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Mechanistic study of the formation of ring-retaining and ring-opening products from the oxidation of aromatic compounds under urban atmospheric conditions

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1 Inlet Losses in CIMS Instruments

Concentrations of gaseous analytes can be perturbed by gas-wall interactions occurring in the tubing used for sampling gases from the environmental chamber or inside the instruments. In order to estimate the response timescale of CIMS instruments (PTR3, Vocus, and I- CIMS), we follow the procedure described in detail by Pagonis et al. (2017). At the beginning of the procedure, the instruments sampled air from the environmental chamber containing decane photooxidation products. Later, the instruments sampling lines were abruptly reconnected to zero air resulting in step-function decrease in the concentrations of the oxidation products. PTR3, Vocus and I- CIMS time responding profiles measured in response to this step-function decrease were used to calculate delay times for the three instruments. Inlet delay times for all measured compounds did not exceed 20 seconds (Fig. S1).

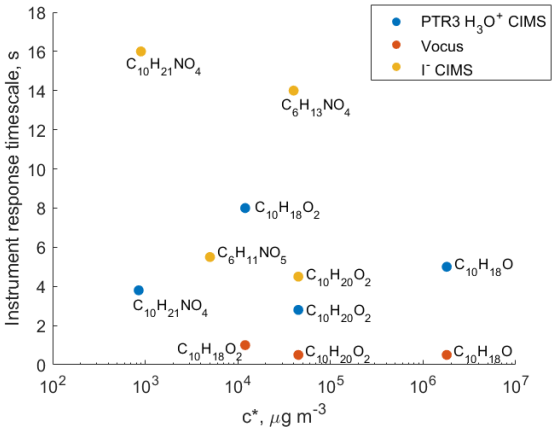

Figure S1: Measured instrument delay times as a function of SIMPOL c* for CIMS instruments.

2 Additional Figures and Tables

Table S1: Description of experiments.

Expt. no.	VOC	Initial VOC concentration, ppbv	Initial HONO injection, ppbv	Additional HONO injections[a], ppbv	Particle loading after seed injection[b], cm^{-3}	Temp., K	RH, %	Total dilution
1	toluene	89	28	16 (124); 28 (220)	$2.6 \cdot 10^4$	292	2%	0.44
2	toluene	89	30	17 (140); 6 (180); 12 (290)	$4.2 \cdot 10^4$	292	2%	0.62
3	toluene	89	31	21 (125); 18 (290)	$3.2 \cdot 10^4$	292	2%	0.65
4	toluene	89	28	23 (180)	100[c]	292	3%	0.45
5	1,2,4-TMB	69	30	5 (155); 10 (300)	$3.6 \cdot 10^4$	292	2%	0.56
6	1,2,4-TMB	69	31	13 (145); 10 (245); 5 (345)	$3.8 \cdot 10^4$	292	2%	0.72
7	1,2,4-TMB	69	34	18 (150); 6 (265); 13 (390)	$5.7 \cdot 10^4$	292	2%	0.74
8	1,2,4-TMB	69	60	-	100[c]	292	2%	0.27

[a] The following format is used: HONO injection in ppbv (time since the beginning of the experiment in min).

[b] Particle loading was measured before the chamber lights were turned on.

[c] No seed was injected in the two experiments.

Table S2: Sensitivities of I^- CIMS for calibrated species

Species	Ion formula	m/z	Sensitivity (ndcps/ppb)
Formic acid	$CH_2O_2I^-$	172.91	3000
Acetic acid	$C_2H_4O_2I^-$	186.93	130
Acrylic acid	$C_3H_4O_2I^-$	198.93	63
Glycolic acid	$C_2H_4O_3I^-$	202.92	880
cis-2-butene-1,4-diol	$C_4H_8O_2I^-$	214.96	1600
1,2-butanediol	$C_4H_{10}O_2I^-$	216.97	110
Phenol	$C_6H_6OI^-$	220.95	180
Malonic acid	$C_3H_4O_4I^-$	230.92	74
o-cresol	$C_7H_8OI^-$	234.96	65
Nitrophenol	$C_6H_5NO_3I^-$	265.93	38500

Table S3: Sensitivities of PTR3 H_3O^+ CIMS and PTR3 NH_4^+ CIMS for calibrated species

Species	PTR3 H_3O^+ CIMS			PTR3 NH_4^+ CIMS		
	Ion formula	m/z	Sensitivity (ndcps/ppb)	Ion formula	m/z	Sensitivity (ndcps/ppb)
Acetone	$C_3H_6OH^+$	59.05	12900	$C_3H_6ONH_4^+$	76.08	10600
Acetic acid	$C_2H_4O_2H^+$	61.03	9600	$C_2H_4O_2NH_4^+$	78.06	840
Methacrolein	$C_4H_6OH^+$	71.05	15300	$C_4H_6ONH_4^+$	88.08	4900
2-furanone	$C_4H_4O_2H^+$	85.03	20700	$C_4H_4O_2NH_4^+$	102.06	10300
Diacetyl	$C_4H_6O_2H^+$	87.04	5000	$C_4H_6O_2NH_4^+$	104.07	5200
Angelica lactone	$C_5H_6O_2H^+$	99.04	19400	$C_5H_6O_2NH_4^+$	116.07	20800
Benzaldehyde	$C_7H_6OH^+$	107.05	16200	$C_7H_6ONH_4^+$	124.07	14500
o-cresol	$C_7H_8OH^+$	109.07	6900	$C_7H_8ONH_4^+$	126.09	370
1,2,4-TMB	$C_9H_{12}H^+$	121.10	1640	$C_9H_{12}NH_4^+$	138.13	800
3-decanone	$C_{10}H_{20}OH^+$	157.16	13600	$C_{10}H_{20}ONH_4^+$	174.19	23200

Table S4: Estimated NH_4^+ CIMS sensitivity factors for species detected in toluene experiments.

Compound	*m/z*	$KE_{cm\ 50}$, eV	Sensitivity factor
$C_7H_7NO_3$	171.077	0.166	0.69
$C_7H_8O_4$	174.077	0.185	0.89
$C_7H_5NO_4$	185.056	0.166	0.69
$C_7H_7NO_4$	187.072	0.293	1
$C_7H_6O_5$	188.056	0.192	0.97
$C_7H_8O_5$	190.072	0.208	1
$C_7H_{10}O_5$	192.087	0.192	0.97
$C_7H_5NO_5$	201.051	0.175	0.79
$C_7H_6O_6$	204.051	0.198	1
$C_7H_9NO_5$	205.083	0.183	0.87
$C_7H_8O_6$	206.067	0.197	1
$C_7H_{10}O_6$	208.082	0.193	0.98
$C_7H_7NO_6$	219.062	0.188	0.93
$C_7H_9NO_6$	221.077	0.187	0.92

$C_7H_7NO_7$	235.057	0.185	0.89
$C_7H_9NO_7$	237.072	0.195	1

Table S5: Estimated NH_4^+ CIMS sensitivity factors for species detected in 1,2,4-trimethylbenzene experiments.

Compound	*m/z*	$KE_{cm\ 50}$, eV	Sensitivity factor
$C_9H_{10}O_4$	200.092	0.236	1
$C_9H_{12}O_4$	202.108	0.204	1
$C_9H_{14}O_4$	204.124	0.184	0.89
$C_9H_{11}NO_4$	215.103	0.217	1
$C_9H_{10}O_5$	216.087	0.222	1
$C_9H_{12}O_5$	218.103	0.225	1
$C_9H_{14}O_5$	220.119	0.195	1
$C_9H_9NO_5$	229.083	0.134	0.36
$C_9H_{11}NO_5$	231.098	0.199	1
$C_9H_{12}O_6$	234.098	0.207	1
$C_9H_{14}O_6$	236.114	0.225	1
$C_9H_{13}NO_6$	249.109	0.153	0.56
$C_9H_{11}NO_7$	263.088	0.207	1
$C_9H_{13}NO_8$	281.099	0.207	1

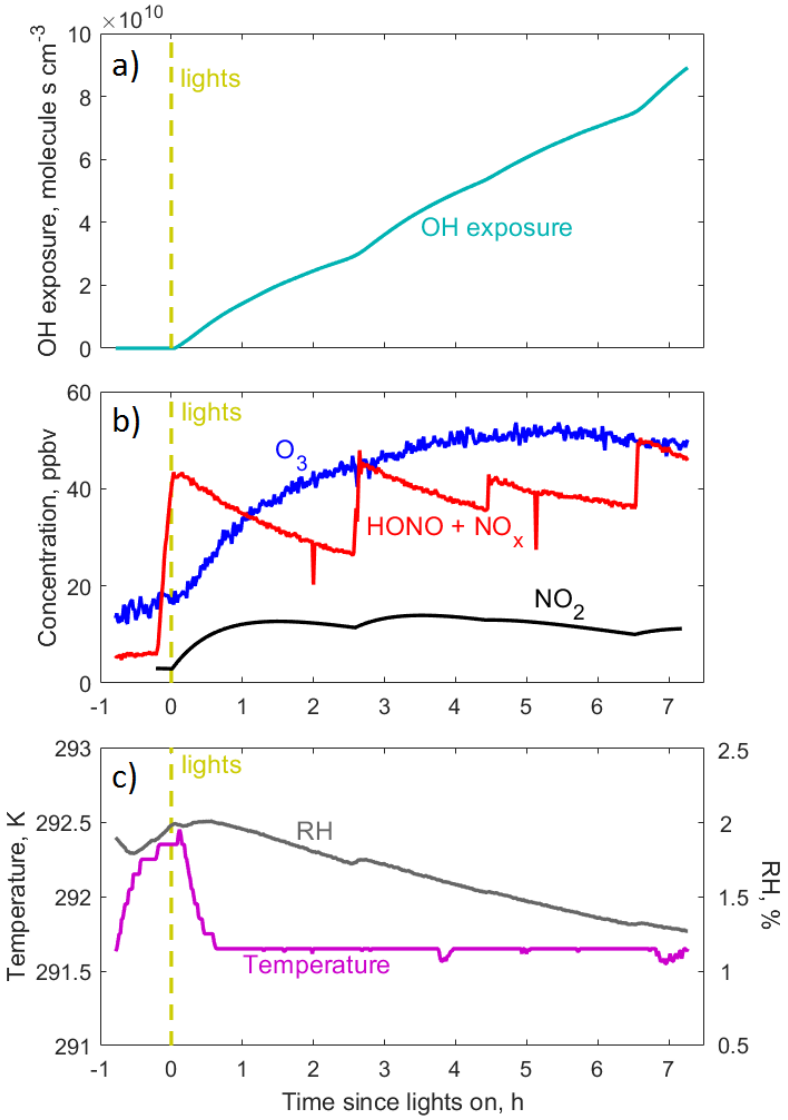

Figure S2: (a) OH exposure, (b) concentrations of O_3, NO_2, HONO+NO_x, and (c) temperature and RH for a typical photooxidation experiment. NO_2 concentration was estimated using F0AM (Wolfe et al., 2016) based on MCM v3.3.1 (Bloss et al., 2005).

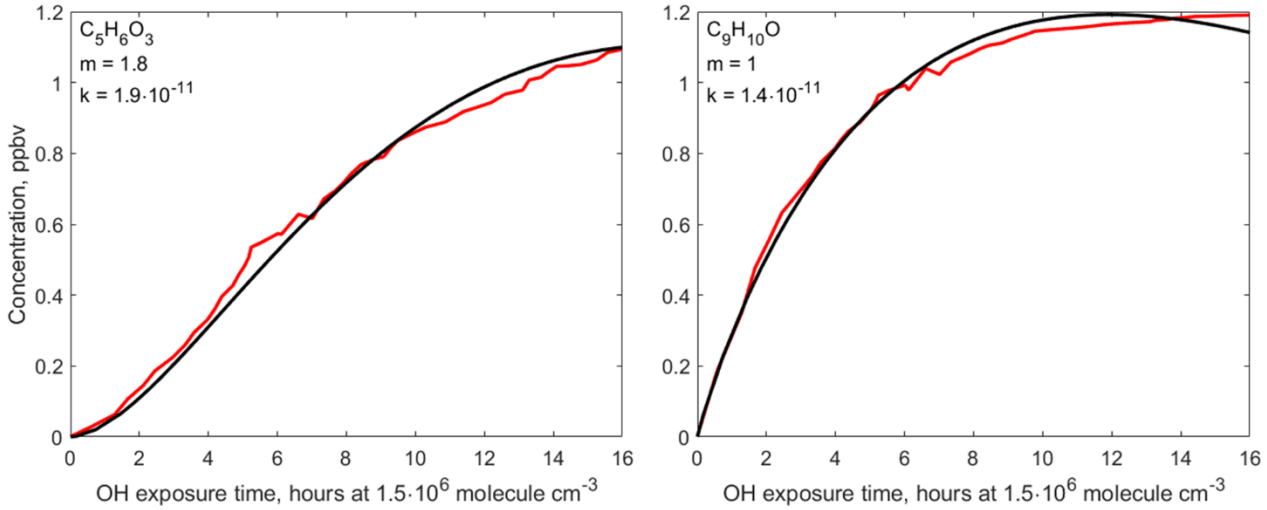

Figure S3: Species measured by NH_4^+ CIMS in 1,2,4-TMB photooxidation experiment (red) and kinetic best fit (black).

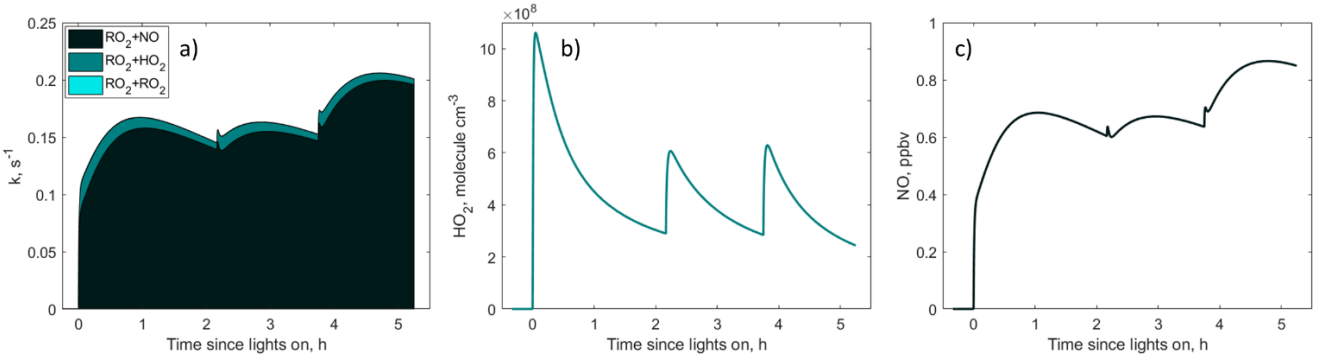

Figure S4: (a) Loss of bicyclic peroxy radicals calculated from the modelled concentrations of NO, HO_2, and RO_2; (b) and (c) modelled concentrations of NO and HO_2 during photooxidation of toluene.

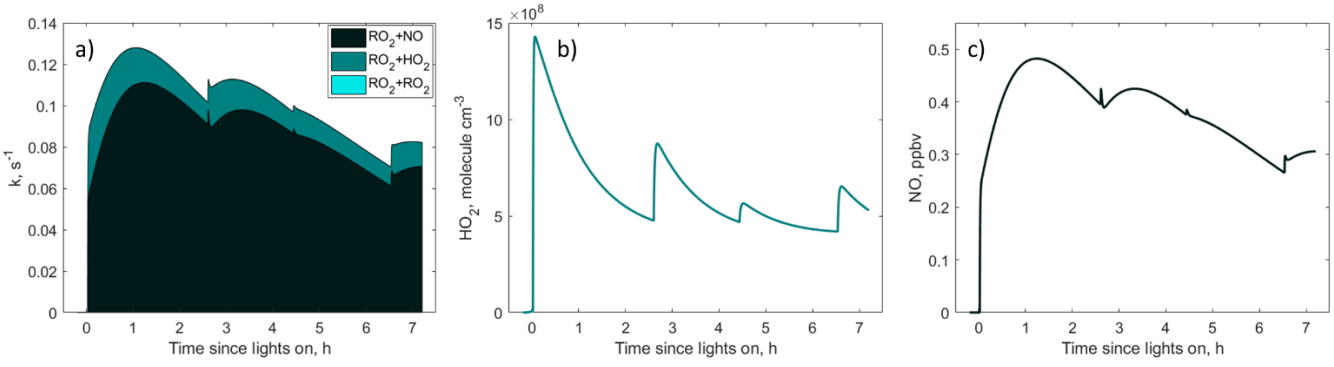

Figure S5: (a) Loss of bicyclic peroxy radicals calculated from the modelled concentrations of NO, HO_2, and RO_2; (b) and (c) modelled concentrations of HO_2 and NO during photooxidation of 1,2,4-TMB.

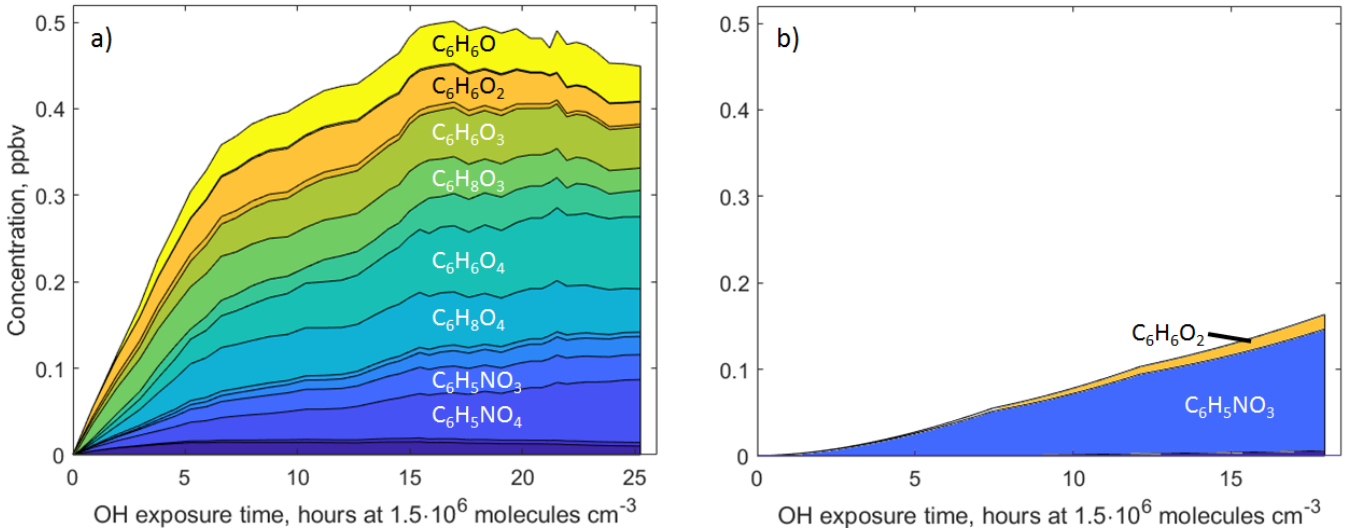

Figure S6: C_6 gas-phase products (a) detected by PTR-MS and NH_4^+ CIMS and (b) predicted by MCM v3.3.1 during oxidation of toluene.