Response to Reviewer #2

General comments:

Liu et al. describe photochemical oxidation experiments of gasoline vehicle exhaust with and without SO_2 gas. This manuscript is technically sound, provides detailed methodology, and addressed a highly relevant topic in the field of atmospheric chemistry. I recommend its acceptance for publication in Atmospheric Chemistry and Physics pending an adequate response to the comments listed below.

In this reviewer's opinion, this paper could use some copy-editing for language. While the text is comprehendible at present, it is, in some cases, awkwardly worded.

Reply: The language of the revised manuscript has been edited by a native speaker.

Specific comments:

Q1- Page 23620, line 8: What molecular weight was assumed for hydrocarbons? Was this a weighted-average based on the gas-phase analyses?

Reply: The hydrocarbons measured in this study include methane and C_2-C_{12} hydrocarbons. The carbon content of different hydrocarbon was respectively calculated. Thus, $[\Delta HC]/MW_{HC}$ in the equation represents the sum of different hydrocarbons.

To clarify this, we add the following text to the revised manuscript.

"The carbon content of each hydrocarbon was respectively calculated and then summed in Eq. (1)."

Q2- Page 23620, line 17: It may be worth stating the reference from which the authors are obtaining the rate constant for the toluene + OH radical reaction, since this appears to be known a priori (or at least the assumed value).

Reply: The following text has been added to the revised manuscript.

"The value of *k* is obtained from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) (Jenkin et al., 2003)."

Q3- Page 23621, line 16-page 23622, line 7: It may be useful to provide examples of which compounds may be participating in this chemistry (e.g., ethene, 1,2-butadiene, 2-methyl-propene, cyclohexene). Given that the authors have input these species to the MCM, this should be relatively straightforward, and it could be as simple as saying XX% straight alkenes, YY% branched alkenes, and ZZ% cycloalkenes.

Reply: Table 2 (Table 4 in the revised manuscript) shows the concentrations of alkenes included in the model and the category of sCIs. N-alkenes and branched alkenes respectively contributed 89.9%-93.0% and 7.0%-10.1% of the alkenes, with ethene and propene as two main components accounting for as high as 66.8%-81.3%.

Table 2. Concentrations of alkenes included in the model and the category of sCIs.

Sepecies	Concentration (ppb)			sCIs
	I-2	II-2	III-2	
ethene	333.1	113.8	202.0	CH_2OO
propene	95.8	50.3	52.6	CH_2OO, CH_3CHOO
1-butene	30.9	49.1	13.1	CH_2OO, C_2H_5CHOO
cis-2-butene	7.6	4.8	7.1	CH_3CHOO
trans-2-butene	9.9	6.4	9.6	CH_3CHOO
1-pentene	3.8	0.3	3.1	CH_2OO, C_3H_7CHOO
cis-2-pentene	5.2	1.2	5.2	CH_3CHOO, C_2H_5CHOO
trans-2-pentene	8.5	2.6	9.4	CH_3CHOO, C_2H_5CHOO
2-methyl-1-butene	11.9	5.4	12.4	CH_2OO, $C_2H_5(CH_3)COO$
3-methyl-1-butene	2.4	0.8	2.4	CH_2OO, $(CH_3)_2CHCHOO$
2-methyl-2-butene	17.8	10.9	22.7	CH_3CHOO, $(CH_3)_2COO$
cis-2-hexene	0.8	0	1.5	CH_3CHOO, C_3H_7CHOO

The following text has been added to the revised manuscript.

“The concentrations of alkenes included in the model and the category of sCIs are presented in Table 4. N-alkenes and branched alkenes respectively contributed 89.9%-93.0% and 7.0%-10.1% of the alkenes, with ethene and propene as two main components accounting for as high as 66.8%-81.3%.”

Q4- Another comment related to the MCM work: Given that alkenes are only ~10-20% of the total VOCs, how might these reactions be biased due to neglecting the presence of alkanes, aromatics, etc.? This answer may that there is no bias, due to the constraints placed on OH, SO_2, O_3, and NO_2, but perhaps the authors should explicitly state this. Maybe this could be validated by re-running the MCM simulations including aromatics in addition to alkenes to assess any differences in model outputs.

Reply: According to the Eq. (5), the steady state concentrations of sCIs depend on the concentrations of O_3, alkenes, OH, SO_2, O_3 and NO_2. Due to the constraints of OH, SO_2, O_3 and NO_2, the neglect of alkanes and aromatics would not influence the concentrations of sCIs. Re-running the MCM simulations including aromatics and alkanes did not change the steady state concentrations of sCIs. The following text has been added to the revised manuscript:

"Thus, the neglect of alkanes and aromatics would not influence the steady state concentrations of sCIs, as was confirmed by running the models including alkanes and aromatics."

Q5- Page 23623, lines 3-8: Is this how the authors are accounting for collection efficiency? Presumably, this approach biases the concentrations of OA, sulfate, ammonium, and nitrate high because LDGVs also emit black carbon (Forestieri et al., 2013; Kamboures et al., 2013; May et al., 2014). In the cited Gordon et al. (2014) reference, those authors do account for black carbon. An approach such as the Middlebrook et al. (2012) composition-dependent CE may be necessary.

Reply: Theoretically, the difference of PM mass measured by AMS and SMPS should be attributed to black carbon (BC). As shown in Figure 1, the initial mass of PM measured by SMPS was comparable with that measured by HR-TOF-AMS, thus we assumed that the mass of BC in the reactor was negligible. It is then reasonable to use AMS data combined with SMPS data to derive the time-resolved concentrations of OA, sulfate, ammonium and nitrate.

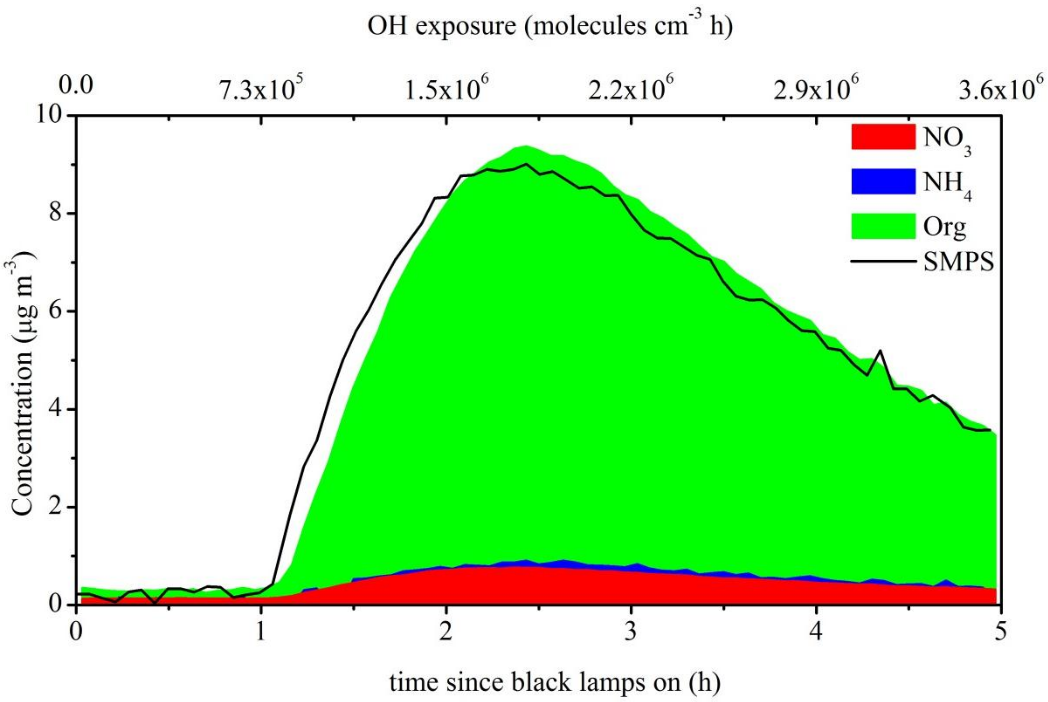


Figure 1. Comparison of the sum of organics, nitrate and ammonium (measured by AMS) against the total particle mass measured by the SMPS for experiment III-1.

The following text has been added to the revised manuscript:

"The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015), thus…"

Q6- Page 23623, line 23-page 23624, line 6: Previously, the authors state that NMHCs, NOx, and average OH are different than typical urban conditions. How similar is the injected SO_2 concentration (~150 ppb) to urban or urban-downwind conditions? Could these discrepancies resolve the large differences between chamber observations and field observations? Due to potential differences in these conditions, it may be useful to normalize the sulfate production rate (e.g., µg-m^{-3}-sulfate hr^{-1} ppt-OH^{-1} or similar) to explore any biases. If the differences still exist, this may enhance the argument related to the role of Creigee intermediates.

Reply: The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study. We still reported the sulfate production rates in μg m^{-3} h^{-1} in order that they can be easily compared with those in previous studies, like Xiao et al. (2009) and Zhang et al. (2011).

The following text has been added to the revised manuscript:

"The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study."

Q7- Page 23625, lines 10-17: Given that there is routine analysis for calcium, magnesium, potassium, and sodium in motor vehicle exhaust (California Air Resources Board, 2011), how might the presence of these additional cations affect the H+ calculations? I do not think this will change the authors conclusions, but it may be worth noting that the reported values of H+ can be considered an upper bound.

Reply: As shown in Figure 1, the mass of primary particles was negligible compared with the formed secondary inorganic aerosols. This indicated that other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+), only part of the primary particles, had negligible influence on the aerosol acidity. But we agree with the referee that the reported values of H^+ are upper bounds.

The following text has been added to the revised manuscript.

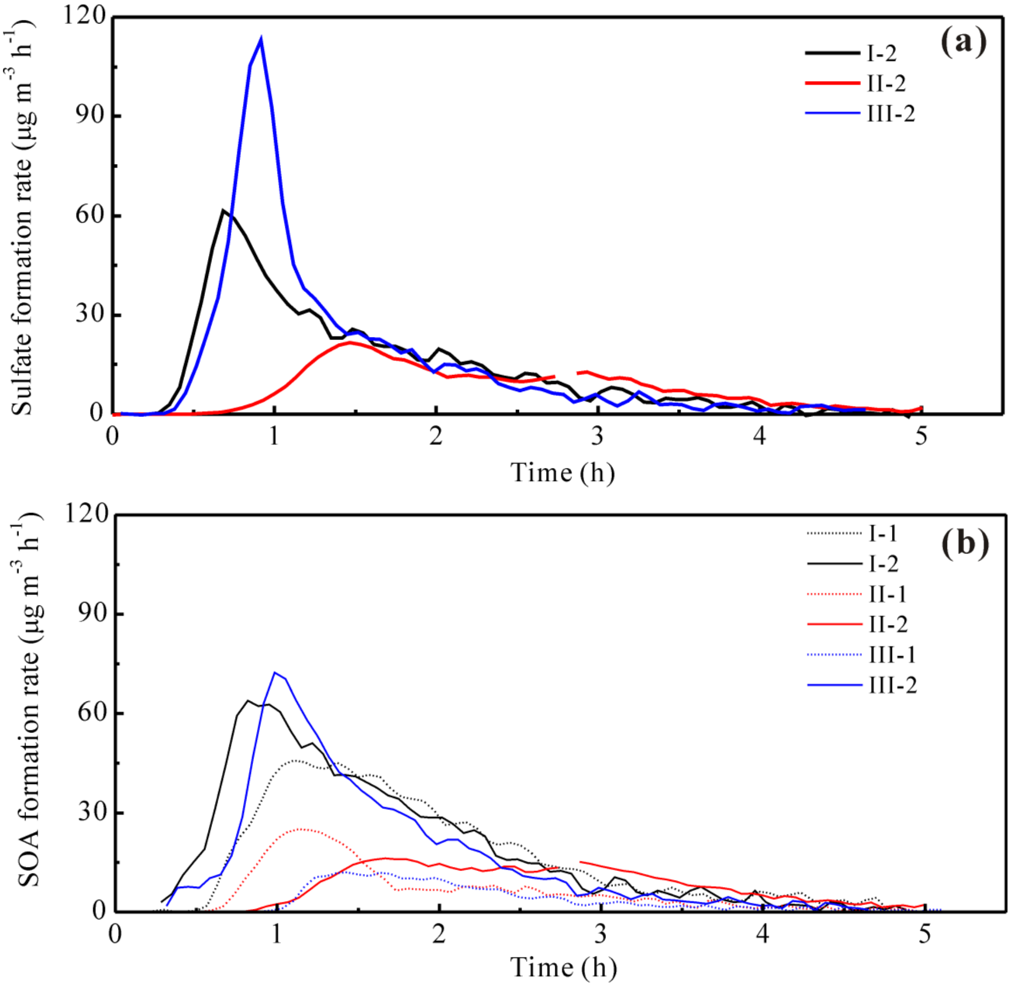
"SO_4^{2-}, NH_4^+ and NO_3^- contributed virtually all of the aerosol phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+) had negligible influence on the aerosol acidity, it is worth noting that the reported values of H^+ may be the upper bound."

Q8- Figures 1-4: Presumably, particle concentrations are wall-loss-corrected. It may be worth explicitly stating this in the caption.

Reply: The concentrations of particle-phase species are wall-loss corrected. This has been clarified in the revised manuscript.

Q9- Figure 5: I would recommend using the same y-axis scale for both figures. This can facilitate direct comparisons between the time series of sulfate and SOA production rates.

Reply: Revised as suggested.



Q10- Figure 6: Maybe this is discussed in the text, and I have missed it, but why is there a large difference between the total loss rate and the sum of sCI and OH oxidation for vehicle II? The results for this vehicle are more drastic than the two others. Could the authors use the results from He et al. (2014) to estimate surface reactions on particles for the present study?

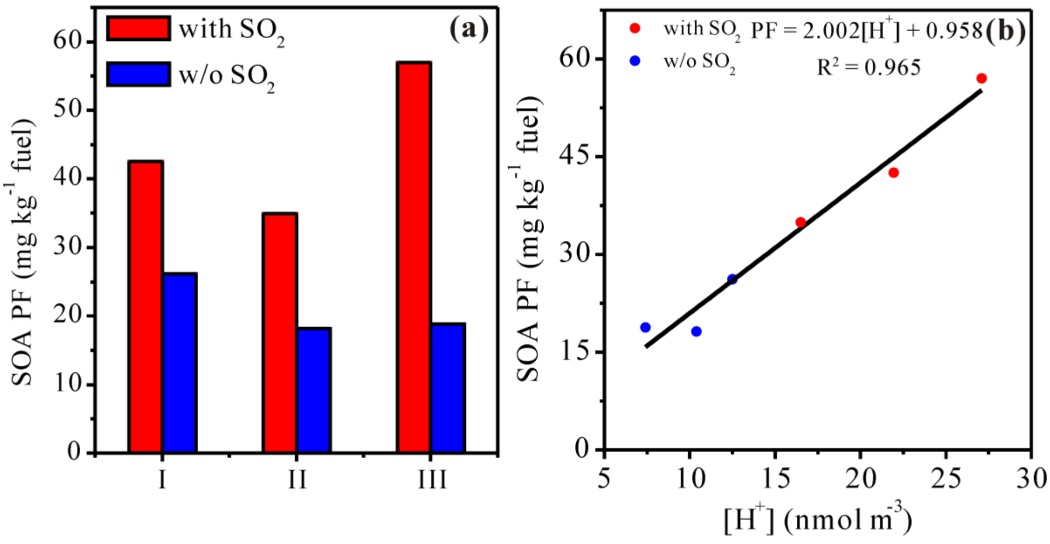
Reply: The difference between the total loss rate and the sum of sCIs and OH oxidation for vehicle II indicated that there might be other oxidation pathways for SO_2. As discussed in the manuscript, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be an explanation. As shown in Fig. 5 in the revised manuscript, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). Thus we speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II.

The sentence "*In this study, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be a pathway to lead to the formation of sulfate.*" has been revised and now reads:

"As shown in Fig. 5, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). We speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II."

Q11- Figure 7b: It may be worthwhile to color the markers in this figure to be consistent with the bar colors in Figure 7a in order to distinguish between "with SO_2" and "w/o SO_2". This should be obvious to the reader, but it will really drive the point home.

Reply: Revised as suggested.



Q12-Figure 9: If I understand this correctly, these figures are discrete points corresponding to data selected from Figure 5? I would recommend some clarification of this in the text. Furthermore, can the authors explain why the slopes are vastly different (i.e., ~4 vs. ~1 vs. ~3)? Given that the initial conditions were largely similar (i.e., Table 2), why might the results be the way that they are? Could this be a function of alkene abundance, or might some other factor play a role?

Reply: Yes, these discrete points are corresponding to data selected from Figure 5. This has been clarified in the revised manuscript. The difference in slopes suggested that there were some other factors influencing the SOA formation rate. We agree with the referee that the alkene abundance might play an important role. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfate and thus influence the aerosol acidity.

The sentence "*Significant linear correlations (P<0.05, $R^2>0.88$) between SOA formation rate and particle acidity (Fig. 9) during this stage for experiments with SO_2 suggest that acid-catalyzed heterogeneous reactions might play an important role on the fast formation of SOA (Jang et al., 2002)*" has been revised and now reads:

"Fig. 10 shows the correlation between SOA formation rate and particle acidity. Plotted data corresponded to data selected from Fig. 6 when SOA formation rate was higher than zero to when the rate reached the maximum value. Significant linear correlations ($P<0.05$, $R^2>0.88$) between SOA formation rate and particle acidity during this stage for experiments with SO_2 suggest that acid-catalyzed heterogeneous reactions might play an important role in the rapid formation of SOA (Jang et al., 2002)"

The following text has been added to the revised manuscript.

"The fitted slopes for vehicle I, II and III were 3.96, 0.82 and 3.14, respectively, suggesting other factors, including alkene abundance, may influence the SOA formation rate. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfuric acid, thus influence the aerosol acidity."

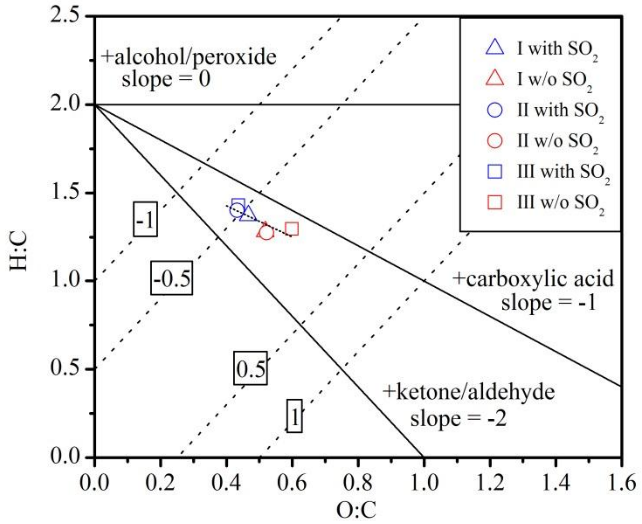
Q13- Figure 10: Do the authors have sufficient signal in the AMS results to calculate an initial H:C and O:C? These may be uncertain because POA concentrations were low. Based on the figure, it appears that the six data points have a slope of -1 and a y-intercept of roughly 1.8, so I am curious for this reason.

Reply: Concentrations of POA in this study were lower than 0.5 μg m^{-3}, typically regarded as not appreciable (Presto et al., 2014) and insufficient to determine the initial H:C and O:C. The six data points fall along a line with a slope of -0.87. This suggests that SOA formation in these experiments is a combination of carboxylic acid and alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). The slope for the mixture of SO_2 and exhaust is slightly higher than those for exhausts alone (Liu et al., 2015). The slope of -0.87 and intercept of around 1.8 are similar to the observation for ambient data with a slope of approximately -1 and intercept approximately 1.8 (Heald et al., 2010), suggesting that SOA chemistry for the mixture of SO_2 and gasoline vehicle exhaust is atmospheric relevant.

The following text has been added to the revised manuscript.

"Concentrations of POA were lower than 0.5 μg m^{-3}, typically regarded as not appreciable (Presto et al., 2014) and insufficient to determine the initial H:C and O:C, thus only SOA data were plotted on the diagram."

"The slope of -0.87 (Fig. 11) for the mixture of SO_2 and exhaust, slightly higher than those for exhaust alone (Liu et al., 2015), indicates that SOA formation in these experiments is a combination of carboxylic acid and alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). The slope of -0.87 and intercept of approximately 1.8 are similar to the observation for ambient data with a slope of approximately -1 and intercept approximately 1.8 (Heald et al., 2010), suggesting that SOA chemistry for the mixture of SO_2 and gasoline vehicle exhaust is atmospheric relevant."



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