

1. Executive Summary

Terrestrial vegetation emits large quantities (~500 teragrams Carbon (C)) into the atmosphere of a chemical called isoprene (C_5H_8). Isoprene emissions in eastern Texas and northern Louisiana are some of the largest in the United States. The photochemical oxidation of emitted isoprene leads to significant yields of gas-phase intermediates that then contribute to particulate matter (PM) through secondary organic aerosols (SOA). The production of isoprene-derived PM is enhanced when mixed with anthropogenic emissions from urban areas like those found in Houston. To quantify the contribution that PM production from isoprene has in Texas requires air quality models to predict the oxidation chemistry that produces the gas phase PM precursors. These models must also be updated with the fundamental parameters needed to describe the efficiency that these gas phase precursors react on the surface of PM. The goal of this project was to provide new information on these two critical processes. The following four tasks were completed to accomplish this goal:

1. Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into our smog chamber box model
2. Synthesis of Isoprene-derived Epoxides and Known SOA Tracers
3. Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides
4. Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers

Upon successful completion of these tasks we have already published two articles. The two completed manuscripts are listed here and the results and findings can be found in Chapters 2-3 of this report.

1. Chen, Y.Z., et al., Assessment of SAPRC07 with updated isoprene chemistry against outdoor chamber experiments. *Atmospheric Environment*, 2015. **105**: p. 109-120.
2. Riedel, T.P., et al., Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates. *Environmental Science & Technology Letters*, 2015. **2**(2): p. 38-42.

A third draft manuscript that is listed below is currently in review and its draft is presented in Chapter 4 of this report.

3. Riedel, T. P., Z. Zhang, K. chu, J. Thornton, W. Vizuete, A. Gold and j. d. Surratt, Constraining Condensed-Phase Formation Kinetics of Secondary

A. Key Findings

1. Gas Phase Oxidation of Isoprene

We have evaluated against outdoor chamber experiments the state of the science Community Multi-scale Air Quality (CMAQ) modeling system version of the Statewide Air Pollution Research Center (SAPRC07) mechanism we have called the Xie mechanism and published our results [1]. This research version of the SAPRC07 chemical mechanism is a combination of improved isoprene oxidation pathways by EPA researchers [2] and the base mechanism SAPRC07T [3]. Our model performance results suggest that the new Xie mechanism produces more ozone (O_3) and predicts an earlier Nitrous Oxide (NO)/ Nitrous Dioxide (NO_2) crossover time than SAPRC07 for all experiments. Under lower-NO+ NO_2 conditions, both mechanisms over-predict O_3 observations; the Xie mechanism worsens performance and increases the bias of O_3 from 4.9% to 9.4%. Overall, the Xie mechanism reacts more Volatile Organic Carbons (VOCs) due to a more explicit representation of isoprene oxidation products and therefore increases subsequent hydroxyl radical (OH) formation. The increased reaction rate of VOCs results in more NO to NO_2 conversions by peroxy radicals and more production of aldehyde. The Xie mechanism also increases NO_2 recycling from nitrogen termination species, which accounts for the increase in the afternoon O_3 peak concentrations in the lower- NO_x experiments. The increase in NO_2 recycling from peroxyacetyl nitrate species (PAN) accounts for 85% of the total increase in NO_2 recycling.

This data suggests a continued focus on the production of radical and SOA precursor species to improve the ability of the mechanism to simulate ozone chemistry while maintaining explicit gas phase precursors for isoprene SOA. The significantly larger concentrations in our experiments allow for all day oxidation. Our results, however, may not be applicable for ambient conditions at low NO_x concentrations. Chamber experiments at ambient NO_x concentrations are needed to obtain a complete understanding of the performance of the Xie mechanism under ambient-relevant conditions.

2. Formation of PM

A combination of flow reactor studies and chamber modeling was used to constrain two uncertain parameters central to SOA formation from isoprene-derived gas phase precursors:

- (1) Rate of epoxide heterogeneous uptake to the particle phase

(2) Molar fraction of gas phase precursors that are reactively taken up and contribute to SOA (ϕ_{SOA}).

Flow reactor measurements of the *trans*- β -isoprene epoxydiol (*trans*- β -IEPOX) and methacrylic acid epoxide (MAE) aerosol reaction probability (γ) were completed on atomized aerosols with compositions similar to those used in chamber studies [4]. Observed γ ranges for *trans*- β -IEPOX and MAE were 6.5×10^{-4} –0.021 and 4.9×10^{-4} – 5.2×10^{-4} . Through the use of a time-dependent chemical box model initialized with chamber conditions and the γ measurements, ϕ_{SOA} for *trans*- β -IEPOX and MAE on different aerosol compositions was estimated between 0.03–0.21 and 0.07–0.25, with MAE ϕ_{SOA} showing more uncertainty.

As discussed above, it is unclear how γ and ϕ_{SOA} are affected when a significant fraction of surface area (S_a) is represented by epoxide-derived SOA. This warrants further investigation as it could be relevant in regions like eastern Texas during summer where isoprene SOA can account for a substantial portion of $\text{PM}_{2.5}$ mass and therefore S_a . The results presented here, and in our previous study [5] that constrained all reactions contributing to IEPOX- and MAE-derived SOA, could be beneficial in regional and/or global models to help constrain predictions of IEPOX- and MAE-derived SOA. This is especially true since only a few known aqueous-phase reaction rates constrain current models.

We have completed our chemical box model simulations that explicitly predict the gas- and aqueous-phase reactions during chamber experiments of SOA growth from IEPOX uptake onto acidic sulfate aerosol. These reactions are listed in Figure 1.1. Specifically, the model is constrained by recent measurements of the IEPOX reactive uptake coefficient [4, 5], experimentally obtained aqueous-phase rate constants [6], chamber-measured aerosol mass and surface area concentrations, aerosol thermodynamic model calculations with Extended AIM Aerosol Thermodynamics Model (E-AIM III) [7], and offline filter measurements of SOA of a number of the aforementioned tracers.

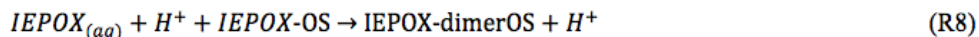
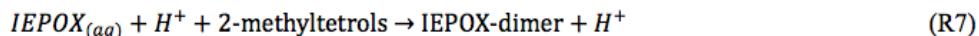
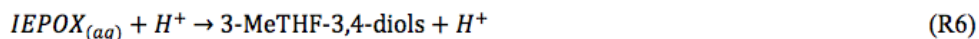


Figure 1.1 Reactions used in box model.

The resulting model-predicted tracer formation rate constants for these reactions are given in Table 1.1. These are averaged over all experiments and the listed errors correspond to one standard deviation. For the purpose of comparison, we have also included the existing literature values [8, 9] in the top portion of the table.

Table 1.1 Model-predicted tracer formation rate constants (k) where “OS” is defined as IEPOX-derived organosulfates.

SOA tracer formed	k	reaction
2-methyltetrols	$9.0 \times 10^{-4} \text{ M}^{-2} \text{ s}^a$	(R1)
2-methyltetrols	$1.3 \times 10^{-5} \text{ M}^{-2} \text{ s}^a$	(R2)
IEPOX-OS	$2.0 \times 10^{-4} \text{ M}^{-2} \text{ s}^a$	(R3)
IEPOX-OS	$2.9 \times 10^{-6} \text{ M}^{-2} \text{ s}^a$	(R4)
C ₅ -alkene triols	$7.8 \pm 0.4 \times 10^{-4} \text{ M}^{-1} \text{ s}$	(R5)
3-MeTHF-3,4-diols	$9.2 \pm 1.2 \times 10^{-4} \text{ M}^{-1} \text{ s}$	(R6)
IEPOX-dimer	$7.7 \pm 2.7 \times 10^{-7} \text{ M}^{-2} \text{ s}$	(R7)
IEPOX-dimerOS	$8.1 \pm 3.3 \times 10^{-6} \text{ M}^{-2} \text{ s}$	(R8)
other SOA	$5.4 \pm 0.2 \times 10^{-3} \text{ M}^{-1} \text{ s}$	(R9)

^afrom Eddingsaas et al., 2010; see also Pye et al., 2013

Figure 1.2 shows a tracer-specific model simulation and the corresponding offline filter measurements from the chamber experiment. Through the use of offline filter measurements collected during the chamber experiments, we are able to place estimates on the tracer formation reaction rate constants that have yet to be measured for bulk solutions. By varying the aqueous-phase reaction rate constants in the model that lack experimental constraints until the modeled SOA tracer mass loadings closely match those of the filter measurements we are able to constrain the kinetics of the aerosol-phase species that have been quantified through offline techniques but lack formation rate information. Additionally, those species that are not quantified through filter analyses, which we term “other SOA”, are also examined and a preliminary formation rate constant for the sum of those species can be obtained.

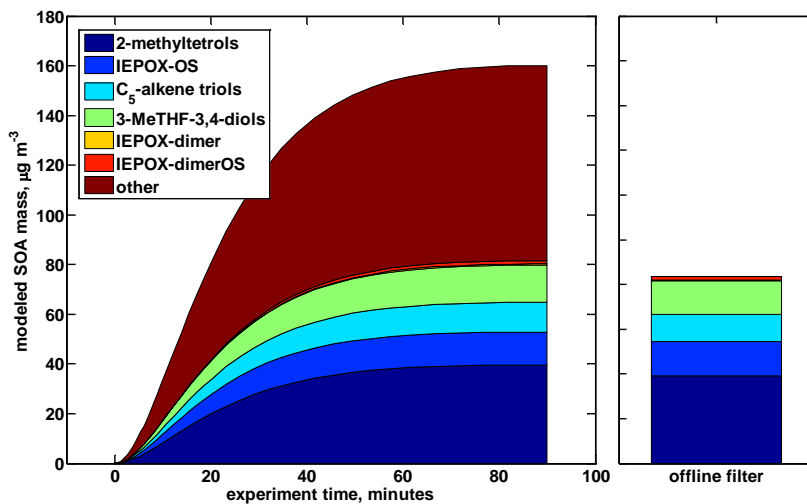


Figure 1.2 Model simulation of speciated SOA growth during a chamber experiment (left panel). Corresponding filter measurements during the chamber experiment (right panel). “other SOA” represents tracers not quantified by the filter analyses.

B. Project Deliverables

The critical information generated by this project has been disseminated in two published publications [1, 4] in the peer-reviewed literature, and a third manuscript that is currently in progress of being drafted [10]. The two published manuscripts are provided in chapters 2-3 and the draft manuscript in chapter 4. Each chapter provides detailed methodological and supporting information for the key findings described in this summary. Following are other key deliverables provided by this project.

- We have developed evaluation software that allows a user to evaluate chemical mechanisms against UNC’s experimental chamber runs. This includes incorporating data into the software from 40 experiments (16 characterization runs and 24 isoprene runs) that were conducted in the UNC Dual Gas-phase Chamber (Pittsboro, NC). These experimental runs include real-time concentration data of NO_x , VOCs and O_3 . Other data from these experiments include temperature, relative humidity, and light intensity. Using this evaluation software we have generated data evaluating two chemical mechanisms: the standard SAPRC07 [3] and the updated Xie mechanism [2].
- We have generated new experimental data that quantitatively measures the reactive uptake of two predominant isoprene-derived gas phase intermediates to PM. These new fundamental measurements provide for the first time the data needed to directly evaluate the aerosol-phase processes in an air quality model. These experiments include *trans*- β -IEPOX and MAE chamber runs where SOA

growth was measured with various relative humidity (RH) levels and seed aerosol types. These data were used to generate γ results for *trans*- β -IEPOX and MAE including the 1σ error for each measurement.

- A 0-Dimension time-dependent box model was developed and data generated that simulated the chamber experiments and estimated ϕ_{SOA} .
- Techniques for the synthesis of isoprene-derived epoxides and known SOA tracers were developed and quality assured.
- We have estimated reaction rate constants needed for the model to predict SOA tracer loadings.

C. References

1. Chen, Y.Z., et al., *Assessment of SAPRC07 with updated isoprene chemistry against outdoor chamber experiments*. Atmospheric Environment, 2015. **105**: p. 109-120.
2. Xie, Y., et al., *Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality*. Atmospheric Chemistry and Physics, 2013. **13**(16): p. 8439-8455.
3. Hutzell, W.T., et al., *Interpreting predictions from the SAPRC07 mechanism based on regional and continental simulations*. Atmospheric Environment, 2012. **46**: p. 417-429.
4. Riedel, T.P., et al., *Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates*. Environmental Science & Technology Letters, 2015. **2**(2): p. 38-42.
5. Gaston, C.J., et al., *Reactive Uptake of an Isoprene-Derived Epoxydiol to Submicron Aerosol Particles*. Environmental Science & Technology, 2014. **48**(19): p. 11178-11186.
6. Eddingsaas, N.C., D.G. VanderVelde, and P.O. Wennberg, *Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols*. The Journal of Physical Chemistry A, 2010. **114**(31): p. 8106-8113.
7. Wexler, A.S. and S.L. Clegg, *Atmospheric aerosol models for systems including the ions H^+ , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , Br^- , and H_2O* . Journal of Geophysical Research-Atmospheres, 2002. **107**(D14).
8. Pye, H.O., et al., *Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation*. Environ Sci Technol, 2013. **47**(19): p. 11056-64.
9. Eddingsaas, N.C., D.G. VanderVelde, and P.O. Wennberg, *Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols*. Journal of Physical Chemistry A, 2010. **114**(31): p. 8106-8113.
10. Riedel, T.P., et al., *Constraining Condensed-Phase Formation Kinetics of Secondary Organic Aerosol Components from Isoprene Epoxydiols*. Atmospheric Chemistry and Physics, 2015.