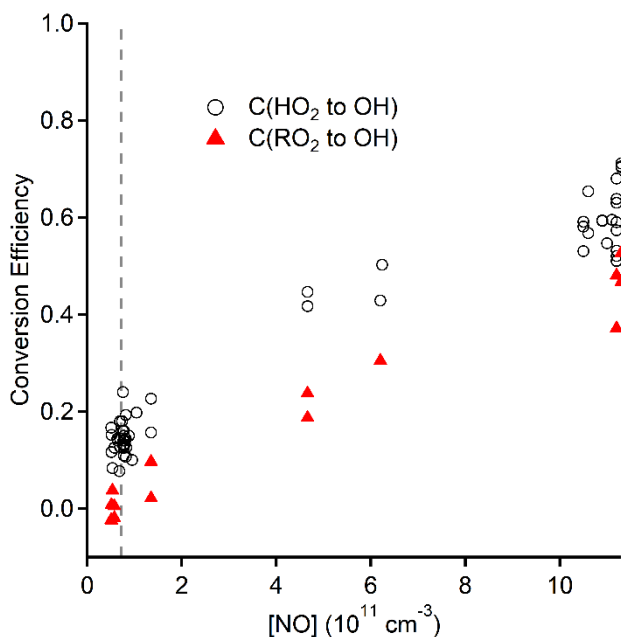
One reason for this excellent agreement (within 3%) is that the largest source of uncertainty for the calibration gas concentration - the product of the UV lamp actinic flux and the irradiation time ("Ft") - was tied to readings from ECHAMP as it was determined by the measurement of O$_3$ in the ECHAMP background channel when sampling dry zero air (Kundu et al., 2019). The Licor 6262 H$_2$O measurements used for the IU calibration source also agreed with the water vapor mixing ratios determined using the ECHAMP RH/T probe within 5%.

Table S1: Measured compounds used as model constraints within RACM and respective measurement sources (CU: University of Colorado, UH: University of Houston, NE: IMT Nord Europe, UM: University of Minnesota, HU: Harvard University, NCAR: National Center for Atmospheric Research, SUNY: University at Albany)

RACM input	Grouped compounds	Source	RACM input	Grouped compounds	Source
H2	hydrogen	Calc.	NO	nitrous oxide	NCAR
O3	ozone	CU	NO2	nitric oxide	NCAR
CO	carbon monoxide	UH	HONO	nitrous acid	SUNY
SO2	sulfur dioxide	UH	ISO	isoprene	UM
H2O	water vapor	UH	MVK	methylvinylketone	UM
CH4	methane	Calc.	MACR	methacrolein	UM/NE
ETH	ethane	NE	API	monoterpenes	UM
HC3	propane, n-butane, isobutane	NE	BALD	benzaldehyde	UM
			ACD	acetaldehyde	UM
HC5	isopentane, n-pentane, n-heptane, dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane	NE	ACT	acetone	UM
			HCHO	formaldehyde	HU/NE
			ALD	propanal, butanal	NE
			GLY	glyoxal	NE
HC8	ethyne, nonane	NE	MGLY	methylglyoxal	NE
ETE	ethene	NE	BEN	benzene	UM
OLI	trans-2-butene	NE	TOL	toluene, ethylbenzene, 2-ethyltoluene	UM/NE
OLT	propene, 1-butene	NE			
DIEN	butadiene	NE	XYP/XYM	m,p-xylene	NE
MEK	methylethylketone	NE	XYO	o-xylene	NE

Table S2: Model constraints, their designation within MCM, and respective measurement sources.

MCM Designation	Measured Constraint	MCM Designation	Measured Constraint
University of Houston		**IMT Nord Europe**	
T	temperature	HCHO	formaldehyde
RH	relative humidity	C2H2	ethyne
P	pressure	C2H4	ethene
j(NO$_2$)	photolysis rate constant	C2H6	ethane
SO2	sulfur dioxide	C3H6	propene
CO	carbon monoxide	C3H8	propane
		NC4H10	n-butane
University of Colorado		IC4H10	isobutane
O3	ozone	BUT1ENE	1-butene
		TBUT2ENE	trans-2-butene
National Center for Atmospheric Research		C4H6	1,3-butadiene
NO	nitric oxide	M22C4	2,2-dimethylbutane
NO2	nitrogen dioxide	M3PE	3-methylpentane
		M2PE	2-methylpentane
University of Minnesota		NC5H12	n-pentane
C5H8	isoprene	IC5H12	isopentane
APINENE	monoterpenes	NC6H14	hexane
CH3CHO	acetaldehyde	NC7H17	n-heptane
CH3COCH3	acetone	NC9H20	nonane
BENZENE	benzene	MEK	methyl ethyl ketone
CH3OH	methanol	MGLYOX	methylglyoxal
TOLUENE	toluene	C2H5CHO	propanal
MVK	methyl vinyl ketone	C3H7CHO	butanal
MACR	methacrolein	BENZAL	benzaldehyde
		EBENZ	ethylbenzene
Harvard University		TM135B	mesitylene
HCHO	formaldehyde	OETHTOL	2-ethyltoluene
		OXYL	o-xylene
SUNY		MXYL	m-xylenes
HONO	nitrous acid	STYRENE	styrene

Figure S1: Conversion efficiencies of HO₂ to OH (black open circles) and isoprene RO₂ to OH (red triangles) as a function of the NO concentration inside the sampling cell. The measured values were obtained from calibrations performed before and during the campaign. The vertical dashed line indicates the NO concentration used for HO₂ measurements.
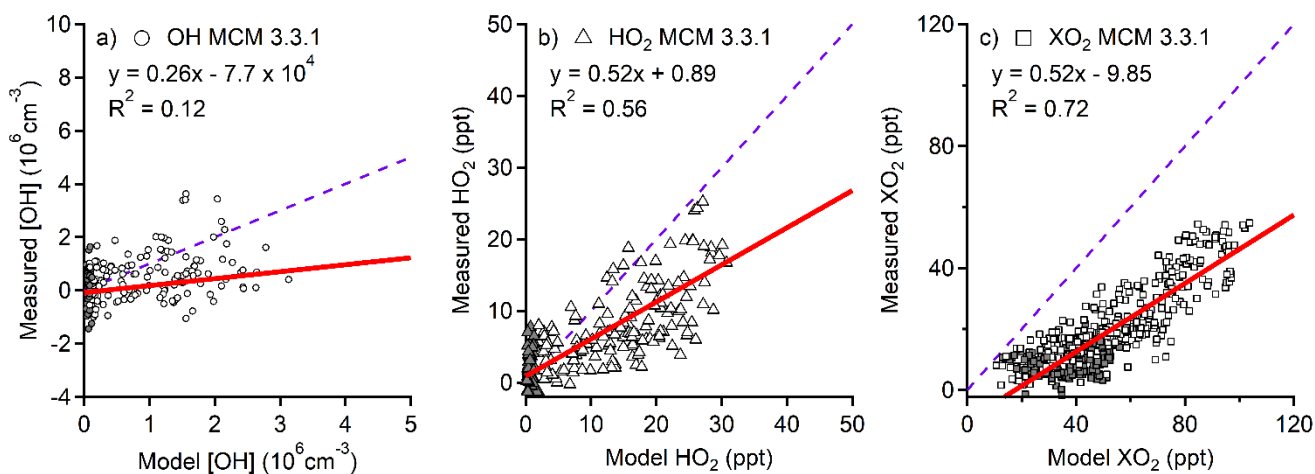
Figure S2: Correlation plots of modeled radical concentrations (MCM-3.3.1) against measurements of a) OH (circles), b) HO₂ (triangles), and c) XO₂ (squares). Filled symbols denote nighttime and open symbols indicate measurements made during the day. The dashed purple line indicates a 1:1 correlation and the red lines show measurement vs. model regressions of the data weighted by both the precision of the measurements and the uncertainty of the model concentrations.
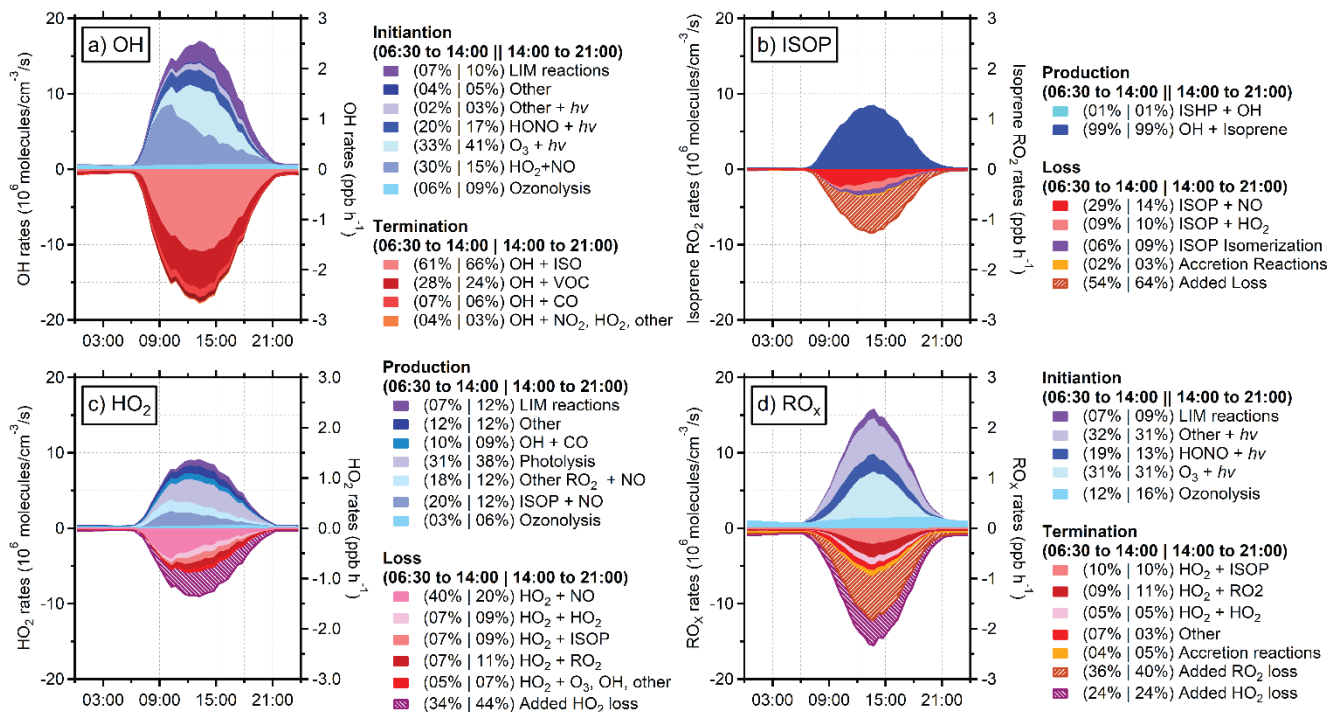
Figure S3: Radical budgets for a) OH, b) HO₂, c) isoprene-RO₂, and d) total ROₓ radical budget from the RACM2-ACC model with added loss mechanisms for HO₂ and isoprene RO₂. Shades of blue represent reactions that produce OH, and shades of red represent loss rates, including reactions that propagate to RO₂ or HO₂. Percentages represent the relative initiation or termination rates of each respective process in the morning (06:30: to 14:00) and during the evening (14:00 to 21:00) which are indicated by the vertical dashed lines.
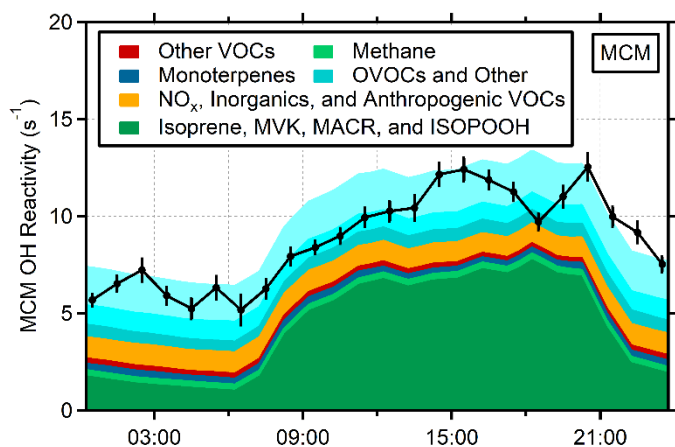

Figure S4: Diurnal average of the measured (IU-TOHLM instrument) and modeled total OH reactivity at the top of the tower during PROPHET-AMOS. Modeled reactivity is largely based on measured species that are used as constraints in the model but also includes contributions from unmeasured oxidation products in the MCM 3.3.1 model.

References

Kundu, S., Deming, B. L., Lew, M. M., Bottorff, B. P., Rickly, P., Stevens, P. S., Dusanter, S., Sklaveniti, S., Leonardis, T., Locoge, N., and Wood, E. C.: Peroxy radical measurements by ethane – nitric oxide chemical amplification and laser-induced fluorescence during the IRRONIC field campaign in a forest in Indiana, Atmos. Chem. Phys., 19, 9563-9579, https://doi.org/10.5194/acp-19-9563-2019, 2019.