

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_x 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}).”

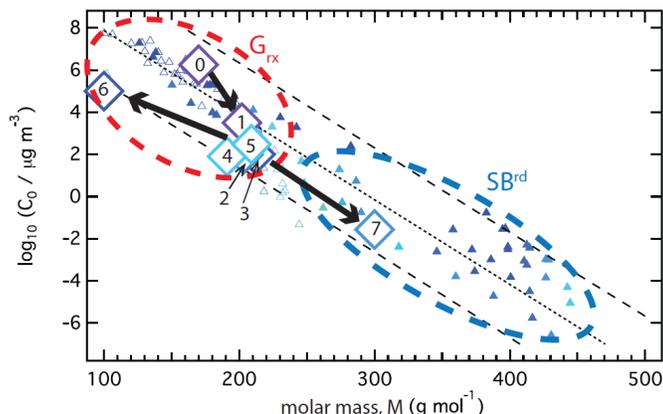


Figure 5. Evolution of reaction pathways over the molecular corridor of dodecane SOA under low NO condition. The large diamonds indicate the surrogate compounds used in the KM-GAP simulations (Appendix D; Shiraiwa et al., 2013a), including the precursor (dodecane, 0), 1st – 5th generations of surrogate 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, α -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_x, and seed aerosol conditions. Is that true? Do we even know that these plots would hold up under all conditions? In isoprene SOA, NO_x 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_x 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_x level, acidity) affect molecular corridor should warrant future studies.

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

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

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_{rx}, 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}).”

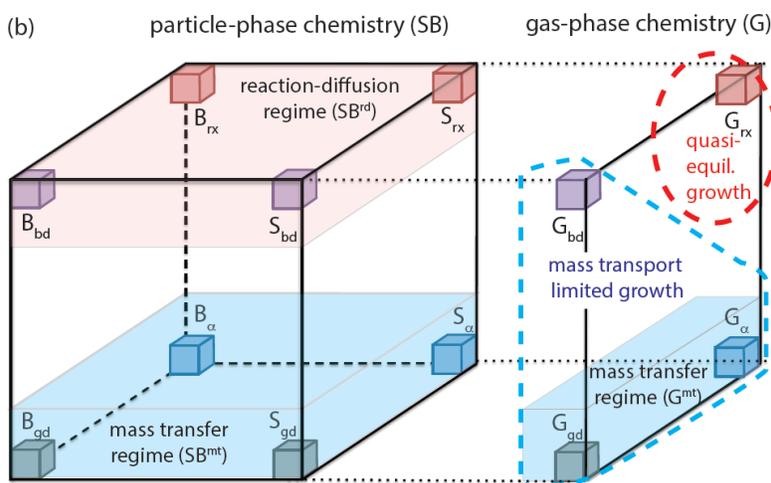


Figure 3. (b) The left side of the cuboid can be regarded as a particle-phase chemistry regime (SB) and subdivided into a reaction-diffusion regime (SB^{rd}) and a mass transfer regime (SB^{mt}). The right side of the cuboid can be regarded as a gas-phase chemistry regime (G) and subdivided into a traditional 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}).

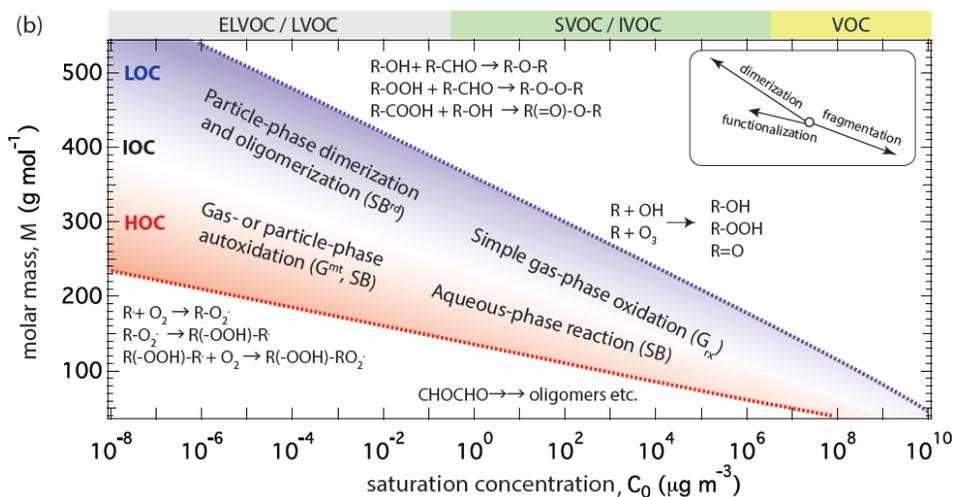


Figure 4. (b) Characteristic reaction pathways with most probable kinetic regimes. Molecular corridors consists of high, intermediate, and low O:C corridors (HOC, red shaded area; IOC, white area; LOC, blue shaded area). SOA products evolve over the molecular corridor driven by three key reaction types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