Supplemental Information

"Effect of NOx on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation"

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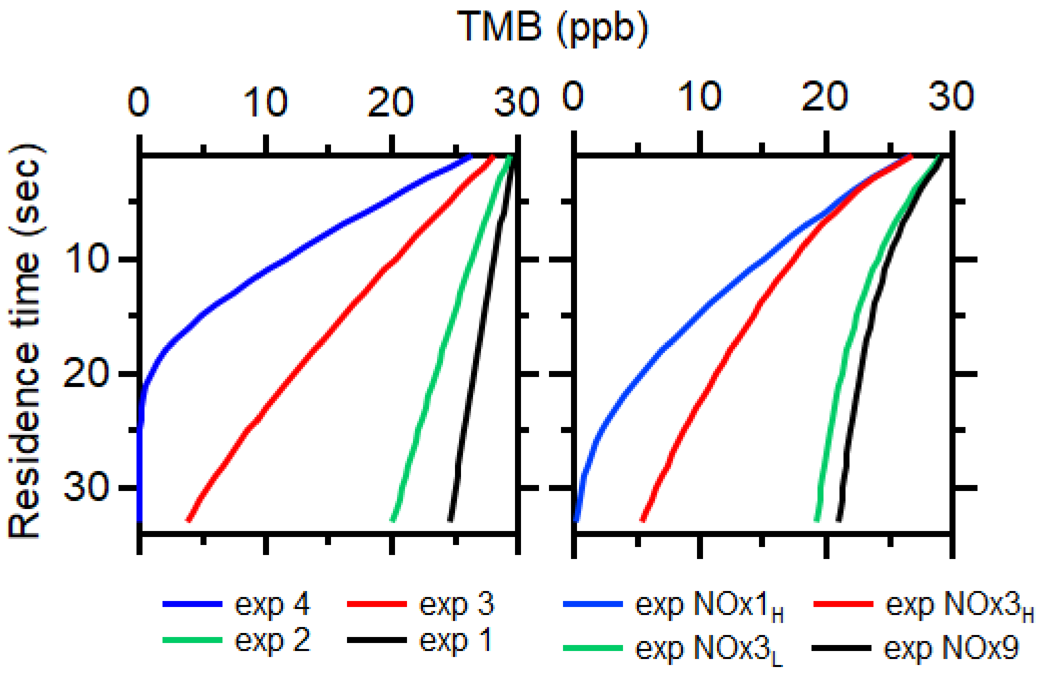

Figure S1: Top: Vertical profile of TMB (ppb) in the PAM chamber without (left) and with NO_x (right). Bottom: Modelled product distribution for all 8 experiments. Left panels show experimetns without NOx and the right panels experments with NOx.

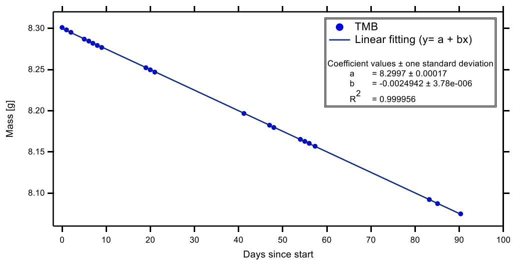

Figure S2: Characterization of TMB evaporation rate from the diffusion vial at a temperature of 20ºC.

Table S1: Contribution of the highest 10 compounds depending on experimental condition.

1		**2**		**3**		**4**	
$C_9H_{12}O_{10}$	4.44	$C_{18}H_{26}O_{10}$	4.76	$C_{18}H_{26}O_{10}$	5.68	$C_9H_{14}O_7$	5.48
$C_{18}H_{26}O_{10}$	4.04	$C_{18}H_{28}O_{11}$	4.53	$C_{18}H_{28}O_{11}$	4.86	$C_9H_{16}O_9$	4.64
$C_{18}H_{28}O_{11}$	3.46	$C_9H_{15}O_8$	3.83	$C_{18}H_{28}O_{12}$	4.55	$C_9H_{14}O_8$	4.49
$C_9H_{15}NO_{10}$	3.07	$C_9H_{14}O_7$	3.19	$C_9H_{14}O_7$	4.27	$C_9H_{16}O_8$	4.48
$C_9H_{13}NO_8$	2.87	$C_9H_{14}O_8$	3.04	$C_9H_{16}O_8$	4.02	$C_{18}H_{28}O_{12}$	3.60
$C_9H_{15}O_8$	2.87	$C_9H_{15}NO_{10}$	2.93	$C_9H_{16}O_9$	3.70	$C_9H_{14}O_6$	3.10
$C_9H_{14}O_8$	2.82	$C_9H_{12}O_{10}$	2.62	$C_9H_{14}O_8$	3.31	$C_9H_{14}O_9$	2.91
$C_9H_{12}O_9$	2.30	$C_9H_{16}O_8$	2.42	$C_9H_{15}O_8$	2.94	$C_9H_{16}O_7$	2.85
$C_{18}H_{25}O_{13}$	2.13	$C_9H_{15}O_7$	2.20	$C_9H_{16}O_7$	2.69	$C_{18}H_{26}O_{10}$	2.84
$C_9H_{15}NO_8$	2.11	$C_9H_{16}O_9$	2.18	$C_{18}H_{26}O_{12}$	2.64	$C_{18}H_{26}O_{12}$	2.68
total	28.6		29.8		38.7		35.9
NOx3$_L$		**NOx9**		**NOx1**		**NOx3$_H$**	
$C_9H_{14}N_2O_{10}$	10.0	$C_9H_{14}N_2O_{10}$	16.0	$C_9H_{15}NO_{10}$	6.1	$C_9H_{15}NO_{10}$	10.4
$C_9H_{13}NO_7$	7.0	$C_9H_{13}NO_7$	15.6	$C_9H_{14}O_7$	3.7	$C_9H_{14}N_2O_{10}$	5.8
$C_9H_{15}NO_8$	6.6	$C_9H_{13}NO_8$	6.1	$C_9H_{16}O_9$	3.4	$C_9H_{13}NO_8$	3.9
$C_9H_{13}NO_8$	5.2	$C_9H_{12}O_{10}$	3.1	$C_9H_{14}O_8$	3.4	$C_9H_{15}NO_8$	2.4
$C_9H_{12}O_{10}$	4.0	$C_9H_{13}NO_9$	2.4	$C_9H_{16}O_8$	3.0	$C_9H_{14}O_7$	2.2
$C_9H_{14}O_8$	2.1	$C_9H_{15}NO_{10}$	2.3	$C_9H_{14}O_6$	2.5	$C_9H_{14}O_8$	2.1
$C_9H_{15}NO_8$	2.1	$C_9H_{12}O_9$	1.9	$C_9H_{14}O_9$	2.3	$C_9H_{13}NO_9$	2.0
$C_9H_{13}NO_9$	2.0	$C_9H_{14}O_8$	1.8	$C_{18}H_{28}O_{12}$	2.1	$C_9H_{14}O_6$	2.0
$C_9H_{12}O_9$	1.8	$C_9H_{14}N_2O_9$	1.7	$C_9H_{15}O_8$	2.0	$C_9H_{12}O_{10}$	1.8
$C_9H_{13}NO_8$	1.7	$C_9H_{13}NO_{10}$	1.6	$C_{18}H_{26}O_{10}$	1.9	$C_9H_{13}NO_7$	1.6
total	42.3		52.4		30.5		34.2

Kinetic model of HOM and ON formation in PAM chamber

A chemical model, describing comprehensively the ozone photolysis at 254nm and NO_x chemistry as well as the general scheme for HOM formation by 1,3,5 trimethylbenzene (TMB) in the Go:PAM, was used. The main structure of the model is based on Watne et al. (2018), where the rate coefficients are adapted from Sander et al. (2011) and Li et al. (2015). The new NO_x chemistry are based on Atkinson et al. (1992); Finlayson-Pitts (1999) and Berndt et al. (2018), while the regular TMB oxidation scheme was taken from the MCM v3.3.1 (Jenkin et al., 2003) and the more oxidized one from Ehn et al. (2014); Berndt et al. (2018) and Zhao et al. (2018). All the reaction and the corresponding rate constants are given in Table S2. FACSIMILE 4 (FACSIMILE for Windows 4, 2009) was used to implement the model and solve the ordinary differential equations.

The photon flux at 254nm used in the simulations was tuned to match measured decay of O_3 and was calculated to be $P_{FLUX254} = 1.31\times10^{16}$ $cm^{-2}s^{-1}$. A OH sink was added to match the observed OH production in the background experiment, i.e. without the addition of TMB. The model was run for all experiments with and without NO_x. HOM (MONOMER) were produced as a termination product from $HOMRO_2$ or the corresponding alkoxy radical (HOMRO). The oxidized peroxy radicals ($HOMRO_2$) were considered to be formed after 3 autoxidation steps (Ehn et al., 2014) of a general RO_2 with a rate constant of 0.1667 s^{-1}. The oxidation state of produced dimers was defined as low, medium or high, depending on the cross reactions. A cross reaction between a general RO_2 and another RO_2 leads to low oxidized dimer (LODIMER)., between a RO_2 and $HOMRO_2$ leads to medium oxidized dimer (MODIMER).and between a $HOMRO_2$ and another $HOMRO_2$ leads to high oxidized dimer (HODIMER). Highly oxygenated nitrates (ON) was formed via $HOMRO_2$ reaction with NO.

Three different cases were tested, in which the rate coefficients of the cross reactions (Reactions 63 – 68) were varied. During the 1st case the rate coefficients of the following reactions (Reactions 63, 64, 66 and 67) was 8.8×10^{-13} cm3 $molecules^{-1}$ s^{-1} (MCM) and the dimer formation reactions (Reactions 65 and 68) were based on Berndt et al. (2018). In that case either we overestimate the production of dimers, underestimate the production of monomers or both of them. The concentration of dimers dominates even in the experiments with high NO_x, which is not consistent with our measurements. In the 2nd case the rate coefficient of Reactions 65 and 68 were kept constant, but for the rest of them changed to 1×10^{-12} cm^3 $molecules^{-1}$ s^{-1} based on Zhao et al. (2018). The concentration of the dimers was still quite higher than the monomers and nitrates, even in the high NO_x experiments. This overestimation suggests that the rate coefficients of the reactions, in which dimers are produced, are lower. Thus, during the 3rd case the rate coefficients for the reactions 65 and 68 were decreased to 2×10^{-12} cm^3 $molecules^{-1}$ s^{-1} (Zhao et al., 2018). The same value was used for both dimer formation reactions, in contrast to the 1st and 2nd cases. The 3rd case gives the best results compared to our measurements (see main text).

Table S2: Reactions and rate coefficients for model calculations. Rate constants were taken from Sander et al. (2011), Li et al. (2015). and Jenkin et al., (2013) unless otherwise stated. The temperature was 298 K, the relative humidity was 38% and the pressure ($M = 2.46\times10^{19}$ molecules cm^{-3}).

No.	*Reaction*	*k*	*Comments*
1	O3 + hν = O2 + O(1D)	0.15	$\sigma_{254}=1.148\times10^{-17} cm^{-2}$
2	O(1D) + H2O = OH + OH	1.99×10^{-10}	
3	O(1D) + O2 = O(3P) + O2	3.97×10^{-11}	
4	O(1D) + O3 = O2 + O(3P) + O(3P)	1.2×10^{-10}	
5	O(1D) + O3 = O2 + O2	1.2×10^{-10}	
6	O(1D) + N2 = O(3P) + N2	3.11×10^{-11}	
7	O(3P) + O2 + M = O3 +M	6.1×10^{-34}	
8	O(3P) + O3 = O2 + O2	7.96×10^{-15}	
9	O(3P) + OH = H + O2	3.29×10^{-11}	
10	H + O2 = HO2	9.57×10^{-13}	
11	H + HO2 = OH + OH	7.2×10^{-11}	
12	H + HO2 = O(3P) + H2O	1.6×10^{-12}	
13	H + HO2 = H2 + O2	6.9×10^{-12}	
14	OH + OH = H2O + O(3P)	1.8×10^{-12}	
15	OH + OH = H2O2	6.29×10^{-12}	
16	OH + O3 = HO2 + O2	7.25×10^{-14}	
17	HO2 + HO2 = H2O2 + O2	3.28×10^{-12}	$(k_{17} = 3\times10^{-13}\times e^{(460/T)}+2.1\times10^{-33}\times e^{(920/T)}\times M) \times (1+1.4\times10^{-21}) \times H_2O\times e^{(2200/T)})$
18	OH + TMB = 0.82 RO2	5.67×10^{-11}	MCM
19	OH + TMB = 0.18 HO2	5.67×10^{-11}	MCM
20	NO + O(3P) = NO2	1.66×10^{-12}	
21	O(3P) + OH = H + O2	3.29×10^{-11}	
22	NO2+ hν = NO + O(3P)	1.37×10^{-4}	$\sigma_{254}=1.05\times10^{-20}$
23	OH + NO2 = HNO3	1.06×10^{-11}	
24	OH + NO2 = HOONO	1.79×10^{-12}	
25	HO2 + NO = OH + NO2	8.16×10^{-12}	
26	RO2 + NO = RO + NO2	9.0×10^{-12}	MCM
27	O(1D) + N2 + M = N2O + M	2.82×10^{-36}	
28	N2O + O(1D) = N2 + O2	5.09×10^{-11}	
29	N2O + O(1D) = NO + NO	7.64×10^{-11}	
30	O(3P) + HO2 = OH + O2	5.87×10^{-11}	
31	O(3P) + H2O2 = OH + HO2	1.7×10^{-15}	
32	H + O3 = OH + O2	2.89×10^{-11}	
33	HO2 + O3 = OH + O2 +O2	1.93×10^{-15}	
34	HO2 + OH = H2O + O2	1.11×10^{-10}	
35	H2O2 + hν = OH +OH	8.75×10^{-4}	$\sigma_{254}=6.7\times10^{-20}$
36	HO2 + hν = OH + O(1D)	3.4×10^{-4}	$\sigma_{254}=2.6\times10^{-19}$
37	H2O2 + OH = HO2 + H2O	1.8×10^{-12}	
38	NO + O3 = NO2 + O2	1.95×10^{-14}	
39	O(1D) + H2 = OH + H	1.2×10^{-10}	

40	OH + H2 = H2O + H	6.67×10^{-15}	
41	NO2 + O(3P) = NO + O2	1.03×10^{-11}	
42	NO2 + O(3P) = NO3	1.61×10^{-12}	
43	H + NO2 = NO + OH	1.28×10^{-10}	
44	NO + NO3 = NO2 + NO2	2.65×10^{-11}	
45	NO2 + O3 = NO3 + O2	3.2×10^{-17}	
46	OH deposition/loss	2.685	
47	RO2 + HO2 = ROOH + O2	2.28×10^{-11}	MCM
48	RO2 + RO2 = 0.38 (Carbonyl + Alcohol + O2)	8.8×10^{-13}	MCM
49	RO2 + RO2 = 0.58 (RO + RO + O2)	8.8×10^{-13}	MCM
50	RO2 + RO2 = 0.04 (LODIMER + O2)	8.8×10^{-13}	Low Oxidized dimer, MCM, Zhao et al. (2018)
51	RO2 + NO2 = RO2NO2	9.0×10^{-12}	p 187 Finlayson - Pitts & Pitts (2000)
52	RO2 = HOMRO2	0.1667	3 steps, Ehn et al. (2018)
53	RO = 0.3 (Carbonyl + HO2)	$1.0\times10^{+6}$	MCM, Fraction is empirically determined
54	RO = 0.7 RO2	$1.0\times10^{+6}$	MCM, Fraction is empirically determined
55	HOMRO2 + HO2 = MONOMER	2.28×10^{-11}	MCM
56	HOMRO2 + NO = 0.3 ONs	1.0×10^{-11}	Berndt et al. (2018)
57	HOMRO2 + NO = 0.7 (HOMRO + NO2)	1.0×10^{-11}	Berndt et al. (2018)
58	HOMRO = 0.3 (MONOMER + HO2)	$1.0\times10^{+6}$	MCM, Fraction is empirically determined
59	HOMRO = 0.7 HOMRO2	$1.0\times10^{+6}$	MCM, Fraction is empirically determined
60	HOMRO2 + NO2 = HOMRO2NO2	9.0×10^{-12}	p 187 Finlayson - Pitts & Pitts (2000)
61	RO2NO2 = RO2 + NO2	3.99	Atkinson et al. (1992)
62	HOMRO2NO2 = HOMRO2 + NO2	3.99	Atkinson et al. (1992)
Case 1			
63	HOMRO2 + RO2 = 0.4 (MONOMER + Carbonyl/Alcohol + O2)	8.8×10^{-13}	MCM
64	HOMRO2 + RO2 = 0.6 (HOMRO + RO + O2)	8.8×10^{-13}	MCM
65	HOMRO2 + RO2 = MODIMER + O2	8.0×10^{-11}	Medium Oxidized dimer, Berndt et al. (2018)
66	HOMRO2 + HOMRO2 = 0.4 (MONOMER + MONOMER + O2)	8.8×10^{-13}	MCM
67	HOMRO2 + HOMRO2 = 0.6 (HOMRO + HOMRO + O2)	8.8×10^{-13}	MCM
68	HOMRO2 + HOMRO2 = HODIMER + O2	2.6×10^{-10}	Highly Oxidized dimer, Berndt et al. (2018)
Case 2			
63	HOMRO2 + RO2 = 0.4 (MONOMER + Carbonyl/Alcohol + O2)	1.0×10^{-12}	Zhao et al. (2018)
64	HOMRO2 + RO2 = 0.6 (HOMRO + RO + O2)	1.0×10^{-12}	Zhao et al. (2018)
65	HOMRO2 + RO2 = MODIMER + O2	8.0×10^{-11}	Medium Oxidized dimer, Berndt et al. (2018)
66	HOMRO2 + HOMRO2 = 0.4 (MONOMER + MONOMER + O2)	1.0×10^{-12}	Zhao et al. (2018)
67	HOMRO2 + HOMRO2 = 0.6 (HOMRO + HOMRO + O2)	1.0×10^{-12}	Zhao et al. (2018)
68	HOMRO2 + HOMRO2 = HODIMER + O2	2.6×10^{-10}	Highly Oxidized dimer, Berndt et al. (2018)

Case 3			
63	HOMRO2 + RO2 = 0.4 (MONOMER + Carbonyl/Alcohol + O2)	1.0×10^{-12}	Zhao et al. (2018)
64	HOMRO2 + RO2 = 0.6 (HOMRO + RO + O2)	1.0×10^{-12}	Zhao et al. (2018)
65	HOMRO2 + RO2 = MODIMER + O2	2.0×10^{-12}	Medium Oxidized dimer, Zhao et al. (2018)
66	HOMRO2 + HOMRO2 = 0.4 (MONOMER + MONOMER + O2)	1.0×10^{-12}	Zhao et al. (2018)
67	HOMRO2 + HOMRO2 = 0.6 (HOMRO + HOMRO + O2)	1.0×10^{-12}	Zhao et al. (2018)
68	HOMRO2 + HOMRO2 = HODIMER + O2	2.0×10^{-12}	Highly Oxidized dimer, Zhao et al. (2018)

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