Atmospheric
Chemistry
and Physics

Supplement of

Enhanced secondary organic aerosol formation from the photo-oxidation of mixed anthropogenic volatile organic compounds

Junling Li et al.

Correspondence to: Hong Li (lihong@craes.org.cn)

Quality Assurance and Quality Control

The collections and analysis of SOA samples were under strict quality control. The Teflon tube in the sampling device was

30 purged with zero air before sampling, and the membrane holder was cleaned with methanol. Glassware used in the experiments was washed with water and methanol and then dried under high-temperature conditions. Before each injection, the micro syringes were cleaned with methanol to prevent cross-contamination among different samples. The blank PTFE filter analysis showed that there was no serious contamination. The typical mass resolving power of the applied ESI-ToF-MS was > 80000 at m/z 1222. The absolute mass error between the measured m/z and theoretical m/z was below 5 ppm.

35 **Calculation of Vapor Wall Loss**

$$\bar{c} = \sqrt{\frac{8RT}{\pi M_w}} \tag{1}$$

where R was the ideal gas constant (i.e., 8.314 J mol^{-1} K^{-1}), T was the temperature, M_w was the molecular weight.

$$D_{gas} = D_{CO_2} \times \frac{M_{wCO_2}}{M_w} \tag{2}$$

where D_{CO2} was 1.38×10^{-5} m^2 s^{-1}, M_w was set to 300 g mol^{-1} here.

40 $$k_n = \frac{\lambda}{R_p} = \frac{6D_{gas}}{D_p \bar{c}} \tag{3}$$

where K_n was the Knudsen number, R_p was the particle radius, and λ was the gas mean free path.

$$\bar{F}_{FS} = \frac{0.75\alpha(1+k_n)}{k_n^2 + k_n + 0.283 k_n \alpha + 0.75\alpha} \tag{4}$$

where α was the mass accommodation coefficient onto particles, and it was set to 0.002 in this work (Zhang et al., 2014).

Calculation of the Uncertainty of the Gas Phase Correction

45 The error associated with the mass correction here mainly considers the gas phase. For the gas phase wall-loss correction, the gas-particle partitioning timescale ($\bar{\tau}_{g-p}$) and the vapor wall-loss timescale ($\bar{\tau}_{g-w}$) are expressed as the following equation:

$$\bar{\tau}_{g-p} = \frac{1}{2\pi \bar{N}_p \bar{D}_p D_{gas} \bar{F}_{FS}} \tag{5}$$

$$\bar{\tau}_{g-w} = \frac{1}{k_w} \tag{6}$$

$$k_w = \left(\frac{A}{V}\right) \frac{a_w \frac{\bar{c}}{4}}{1.0 + \frac{\pi}{2}\left[\frac{a_w \bar{c}}{4(k_e D_{gas})^{0.5}}\right]} \tag{7}$$

50   For $\bar{\tau}_{g-w}$, the parameters in the formula are fixed values, so only $\bar{\tau}_{g-p}$ is considered here. The two variables N_p and D_p in $\bar{\tau}_{g-p}$ are independent and the uncertainty of them are 10% and 1%, respectively. Considering the propagation of uncertainty, we can obtain the variance formula:

$$\sigma_\tau^2 = \sigma_N^2 \left(\frac{\partial\tau}{\partial N}\right)^2 + \sigma_D^2 \left(\frac{\partial\tau}{\partial D}\right)^2 \tag{8}$$

Then the uncertainty of τ can be calculated as:

55        $$\frac{\sigma_\tau}{\tau} = \sqrt{\left(\frac{\sigma_N}{N}\right)^2 + \left(\frac{\sigma_D}{D}\right)^2} = \sqrt{0.1^2 + 0.01^2} = \sqrt{0.0101} = 10.0\% \tag{9}$$

       The uncertainty of $\bar{\tau}_{g-p}$ is $\pm$ 10.0%, the measurement uncertainty of the precursors' concentration by TD-GC applied in this work is about $\pm$ 5%, thus resulting in the final uncertainty of mass correction to be about $\pm$11.2%.

60

Table S1. $\bar{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ values for the VOCs used in this work.

VOC	AS Seed (Yes or No)	Temperature (°C)	$\bar{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$
1,3,5-TMB	No	35	2.64-4.42
n-dodecane	No	35	4.25-7.34
Mix	No	35	0.19-0.85

Table S2. Initial concentrations of the conducted experiments.

Date	Precursor	Concentration (ppb)	TMB/Dode	NOx (ppb)	ΔVOCs/NOx
2019.0927	n-dodecane	22	--	210	1.26
2019.1009	n-dodecane	20	--	214	1.12
2019.0925(Li et al., 2021)	1.3.5-TMB	178	--	197	8.13
2019.1014(Li et al., 2021)	1.3.5-TMB	170	--	250	6.12
2019.0903(Li et al., 2021)	1.3.5-TMB	105	--	211	4.48
2019.0907	Dod+TMB	28+168	6	231	8
2019.0921	Dod+TMB	22+155	7	212	7.83
2019.0919	Dod+TMB	20+182	9.1	218	8.61

65

3

Table S3. OH reactivity (OHR) of the pure and mixture experiments.

	1,3,5-TMB (ppb)	n-dodecane (ppb)	NO$_X$ (ppb)	OHR$_{VOCs}$[a] (s^{-1})	OHR$_{NOx}$[b] (s^{-1})
Dod-1	--	22	210	7.1	201.9
Dod-2	--	20	214	6.5	200.7
TMB-1	105	--	211	146.5	208.3
TMB-2	178	--	197	248.3	189.6
TMB-3	170	--	250	237.1	238.8
MIX-1	168	28	231	243.4	220.8
MIX-2	155	22	212	223.3	202.4
MIX-3	182	20	218	260.4	205.9
MIX-4	251	35	212	361.5	203.2

a: $k_{OHR_{VOCs}} = \sum k_{OH+VOC_i}[VOC_i]$

b: $k_{OHR_{NOx}} = k_{OH+NO_2}[NO_2] + k_{OH+NO}[NO]$

Table S4. List of functional groups in SOA extracts.

Functional groups	Wavenumber (cm^{-1})
C-OH in alcohol	3360
O-H stretching vibration of carboxylic acid	3192
C-H stretching vibration of alkane	2921, 2850
C=O stretching vibrations	1660, 1633
deformation vibrations of methyl and methylene groups	1465, 1415
nitrate groups in nitrate ester	1268

70

75

80

4

85

90
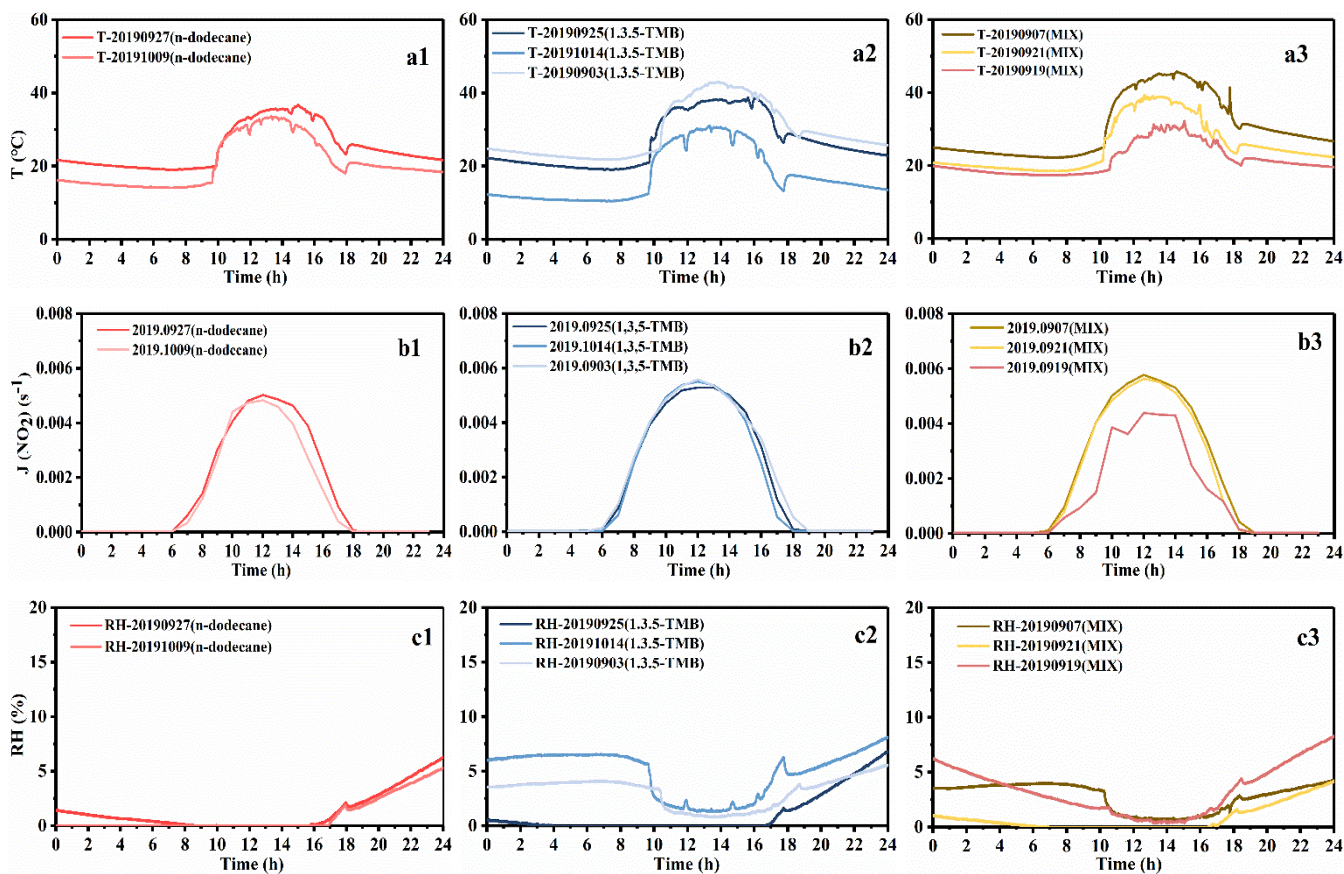
Figure S1. The temperature (T, a), the NO_2 photolysis rate of the experiments ($J(NO_2)$, b), and relative humidity (RH, c); the data of 1.3.5-TMB was referred to Li et al. (2021)) in summer.
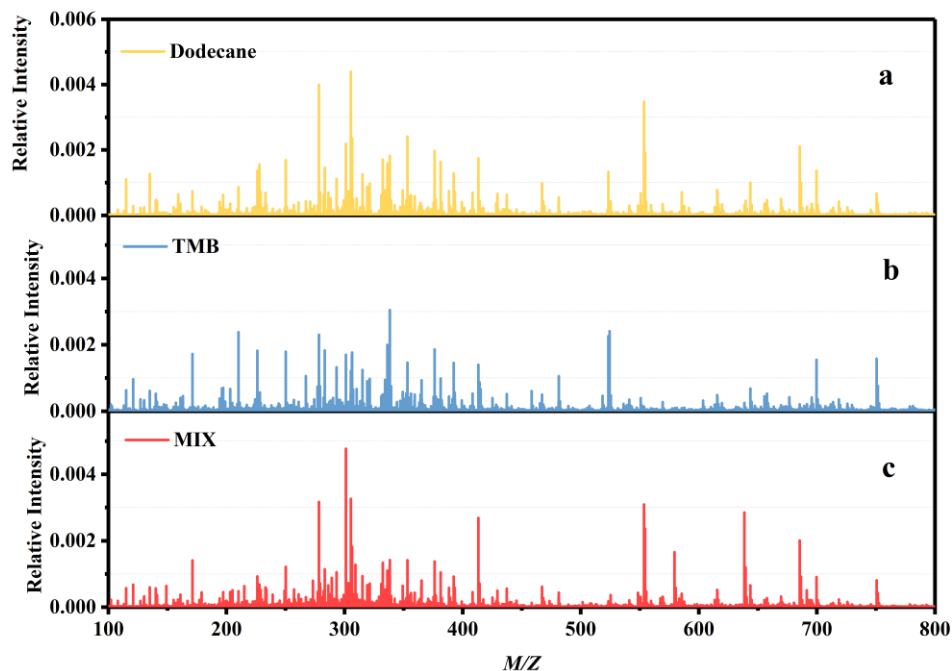
Figure S2. Mass spectra of SOA generated from (a) *n*-dodecane, (b) 1,3,5-TMB, and (c) mixture AVOCs. The Y-axis is the relative intensity normalized by dividing by the total signal strength of the mass spectra.

References

Li, J., Li, H., Wang, X., Wang, W., Ge, M., Zhang, H., Zhang, X., Li, K., Chen, Y., Wu, Z., Chai, F., Meng, F., Mu, Y., Mellouki, A., Bi, F., Zhang, Y., Wu, L., and Liu，Yongchun: A Large-Scale Outdoor Atmospheric Simulation Smog Chamber for Studying Atmospheric Photochemical Processes: Characterization and Preliminary Application, J. Environ. Sci. 102, 185-197, 2021.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proc. Natl. Acad. Sci. USA 111, 5802-5807, 2014.