

Dear Professor Roya Bahreini,

Thank you very much for handling our manuscript submitted to *Atmospheric Chemistry and Physics* (MS No.: acp-2020-1189; Title: Enhanced secondary organic aerosol formation from the photooxidation of mixed anthropogenic volatile organic compounds).

We have addressed all your comments and revised our manuscript very carefully. To proceed, we have uploaded three files, including 1) our point-to-point reply; 2) the revised manuscript with changes highlighted in yellow; 3) the revised manuscript without track-changes.

On behalf of all the co-authors, I would like to thank you and referees for all the invaluable comments. Please feel free to contact me if you need any further information.

Sincerely,

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1. Wall-loss correction: Particle wall loss is size dependent; however, here the correction is based on integrated mass. If you apply size dependent particle loss correction, how different would the results be?

Thank you very much for this question. The wall loss experiments of inert particles (ammonium sulfate) were performed with the chamber applied in this work, and the size-dependent coefficients were obtained (Li et al., 2021):

$$k_{dep}(d) = 6.35 \times 10^{-6} d^{1.56} + \frac{6.38}{d^{0.67}}$$

With the obtained size-dependent coefficients, we re-calibrated the SOA yields. It is shown that the wall-loss correction based on integrated mass is higher than that based on size-dependent coefficients. As size-dependent particle wall-loss correction is more commonly used (Takekawa et al., 2003; Ng et al., 2007; Chen et al., 2019; Chen et al., 2021), we have changed the correction method in this work, and the corresponding parts in the manuscript have been updated:

(Page 5, line 136-140) “The particle growth data was corrected for wall-loss, in which size-dependent coefficients from inert particle wall-loss experiments (ammonium sulfate) were applied to the particle volume data (Li et al., 2021):

$$k_{dep}(d) = 6.35 \times 10^{-6} d^{1.56} + \frac{6.38}{d^{0.67}} \quad (4)$$

where $k_{dep}(d)$ was the wall-loss loss coefficient of particles in the diameter d .”

(Page 21, line 640-647) “Table 1. Summary of the initial conditions and results of the conducted experiments.”

Table 1. Summary of the initial conditions and results of the conducted experiments.

Number	Date	Initial Conditions of the Experiments									General Results of the Experiments					
		1,3,5-TMB (ppb)	<i>n</i> -dodecane (ppb)	NO (ppb)	NO ₂ (ppb)	NO _x (ppb)	ΔVOCs/NO _x (ppbC/ppb)	T (at noon) (°C)	J(NO ₂) (at noon) (s ⁻¹)	RH (%)	O ₃ (ppb)	Mass ^a (μg/m ³)	Mass Predicted ^b (μg/m ³)	Mass Corr. ^c (μg/m ³)	Mass Predicted ^d (μg/m ³)	Yield ^e (%)
Dod-1	2019.09.27	--	22	50	160	210	1.26	37	0.0050	<2	57	6.4	--	35.2	--	23.1
Dod-2	2019.10.09	--	20	77	137	214	1.12	34	0.0048	<2	25	3.7	--	19.1	--	14.1
TMB-1 (Li et al., 2021)	2019.09.03	105	--	23	188	211	4.48	43	0.0056	<4	288	2.1	--	7.68	--	1.5
TMB-2 (Li et al., 2021)	2019.09.25	178	--	46	151	197	8.13	38	0.0053	<4	772	5.1	--	21.11	--	2.4
TMB-3 (Li et al., 2021)	2019.10.14	170	--	68	182	250	6.12	30	0.0055	<5	530	2.5	--	8.99	--	1.1
MIX-1	2019.09.07	168	28	62	169	231	8	46	0.0058	<3	358	59.3	10.3	73.5	49.9	--
MIX-2	2019.09.21	155	22	58	154	212	7.83	39	0.0056	<2	721	47.4	8.5	58.5	40.9	--
MIX-3	2019.09.19	182	20	71	147	218	8.61	31	0.0044	<9	435	11.5	8.6	14.8	40.8	--
MIX-4	2020.08.21	251	35	54	158	212	12.64	39		<7	999	60.2	13.7	74.6	65.8	--
MIX-5	2020.07.14	4 h add	27	61	157	218	--	52	0.0051	<5	289	8	--	27.7	--	--
MIX-6	2020.07.20	4 h add	38	58	198	256	--	43	0.0057	<4	276	6	--	20.8	--	--
MIX-7	2020.07.24	1 h add	39	56	207	263	--	42	0.0058	<6	440	2.3	--	7.9	--	--
MIX-8	2020.07.22	227	1h add	48	167	216	--	43	0.0051	<5	335	4.5	--	15.6	--	--

a: the mass here is the measured value with the SMPS; the density of the formed SOA derived from 1,3,5-TMB is assumed to be 1.4 g/cm³ (Zhang et al., 2016; Nakao et al., 2013); the density of the formed SOA derived from *n*-dodecane is assumed to be 1.06 g/cm³ (Lim and Ziemann, 2009; Li et al., 2017a); the density of the formed SOA derived from the mixed AVOCs is assumed to be 1.23 g/cm³.

b: the predicted mass here is based on the yield that the particle and vapor wall-loss are not considered.

c: the corrected mass here is calculated after taking particle and vapor wall loss into account.

d: the predicted mass here is based on the yield that the particle and vapor wall-loss are considered.

e: the SOA yield here is calculated after taking particle and vapor wall loss into account.

2. What is the estimated OH in the pure and mixture experiments? How similar is the reactivity with respect to OH during pure and mixture experiments? How does this reactivity compare to that of NO₂? Why was so much higher initial conc. of 1,3,5-TMB used compared to dodecane?

Ng et al. (2007) reported that the efficient photolysis of HONO (the same method with this study) could generate relatively high concentrations of OH, 1 ppm NO_x $\sim 2 \times 10^7$ molecules/cm³ OH initially. The NO_x concentration applied in this work is in the range of 190 \sim 260 ppb, resulting in the estimated OH concentration being $(4 - 5.2) \times 10^6$ molecules/cm³ in the pure and mixture experiments. This part has been added in the manuscript (**Page 6, line 157-161**).

Rate constants for the reactions of n-dodecane and 1,3,5-TMB with OH radical at 298 K are 13.2×10^{-12} cm³ molecule⁻¹ s⁻¹ and 56.7×10^{-12} cm³ molecule⁻¹ s⁻¹, respectively (Atkinson and Arey, 2003). As shown in Table 2, OH reactivity of Dod-1 and Dod-2 is about 6.5-7.1 s⁻¹; OH reactivity of TMB-2, and TMB-3 is in the range of 237.1-248.3 s⁻¹; and OH reactivity of MIX-1, MIX-2, MIX-3, and MIX-4 is in the range of 223.3-361.5 s⁻¹. This indicates that OH reactivity of the mixture experiments differs greatly from that of dodecane experiments, but it is very close to that of 1,3,5-TMB experiments. However, the mixture experiments still have a large enhancement in SOA formation compared with 1,3,5-TMB experiments, indicating that this enhancement is likely not due to the different OH reactivity.

Rate constants for the reactions of NO₂ and NO with OH radical at 298 K are 4.1×10^{-11} cm³ molecule⁻¹ s⁻¹ and 3.3×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively (Atkinson et al., 2004). The OH reactivity of NO_x is similar for all experiments (189.6 \sim 238.8 s⁻¹), and therefore likely plays a minor role in influencing SOA concentration.

And this part has been added in the manuscript (**Page 7, line 213-222**).

Table 2. OH reactivity (OHR) of the pure and mixture experiments. (This table has been added in the Supporting Information as Table S3: Page 4, line 67-70)

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

The initial concentration ratio of 1,3,5-TMB and n-dodecane in this work is about 10:1 (ppbv), which is mainly based on the following literature research:

Schauer et al. (2002) reported that 1,3,5-TMB and n-dodecane in the gasoline composition were about 7450 and 136 µg/g, respectively; Gentner et al. (2012) reported that the weight percentage of 1,3,5-TMB and n-dodecane in liquid gasoline were 0.530-0.881 and 0.004-0.045 (% weight by carbon), respectively. According to field observations in China, the measured 1,3,5-TMB concentration at the rural site in the YelRD (Yellow River Delta) region in 2017 could reach 1.447 ppb (Chen et al., 2020), and the measured C12 alkane concentration was 0.122±0.12 ppb at PRD (Pearl River Delta) region, and 0.129±0.086 ppb at NCP (North China Plain) region in 2018 (Wang et al., 2020).

The concentration of 1,3,5-TMB is much higher than that of n-dodecane in both the gasoline compositions and ambient air. Thus, the initial concentration of 1,3,5-TMB used in this work is much higher than n-dodecane.

This part has been added in the manuscript (Page 3, line 67-75).

3. Since the experiments were carried out under high NO_x, it's likely that some nitric acid also partitioned in the aerosols. It seems the total volume increase is assigned

to be due to SOA formation. What is the magnitude of the error associated with this assumption?

According to a previous study (Chen et al., 2019), the formed inorganic nitrate is negligible for the high-NO_x oxidation of gasoline, in which the experimental conditions are similar to this study (NO_x 130 ppb, formed aerosol mass concentration 34.6 µg/m³).

In the pure and mixture experiments, the NO_x concentration is equivalent, so the formed nitric acid should be similar. Therefore, the increase in particle mass concentration in the mixture experiments is likely from the organic aerosols.

Based on the analysis above, we believe that the error associated with this assumption is small.

This part has been added in the manuscript (**Page 6, line 164-168**).

Editorial corrections:

1. L170: sentence after “however” needs to be rephrased.

(**Page 7, line 193**): “however, they only change little on the SOA yield.” → “however, the effect is not obvious”

2. L184: change “likely not this case here” to “likely not the case here”

(**Page 7, line 206-207**): “likely not this case here” → “likely not the case here”

3. L194: products “have”

(**Page 8, line 227**): “products has” → “products have”

4. L195: “coagulate” is not the right phrase here; consider “condense” instead

(Page 8, line 228): “the products of 1,3,5-TMB to coagulate” → “the products of 1,3,5-TMB to condense”

5. L198: consider changing to “different injection experiments....”

(Page 8, line 231): “the injection experiments are performed” → “different injection experiments are performed”

6. L236: change “has” to “have”

This has been corrected in the manuscript.

7. L247: change “are existed” to “exist”

This has been corrected in the manuscript.

8. L248: what do you mean by “and the relative strength is mixed”? Please clarify

The meaning of this sentence is that “and order of the relative strength is mixture AVOCs SOA > n-dodecane SOA > 1,3,5-TMB SOA.”. According to the comments of the reviewers, we have updated the content of this part in the latest version.

9. L253-254: consider deleting “In this work” and “mainly”

(Page 10, line 296): “In this work, the factors affecting ozone generation considered in this work mainly included.....” → “The factors affecting ozone generation included.....”

10. L268: the lines before discuss ozone formation; however the sentence starting with “In conclusion”, discusses results related to particle formation. This logic doesn't

make sense. Please make sure the sentences are not misplaced with that of the next section, i.e., L280-282 that discuss ozone formation.

Thank you for this comment, the sentence in the manuscript has been corrected.

(Page 10, line 310-313): “Higher temperature and higher $\Delta\text{VOCs}/\text{NO}_x$ (ppbC/ppb) ratio in a separate reaction system will promote the generation of ozone; the relative content of reaction precursors (ppb/ppb) in the mixture system will affect the concentration of ozone, with similar $\Delta\text{VOCs}/\text{NO}_x$ ratio, a higher concentration of 1,3,5-TMB will promote ozone generation.”

(Page 11, line 322-325): “Lower temperature and higher $\Delta\text{VOCs}/\text{NO}_x$ (ppbC/ppb) ratio in a separate reaction system will promote the particle formation; the relative content of reaction precursors (ppb/ppb) in the mixture system will affect the formed particles, with similar $\Delta\text{VOCs}/\text{NO}_x$ ratio, a higher concentration of n-dodecane would promote the generation of particles; reaction conditions have little effect on the size of the final particle size.”

11. L276, change “1.3.5” to “1,3,5-”

(Page 11, line 341): “1.3.5-TMB” → “1,3,5-TMB”

12. L594- description for “c” needs to be rephrased.

(Page 21, line 645): “the mass here is the value that the particle and vapor wall-loss are considered.” → “the corrected mass here is calculated after taking particle and vapor wall loss into account”

13. Figure 3 caption: “changement” is not correct. Please use a different word.

(Page 25, line 672-674): “changement” → “time series”

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