

**Cover letter for ACP manuscript acp-2014-146, revised version of 16 June 2014**

Dear Prof. Maria Cristina Facchini:

Please find attached our revised manuscript and our response to the two referees (as published in the interactive discussion in ACPD).

We have answered all referee comments and implemented practically all suggestions for improvement. All changes are marked by red letters.

We are confident that the revised manuscript meets the quality standards of ACP, and we are looking forward to your response.

Many thanks and best regards,

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## Response to the comments of Anonymous Referee #1

Referee General Comment:

General Comments: This manuscript provides a conceptual model: the characteristic “molecular corridors” with a correlation between volatility and molar mass to represent the multiphase chemical evolution of secondary organic aerosol (SOA). Overall, it is a novel proposal to compare the volatility and molar mass of identified SOA constituents in a 2-D map. However, more work needs to be done to demonstrate how the “molecular corridors” could benefit future modeling work and how the detailed chemical mechanisms affect SOA molecule’s positions in the 2-D map. This is a short manuscript and the authors should consider expanding their discussion and building up a linkage between components’ behaviors in the molecular corridors and the SOA formation mechanisms behind them. The comments below should be addressed before consideration for publication in ACP.

Response:

We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. Based on your constructive suggestions for improvement, we will expand discussions in the revised manuscript as detailed below.

Referee Comment 1:

P5931, L5-7: The heterogeneous oxidation reactions are likely triggered by oxidants colliding with particles and the reactions largely occur on particle surface and a limited area at sub-surface. It is not accurate to say “in the particle phase”. Need to clarify.

Response:

As pointed out, heterogeneous reactions may mainly occur at the particle surface or near-surface bulk. Multiphase reactions, particularly cloud processing, may proceed in the particle bulk. We will clarify this point in the revised manuscript.

Referee Comment 2:

P5931, L11-15: The authors claim in both the abstract and introduction that the recent advance in soft ionization mass spectrometry provides molecular information that can be used in the 2-D map for SOA evolution of molar mass vs. volatility. However, in the further discussion, the molecular information for the biogenic SOA (Figure 1a-c) was not from soft ionization mass spectrometry techniques (mostly from GC/EI-MS); the DART-TOF-MS provides molecular formulae for the chamber alkane oxidation shown in Figure 1d-i, but the molecular structures which are necessary to estimate volatility cannot be resolved if not from oxidation of known VOCs. Under such conditions, the authors’ method works only for lab generated SOA, but molecular structure information is essentially needed for a broader use. Thus, I think the linking between soft ionization mass spectrometry and the volatility vs. molar mass map is not fully justified.

Response:

Thanks for pointing this out. We will remove the sentence on soft ionization from the abstract. We will clarify that molecular information of the biogenic SOA were mostly obtained by GC/EI-

MS but also with help of soft ionization mass spectrometry such as ESI-MS and MALDI-MS (Surratt et al., 2006). Even though traditional hard ionization mass spectrometry is capable of identifying molecular structure of oxidation products, the recent advent of soft ionization mass spectrometry (e.g., ESI, MALDI, APCI, DART-MS) and combination with several different instruments have certainly broaden a way to identify chemical composition and molecular structure (e.g., Surratt et al., 2006; Kalberer et al., 2006; Vogel et al., 2013; Chan et al., 2013). To further clarify this point, we will add the below paragraph in the revised manuscript.

“Common techniques applied for the analysis of SOA are gas chromatography/electron impact ionization mass spectrometry (GC/EI-MS) and liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) (e.g., Surratt et al., 2006). Hard ionization, such as electron impact ionization, generally causes significant fragmentation of organic molecules, which makes molecular identification challenging, but can provide molecular structural information. The recent advent of soft ionization methods such as electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI), atmospheric pressure chemical ionization (APCI), and direct analysis in real time (DART) ionization has facilitated the identification of the dominant fraction of the compounds constituting SOA by preserving analytes as intact or nearly intact during ionization (Kalberer et al., 2006; Williams et al., 2010; Laskin et al., 2012a; Laskin et al., 2012b; Chan et al., 2013; Nguyen et al., 2013; Vogel et al., 2013; Schilling-Fahnestock et al., 2014).”

Referee Comment 3:

P5931 L22-27: In Figure 1, the authors show biogenic and anthropogenic SOA constituents. However, it is not entirely clear why the authors choose to present NO<sub>x</sub> dependent data for the anthropogenic, but not for biogenic SOA. Recent studies demonstrate that biogenic SOA have very different constituents under different NO<sub>x</sub> conditions and oxidant types (Lin et al., 2012 ES&T 46, 250-258; Lin et al., 2013 PNAS 110, 6718-6723; Kristensen et al., 2014 ACPD). If the authors are concerned the number of data points will become too small in each figure, I suggest combining the NO<sub>x</sub> dependent figures (i.e., Figure 1 d-e, f-g, and h-i) to be consistent with the biogenic figures.

Response:

In Figure 1 we will include identified oxidation products in the suggested references (Lin et al., 2012, 2013; Kristensen et al., 2014). We combined low and high NO conditions for biogenic SOA, because the number of identified products in previous literatures is not many (<50) and separating into low and high NO conditions make data points small in the each panel. As specified in Table 1, the number of identified compounds of C<sub>12</sub> alkanes by DART-MS in this study is very high (>~100) for both low and high NO conditions. Thus, we prefer to keep figures for low and high NO condition separately for C<sub>12</sub> alkanes.

In the new Table A1 we summarize the experimental conditions (oxidants, NO level, seed) of previous studies that identified biogenic SOA products. Thanks for pointing out that chemical composition of SOA may depend under different NO conditions and oxidants. The molecular corridor for isoprene (Fig. 1a) is relatively tight, even though oxidation products under various conditions are included. Moreover, there are not big differences in the resulting molecular corridors of alkanes under low and high NO conditions. How NO<sub>x</sub> level affects the molecular corridor should be subject to future studies. We will add the below paragraph in the revised manuscript.

“The composition of SOA may vary depending not only on the organic precursor but also on the oxidant and other reaction conditions of formation and aging (Presto et al., 2005; Surratt et al.,

2006; Lin et al., 2012; Lin et al., 2013; Kristensen et al., 2014; Loza et al., 2014; Xu et al., 2014). The atomic O:C ratio tends to be higher at high NO concentrations, partly due to the formation of organonitrates (Nguyen et al., 2011; Schilling-Fahnestock et al., 2014). Even though Fig. 1(g), (h), (i) contain biogenic SOA oxidation products measured under different conditions as specified in Table A1, the molecular corridors are relatively tight with  $R^2 > 0.85$ . The molecular corridors of alkane SOA formed under low and high NO conditions are also quite similar (Figs 1a-f). Thus, the molecular corridors of SOA formation appear to be determined primarily by the organic precursor, and the extent to which they are influenced by reaction conditions warrants further studies.”

Referee Comment 4:

P5933 L12-15: Some of these descriptions can be moved to figure caption.

Response:

Following your suggestion, we will move a part of this sentence to the figure caption.

Referee Comment 5:

P5933 L20-25: In Figure 3, the authors show the molecular corridors of molar mass vs. volatility. However, it is not a surprise that most of the identified SOA compounds locate within the area shown in Figure 3, because: (1) from linear alkane (O:C =0) to sugar alcohol (O:C) is quite a large volatility and mass range and (2) it is generally known as molecular mass increases, volatility decrease (gas phase moving towards particle phase). It is totally expected that most molecules sit in this wide range. However, what is more interesting and I think the authors should spend a little more time (where the authors already briefly discussed a few examples) discussing is the exceptions and the chemistry explanation behind the observations. The rules generally acknowledged based on the multiphase chemistry and Figure 3 can be summarized as: (1) Gas phase products are confined to the lower right area (lower mass and higher volatility); (2) Early generation particle-phase products (or fresh SOA) are semi-volatile and tend to locate in the middle part of the corridors; (3) Particle-phase reactions lead to the formation of high mass, low volatility products, which locate in the upper left area; Here are some examples of exceptions that could be discussed: (1) Some recently observed gas-phase products have low volatility (extreme low volatile organic compounds (ELVOC) from  $\alpha$ -pinene + O<sub>3</sub> reactions (Kristensen et al., 2014 ACPD; Ehn et al., 2014 Nature)). They locate on the upper left even though they are initially formed in the gas phase. This suggests a new chemical pathway that was not captured by traditional understanding: fast formation of low volatility and highly oxygenated products. (2) Semi-volatile compounds undergo gas-particle partitioning, leading to fresh SOA formation and tend to locate in the middle part of the corridors. But some gas phase compounds are quite volatile and they can still participate in SOA formation due to reactive uptake (for example, isoprene epoxydiols (IEPOX)). (3) Particle-phase reactions do not necessarily lead to formation of high mass, low volatility products. The authors mentioned dihydrofurans and furans. The reason for their exception is likely they were formed from dehydration which transferred a -OH group to a double C=C bond and the volatility largely increased. Another example is glyoxal oligomers (lower mass due to the low mass of glyoxal). It would be nice if the authors could expand their discussion and point out a number of possibilities and chemical mechanisms that may cause exceptions, because these are the aspects that current chemical models do not incorporate.

Response:

Thanks for this helpful comment. Based on your comment, we will expand the discussion substantially by including the new panel b in figure 4, which depicts characteristic reaction pathways on the molecular corridor. The main text will be revised substantially to discuss the chemical pathways and location of oxidation products, including exceptions. We will include the below paragraphs in the revised manuscript.

“Characteristic reaction pathways and relevant kinetic regimes are outlined in Fig. 4(b). SOA precursor VOCs with high volatility and low molar mass are located in the lower right corner of the molecular corridor ensemble. As illustrated in the insert in Fig. 4(b), single-step functionalization usually leads to a small increase in molar mass, corresponding to one order of decrease in volatility (Donahue et al., 2006), while dimerization and oligomerization tend to multiply molar mass, and thus decrease volatility by multiple orders of magnitude (Trump and Donahue, 2014) (e.g., three to four orders of magnitude for alkane and terpene SOA, see Fig. 1). Fragmentation, on the other hand, can lead to a substantial decrease of molar mass and increase in volatility (Bertram et al., 2001; Yee et al., 2012; Schilling-Fahnestock et al., 2014). As a result, simple gas-phase oxidation products are confined to the lower right area in the 2D space. Such oxidation products ( $C_0 > 10 \mu\text{g m}^{-3}$ ) tend to fall into the gas-phase reaction limiting case  $G_{rx}$  (quasi-equilibrium growth), as their gas-particle equilibration timescale is on the order of seconds to minutes (Shiraiwa and Seinfeld, 2012) (see Appendix C&D). “

“Aqueous-phase processing of glyoxal and methylglyoxal is an efficient pathway for formation of low volatility and semi-volatile HOC compounds (Liggio et al., 2005; Carlton et al., 2007; Lim et al., 2010; Ervens et al., 2011; Zhao et al., 2012). Uptake of glyoxal into the particle phase leads to hydration and acid catalysis to form hemiacetals, aldols, imines, anhydrides, esters and organosulfates (Lim et al., 2010). Reactive uptake of isoprene epoxydiols (IEPOX) and subsequent formation of oligomers (Surratt et al., 2010; Lin et al., 2012; Lin et al., 2013) also progresses over the HOC corridor. Whether multiphase chemistry of glyoxal and IEPOX is limited by mass transfer or chemical reactions may depend on various factors including reaction rate coefficients, relative humidity, particle pH, and Henry’s law constant (Ervens and Volkamer, 2010; McNeill et al., 2012; Kampf et al., 2013). Recently, highly oxidized extremely low volatility organic compounds (ELVOC) have been detected in field and chamber experiments (Ehn et al., 2012; Schobesberger et al., 2013; Ehn et al., 2014). Such compounds may populate the upper left corner of the HOC corridor.”

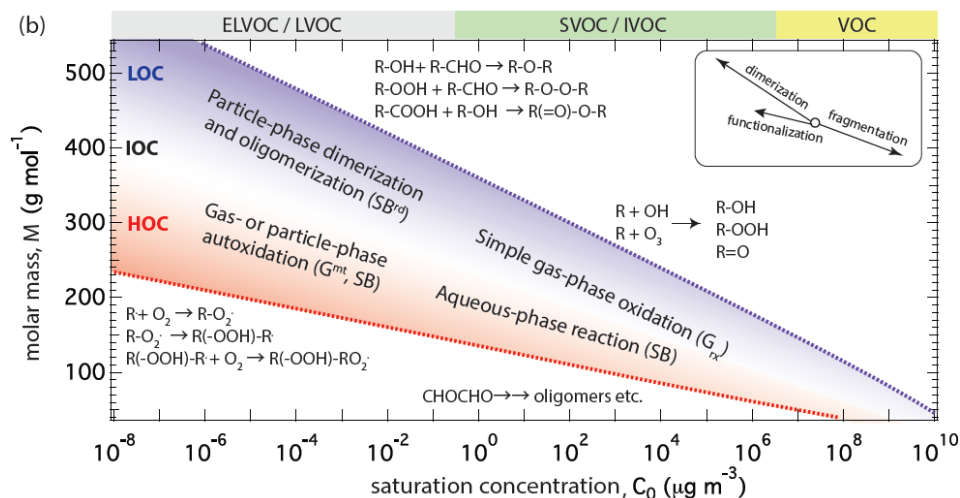


Figure 4. (b) Characteristic reaction pathways with most probable kinetic regimes. The split of molecular corridors between high and low O:C compounds (HOC, red shaded area; LOC, blue shaded area) reflects the median correlation fitted lines from Fig. 1. SOA products evolve over the molecular corridor driven by three key reaction types of functionalization, oligomerization and fragmentation as illustrated in the insert (note different lengths of arrows indicating different intensities of effects on volatility).

Referee Comment 6:

P5935, L6-8: It will be helpful if the authors can specifically point out which precursor system follows which behavior, because the range shown in Figure 1 is different from that in Figure 3. Some explanations would also be helpful (why they follow different behaviors? Biogenic vs. anthropogenic? It takes more oxidation generations for some VOCs to produce semi-volatile products that can partition to the particle phase than the others?).

Response:

Based on your comment, we extend the range of Figure 3 to be consistent with Figure 1. Isoprene SOA follows the HOC corridor; dodecane and cyclododecane follow LOC corridor. We will clarify this point in the revised manuscript as below.

“Many early generation gas-phase oxidation products of alkanes as well as dimers or oligomers with low O:C ratio (LOC) fall into a molecular corridor close to the  $C_nH_{2n+2}$  line, which we designate as LOC corridor ( $-dM/d\log C_0 \geq \sim 25 \text{ g mol}^{-1}$ , blue shaded area). Aqueous-phase reaction and autoxidation products with high O:C ratio (HOC), on the other hand, tend to fall into a corridor near the  $C_nH_{2n+2}O_n$  line, which we designate as HOC corridor ( $-dM/d\log C_0$  of  $\leq \sim 15 \text{ g mol}^{-1}$ , red shaded area). The area in between is characterized by intermediate O:C ratios and accordingly designated as IOC corridor ( $-dM/d\log C_0 \approx \sim 20 \text{ g mol}^{-1}$ ). Among the SOA systems investigated in this study, the small precursor VOCs glyoxal, methylglyoxal and isoprene ( $C_2$ - $C_5$ ) evolve through the HOC corridor, and the terpenes  $\alpha$ -pinene and limonene ( $C_{10}$ ) through the IOC corridor. The alkanes dodecane and cyclododecane ( $C_{12}$ ) evolve through the LOC corridor, while hexylcyclohexane exhibits a branching between the LOC and HOC corridors, suggesting the involvement of different reaction pathways.”

Referee Comment 7:

P5935, L11-13: It is not entirely true that 250-300 g/mol is a threshold between gas and particle-phase products. In addition to furans and glyoxal products, IEPOX products and  $\alpha$ -pinene products are also exceptions. There might be many other exceptions. The interesting question is not where the threshold is, but rather what are the chemical differences that cause different thresholds?

Response:

Thanks for pointing it out. Please also see the response for comment 5. We will revise and include the below paragraph in the revised manuscript:

“Figure 4(a) shows that most identified oxidation products with molar masses higher than 300 g mol<sup>-1</sup> are particle-phase products (solid markers). Thus, the relatively high average molar mass observed for laboratory-generated SOA points to the importance of particle-phase chemistry in these systems. Some SOA compounds with higher molar mass are gas-phase oxidation products including ELVOC and ester dimers observed in  $\alpha$ -pinene oxidation (Ehn et al., 2014; Kristensen et al., 2014), and there are also some particle-phase products with relatively low molar mass including furans and dihydrofurans in dodecane and cyclododecane SOA (Yee et al., 2012; Loza et al., 2014) as well as glyoxal and IEPOX products in isoprene SOA (Lim et al., 2010; Surratt et al., 2010). Nevertheless, the clustering of identified reaction products in molecular corridors may facilitate estimation of the relative importance of gas- vs. particle-phase routes to SOA formation (Fig. 1).”

Referee Comment 8:

Figure 1: Some data points in Figure 1a might be wrong (not updated enough). There are a number of particle-phase products within the 100-200 g/mol range that should be shown in solid markers. Under the low-NO<sub>x</sub> pathway, C<sub>5</sub> alkene triols (M<sub>w</sub> =118), 2-methyltetrols (M<sub>w</sub>=136), 3-methyltetrahydrofuran-3,4-diols (M<sub>w</sub>=118) are all particle phase products; under the high-NO<sub>x</sub> pathway, 2-methylglyceric acid (M<sub>w</sub>=120) is also a particle-phase product (Lin et al., 2012 ES&T 46, 250-258; Lin et al., 2013 PNAS 110, 6718-6723). New observed “ELVOC” should be updated in Figure 1b as well.

Response:

Thanks for pointing out. C<sub>5</sub> alkene triols (M<sub>w</sub> =118), 2-methyltetrols (M<sub>w</sub>=136), and 3-methyltetrahydrofuran-3,4-diols (M<sub>w</sub>=118), and 2-methylglyceric acid (M<sub>w</sub>=120) will be treated as particle-phase products with solid markers. We will add Lin et al., ES&T, 2012; PNAS, 2013 as references. For newly observed ELVOC, we will include dimer ester for  $\alpha$ -pinene observed by Kristensen et al., ACPD, 2014. As Ehn et al., 2013 did not provide molecular identity and volatility of ELVOC compounds (only elemental formula were provided), it is not yet possible to include them in Fig. 1. Kinetic regimes of ELVOC compounds are investigated in Appendix C and Fig. A4(d).

## Response to the comments of Anonymous Referee #2

### Referee General Comment:

This paper presents the novel framework of molecular corridors (based on volatility and molar mass) as a way to capture aspects of SOA formation and aging. This is more of a theory paper that is not directly applied to simulate smog chamber data. The authors mostly use the smog chamber data that exists in the literature to propose this idea. The authors conclude that the molecular corridor theory could serve as a basis for compact representation of SOA formation and aging in models. The manuscript is well written, but I feel lacks many details needed for readers to better understand how this theory was developed from existing smog chamber data. Furthermore, in order to keep my comments concise and not create repetition of what has already been raised by the other reviewer, I want to state here that I completely agree with the other reviewer's concerns and recommend that these be adequately addressed before publication is considered. Besides not applying this theory to simulate SOA formation from existing chamber data at Caltech, my other biggest concern with this paper is how previous chemical data were exactly utilized for estimating volatility. This is not clear at all and I feel should be added in the appendix. The authors say they use prior identified compounds, but it is completely unclear which ones are selected and why others may or may not have been left out. Since I'm an analytical atmospheric chemist, I also warrant caution to the authors about soft ionization mass spectrometry methods. The authors cite the Kalberer et al. (2006, ES&T) study a lot and even use it to determine the average MW of the SOA in Table A1 for isoprene and alpha-pinene systems. With the Kalberer et al. (2006) study, the authors should be aware that MALDI-MS is prone to substantial artifacts. This is also true for other soft ionization methods like ESI-MS. Specifically, cluster ions may form in the ion sources, leading to much higher MW products than might actually exist. In my opinion, the use of chromatography and synthetic standards are the gold standards now and are typically needed to confirm the identity of certain compounds found in SOA systems. I'm surprised that the authors used the Kalberer et al. (2006) study for Table A1 when they say in the text they developed the 2D plots using Surratt et al. (2006; 2010) studies. For isoprene, I would argue that the Surratt et al. studies are more useful since much work was put in to derive the functionality of oligomers under both low- and high-NO<sub>x</sub> conditions. In addition, I'm unclear (and I'm sure other readers would be as well), how exactly aerosol acidity would be utilized in this framework since this is especially important in the isoprene and alphapinene SOA systems (Kleindienst et al., 2006, ES&T; Offenberg et al., 2009, ES&T). Lastly, in addition to these major comments above, I would like to request the authors consider my specific comments below.

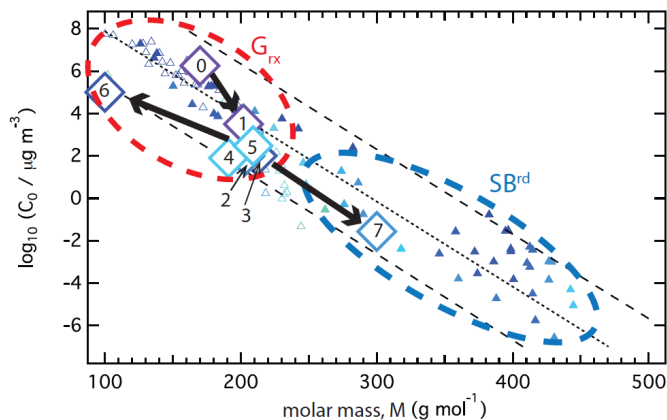
### Response:

The developed theory in this study is actually applied to simulate laboratory data of dodecane photooxidation in Appendix D. To emphasize such application, we have the following new paragraph and new Figure 5 that exhibits evolution of reaction pathways over the molecular corridor of dodecane SOA under low NO condition.

“An example of reaction pathways leading to dimerization is shown in Fig. 5 for dodecane SOA (Appendix D, Shiraiwa et al., 2013a). Within the molecular corridor of dodecane SOA evolution, Fig. 5 illustrates a specific trajectory from the precursor (dodecane, 0) through multiple generations of surrogate products of gas-phase oxidation and functionalization (multifunctional alcohols, ketones, and peroxides, 1-5), gas-phase fragmentation (aldehydes, 6), and particle-phase dimerization between aldehydes and peroxides to peroxyhemiacetals (7). Numerical model results shown in Fig. A2 indicate that the trajectory of chemical evolution passes through different



kinetic regimes, i.e., from limitation by gas-phase reaction ( $G_{rx}$ ) to particle-phase reaction and diffusion ( $SB^{rd}$ ).”



**Figure 5.** Evolution of reaction pathways over the molecular corridor of dodecane SOA under low NO condition. The large diamonds indicate the surrogate compounds used in the KM-GAP simulations (Appendix D; Shiraiwa et al., 2013a), including the precursor (dodecane, 0), 1<sup>st</sup> – 5<sup>th</sup> generations of surrogate products of gas-phase oxidation (1-5), gas-phase fragmentation (aldehydes, 6), and particle-phase dimerization products (7). The smaller symbols indicate identified individual products (as shown in Fig. 1a).

Estimation of volatility of oxidation products was done using the EVAPORATION model (Compernelle et al., 2011), which is described in Appendix A. EVAPORATION model can provide vapor pressure of molecules with the following functionalities: aldehyde, ketone, alcohol, ether, ester, nitrate, acid, peroxide, hydroperoxide, peroxy acyl nitrate and peracid (Compernelle et al., 2011). Thus, for example, organosulfates are not included in the current analysis, even though they are identified as important products in biogenic SOA (Iinuma et al., 2007; Surratt et al., 2008). We agree that this is important information, so that we will add the below paragraph in the main text of the revised manuscript.

“Vapor pressures and saturation mass concentrations of organic compounds were estimated using the EVAPORATION model (“Estimation of vapor pressure of organics, accounting for temperature, intramolecular, and non-additivity effects”, (Compernelle et al., 2011). The EVAPORATION model estimates vapor pressure of molecules with the following functionalities: aldehyde, ketone, alcohol, ether, ester, nitrate, acid, peroxide, hydroperoxide, peroxy acyl nitrate and peracid. Organosulfates and imidazoles are not covered and were thus not included in our analysis, although they have been identified in SOA from biogenic precursors and glyoxal (Iinuma et al., 2007; Surratt et al., 2008; Ervens et al., 2011).”

For SOA oxidation products by biogenic precursors of isoprene,  $\alpha$ -pinene, and limonene, we tried to include as many identified products as we can. In the revised manuscript, we have added several more studies based on comments by Referee 1 and summarized in Table A2.

We used Kalberer et al. (2006) to refer to average molar mass of SOA, as this is the only study that provided such information, to the best of our knowledge. We fully appreciate Surratt et al. (2006, 2010) and all identified products are included in Figure 1.

Thanks for pointing out on aerosol acidity. Aerosol acidity may affect how oxidation products may locate within molecular corridors and certainly affects kinetic regime as reaction may be accelerated by acid-catalyzed reactions. We will add the below sentence in the revised manuscript.

“Whether multiphase chemistry of glyoxal and IEPOX is limited by mass transfer or chemical reactions may depend on various factors including reaction rate coefficients, relative humidity, particle pH, and Henry’s law constant (Ervens and Volkamer, 2010; McNeill et al., 2012; Kampf et al., 2013).”

Referee Comment 1:

I wonder if the Editor and authors would agree if this should really be considered a Technical Note, especially since this theory is not applied to simulate laboratory data? I think many readers would wonder how applicable and useful is this theory in actually simulating SOA formation in the lab. Naturally, I think we would all agree this isn’t ready for prime time in regional or global modeling of SOA until it is validated with laboratory data.

Response:

The developed theory in this study is actually applied to simulate laboratory data of dodecane photooxidation (please see the response to general comments). The classification scheme was also tested/validated by exemplary simulations shown in Figure A2. Thus, we think this study goes beyond technical note and would like to keep it as a regular scientific article.

Referee Comment 2:

Fig 1: I think we have to be careful here. Specifically, I think the authors need to EXACTLY clarify for readers how the different SOA types were generated. For example, is the isoprene SOA in Figure 1 a from photooxidation or ozonolysis? The way these plots read is that these would represent the behaviors for SOA generated under all oxidant, NO<sub>x</sub>, and seed aerosol conditions. Is that true? Do we even know that these plots would hold up under all conditions? In isoprene SOA, NO<sub>x</sub> and seed aerosol type will affect the type (i.e., functionality) and size of oligomers that form (Surratt et al., 2006; 2010).

Response:

Isoprene SOA in Figure 1a is both from photooxidation and ozonolysis. Yes, the current figures for biogenic SOA contains under any condition including oxidants, NO<sub>x</sub> and seed aerosol conditions. We summarized the experimental conditions of each study in the below table, that will be included as Table A2 in the revised manuscript. The molecular corridor for isoprene (Fig. 1a) is relatively tight, even though oxidation products under various conditions are included. Moreover, there are not big differences in molecular corridor of under low and high NO conditions for alkanes. Thus, we think it would not be a big problem to keep all oxidation products in a single panel for biogenic SOA. How these aspects (oxidants, NO<sub>x</sub> level, acidity) affect molecular corridor should warrant future studies.

**Table A1.** Experimental conditions in studies identifying oxidation products of  $\alpha$ -pinene, limonene, and isoprene as included in Figures 1 and 4.

	study	oxidants	NO	seed
dodecane		OH	low / high	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
cyclododecane	this study, Schilling-Fahnestock et al., 2014	OH	low / high	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
hexylcyclohexane		OH	low / high	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
$\alpha$ -pinene	Docherty et al 2005	O <sub>3</sub>	low	no seed
	Claeys et al., 2007	OH	high	no seed
	Claeys et al., 2009	OH, O <sub>3</sub>	high / low	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub>
	Kahnt et al., 2014	O <sub>3</sub>	high	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>
	Kristensen et al., 2014	OH, O <sub>3</sub>	high	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub>
	Zuend & Seinfeld, 2012	O <sub>3</sub>	low	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
limonene	Jaoui et al., 2006	OH, O <sub>3</sub>	high	no seed
	Kundu et al., 2012	O <sub>3</sub>	low	no seed
isoprene	Surratt et al., 2006	OH	high / low	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , no seed
	Surratt et al., 2010	OH	high / low	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , no seed
	Lin et al., 2012	OH	high	no seed
	Lin et al., 2013	OH	low	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub>

Referee Comment 3:

3.) Section 3 - Kinetic regimes for SOA Formation: The authors walk us very clearly through the different limiting cases of kinetic behavior for particle- and gas-phase reactions. Specifically, for the particle-phase reactions, the authors propose there could be 8 limiting cases of kinetic behavior, where as for the gas-phase reactions, the authors propose there to be 4 limiting cases. From prior work on the SOA systems you discuss here in this paper, I wonder if the authors can already rule out any of these limiting cases? I realize they may want to leave these all in to provide flexibility in the future development of the model, especially as more laboratory studies become available.

Response:

We may need to conduct further studies to rule out any of these limiting cases. However, we can already point out the most probable limiting cases inside the molecular corridors. For example, semi-volatile oxidation products generated by simple gas-phase oxidation may most likely adopt G<sub>rx</sub>, and particle-phase oligomerization products may form in the kinetic regime of SB. We will include the below paragraph in the revised manuscript with additional panels in Figures 3 and 4 to emphasize on the relevant kinetic regime in SOA formation in Fig. 3b and point out characteristic reaction pathways and most probable kinetic regimes in Fig. 4b.

“The left part of the cuboid can be regarded as a particle-phase chemistry regime and the right side as a gas-phase chemistry regime. As shown in Fig. 3(b), the particle-phase chemistry regime (SB, including surface (S) or bulk (B) reaction) can be further subdivided into a reaction-diffusion regime ( $SB^{rd}$ ), where the system is limited by reaction or diffusion in the particle-phase, and a mass-transfer regime ( $SB^{mt}$ ) limited by mass accommodation at the interface or diffusion through the gas phase (Berkemeier et al., 2013). The gas-phase chemistry regime (G) comprises the traditional scenario of SOA formation determined by a rate-limiting chemical reaction in the gas phase followed by quasi-instantaneous gas-particle partitioning of the reaction products ( $G_{rx}$ ), corresponding to so-called quasi-equilibrium growth (Shiraiwa and Seinfeld, 2012; Zhang et al., 2012). The rest of the gas-phase chemistry regime is mass transport-limited and corresponds to so-called non-equilibrium growth (Perraud et al., 2012; Zaveri et al., 2014), which can be kinetically limited by gas-to-particle mass transfer (gas-phase diffusion and accommodation at the interface;  $G^{mt}$ ) or retarded diffusion in the particle phase ( $G_{bd}$ ).”

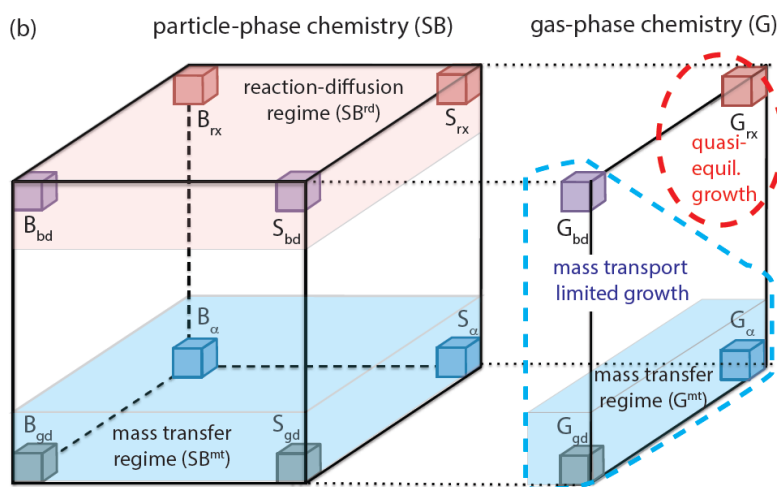


Figure 3. (b) The left side of the cuboid can be regarded as a particle-phase chemistry regime (SB) and subdivided into a reaction-diffusion regime ( $SB^{rd}$ ) and a mass transfer regime ( $SB^{mt}$ ). The right side of the cuboid can be regarded as a gas-phase chemistry regime (G) and subdivided into a traditional scenario of “quasi-equilibrium growth” limited only by a gas phase reaction followed by quasi-instantaneous gas-particle partitioning ( $G_{rx}$ ) and a mass-transport limited regime of “non-equilibrium growth” that may be kinetically limited by gas-to-particle mass transfer ( $G^{mt}$ ) or diffusion in the particle ( $G_{bd}$ ).

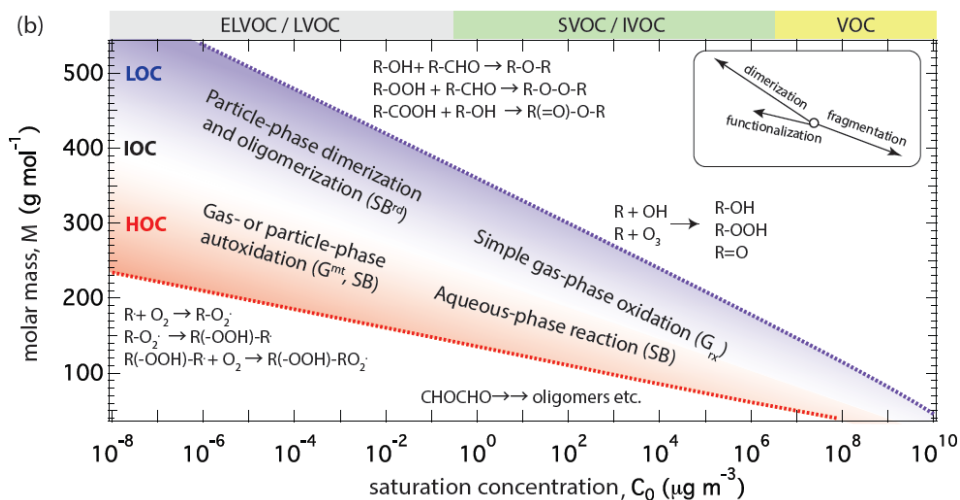


Figure 4. (b) Characteristic reaction pathways with most probable kinetic regimes. Molecular corridors consists of high, intermediate, and low O:C corridors (HOC, red shaded area; IOC, white area; LOC, blue shaded area). SOA products evolve over the molecular corridor driven by three key reaction types of functionalization, oligomerization and fragmentation as illustrated in the insert (note different lengths of arrows indicating different intensities of effects on volatility).