

AQRP Monthly Technical Report

PROJECT TITLE	Update and evaluation of model algorithms needed to predict particulate matter from isoprene	PROJECT #	14-003
PROJECT PARTICIPANTS	UNC-CH	DATE SUBMITTED	12/8/2014
REPORTING PERIOD	From: November 1, 2014 To: November 30, 2014	REPORT #	6

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Task

1. Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model

Preliminary Analysis

We are confident in the QA/QC testing of the algorithms for the predicted uptake of gaseous IEPOX onto an aerosol of variable acidity, temperature, and relative humidity.

Data Collected

We have generated simulations necessary for QA of data from the model including the predicted bulk SOA formation in our indoor chamber using reactive uptake coefficients we recently derived in flow tube studies (Gaston et al., 2014, ES&T).

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

N/A

Goals and Anticipated Issues for the Succeeding Reporting Period

N/A

Detailed Analysis of the Progress of the Task Order to Date

N/A

Task

2. Synthesis of Isoprene-derived Epoxides and Known SOA Tracers

Preliminary Analysis

We have completed all syntheses needed for the project including dealing with the impurity of the organosulfate standards.

Data Collected

QA/QC data verifying synthesis.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Goals and Anticipated Issues for the Succeeding Reporting Period

Detailed Analysis of the Progress of the Task Order to Date

We are confident that this task will be completed in time.

Task

3. Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides

Preliminary Analysis

Our experimental plan is listed in Table 1. We continued to complete more experiments.

Table 1. Indoor experiments to be conducted at UNC.

Expt. #	[Epoxide]		Initial Seed		RH	
	Epoxide	(ppb)	Seed Aerosol Type	Aerosol ($\mu\text{g}/\text{m}^3$)	(%)	T ($^{\circ}\text{C}$)
1	IEPOX	300	$(\text{NH}_4)_2\text{SO}_4$	~20-30	~50-60	~20-25
2		300	$(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$	~20-30	~50-60	~20-25
3	MAE	300	$(\text{NH}_4)_2\text{SO}_4$	~20-30	~50-60	~20-25
4		300	$(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$	~20-30	~50-60	~20-25
5	none		$(\text{NH}_4)_2\text{SO}_4$	~20-30	~50-60	~20-25
6	none		$(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$	~20-30	~50-60	~20-25
7	IEPOX	300	none	none	~50-60	~20-25
8	MAE	300	none	none	~50-60	~20-25

0.6 M $(\text{NH}_4)_2\text{SO}_4 + 0.6 \text{ M H}_2\text{SO}_4$

Data Collected

We have collected data for completed experiments.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

N/A

Goals and Anticipated Issues for the Succeeding Reporting Period

We expect the next 2-3 months will yield enough experimental data to evaluate with the model. This will mean completing all experiments outlined in Table 1.

Detailed Analysis of the Progress of the Task Order to Date

We are currently on schedule to complete this task in time allocated.

Task

4. Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers

Preliminary Analysis

We have completed our first modeling analysis. A combination of flow reactor studies and smog chamber modeling were used to constrain two uncertain parameters central to secondary organic aerosol (SOA) formation from isoprene-derived epoxides: (1) the rate of epoxide heterogeneous reaction with the particle phase and (2) the molar fraction of uptaken epoxides that go on to contribute to the SOA burden – the SOA yield (α_{SOA}). Flow reactor measurements of the *trans*- β -isoprene epoxydiols (IEPOX) and methacrylic acid epoxide (MAE) aerosol reaction probability (γ) were performed on 1 – 2 component atomized aerosols with similar compositions as smog chamber SOA studies. Observed γ ranges for IEPOX and MAE were $6.5 \times 10^{-4} - 0.021$ and $4.9 \times 10^{-4} - 5.2 \times 10^{-4}$, respectively. A range in α_{SOA} for varying aerosol compositions is then estimated through the use of a time-dependent 0-D chemical box model initialized with chamber conditions and the γ measurements. The resulting α_{SOA} for the two epoxides were estimated between 0.03 and 0.22.

Data Collected

Flow Reactor Measurements of γ . Table 1 summarizes the γ results for *trans*- β -IEPOX and MAE including the 1σ error for each measurement. Importantly, the aerosol and RH conditions chosen for the flow reactor was representative of conditions that produced notable SOA growth in the chamber experiments. Table 1 also includes estimates of aerosol acidity obtained from the Extended AIM Aerosol Thermodynamics Model III (E-AIM – <http://www.aim.env.uea.ac.uk/aim/aim.php>) using the atomizer solution composition and RH as inputs.²² As there is no input for magnesium ion concentrations in E-AIM, we instead used 2 sodium ions for the calculations involving MgSO_4 . The largest reaction probability for *trans*- β -IEPOX ($\gamma = 0.021$) was observed on $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ aerosol under dry conditions. The γ values are similar to previous measurements for *trans*- β -IEPOX showing a general increase in γ with higher aerosol acidity, consistent with particle phase acid-catalyzed epoxide ring opening reactions. Moreover, for the same aerosol type at higher RH, decreases in γ are likely attributable to dilution from additional aerosol water. To our knowledge these are the first reaction probability measurements of MAE. γ 's for MAE were significantly lower than those for *trans*- β -IEPOX and likely responsible for the generally smaller observed SOA production. Only at acidities closer to neutral ($[\text{H}^+] \sim 8 \times 10^{-5}$) are the IEPOX and MAE γ 's of similar magnitude with values on the order of 5×10^{-4} .

Chamber Box Modeling of α_{SOA} . As with the atomizer solutions, the RH used in the flow reactor studies were chosen to match the aforementioned chamber studies. In this way the γ 's measured in the flow reactor experiments capture the appropriate γ that one would expect during the chamber experiments thus providing a reliable constraint for epoxide uptake rates in the chamber. However, in order to properly assess the overall SOA production, the α_{SOA} is needed in addition to γ . To this end a 0-D time-dependent box model was used to simulate the chamber experiments and estimate α_{SOA} . The model was initialized with γ 's from the flow reactor measurements, the amount of epoxide injected into the chamber, the chamber-measured aerosol surface area and mass concentrations, the estimated chamber wall-loss rate from epoxide injections in the absence of seed particles, and the user-chosen α_{SOA} . Chemical rate equations for gas and aerosol-phase epoxide concentrations were integrated over the duration of the chamber experiment to determine time-dependent concentrations. The only losses of gas-phase epoxide were to particle surface area and to the chamber walls, and the only source of aqueous-phase

epoxide was the reaction of gas-phase epoxide on the particle surface area. The aqueous-phase epoxide formation rate was scaled by α_{SOA} in order to match the chamber-observed aerosol mass loadings. Aerosol surface area was held constant over the course of a model run despite that the SOA formation does contribute to the surface area. This is less of an issue for MAE given the modest SOA growth compared to *trans*- β -IEPOX. For the *trans*- β -IEPOX experiments the additional SOA resulted in at most a 40% increase in surface area. It is not clear how this additional surface area would affect the modeled SOA growth. Based on previous studies, the presence of aerosol phase semi-oxidized organics in the form of polyethylene glycol tended to inhibit *trans*- β -IEPOX uptake, thereby slowing the SOA growth. Indeed we observed that the modeled SOA growth rate tended to be faster than that observed in the chamber experiments. However, this effect could also be in part a result of the instantaneous mixing assumed by the box model.

As shown in Figure 2, α_{SOA} was adjusted in the model to bracket the observed chamber SOA mass growth and obtain an upper and lower estimate of α_{SOA} . These ranges are reported in Table 1. α_{SOA} for *trans*- β -IEPOX and MAE varied for the different aerosol compositions from 0.03 – 0.16 and 0.05 – 0.22, respectively, with the slightly larger α_{SOA} observations for the ammonium sulfate seed types compared to magnesium sulfate. In general, we would expect aerosol conditions that influence γ – high aerosol acidity, the concentration of general acids like bisulfate, and the concentrations of nucleophiles – to influence α_{SOA} similarly. While γ was largest for the acidified aerosols, α_{SOA} seems to be largely independent of acidity with the largest α_{SOA} for *trans*- β -IEPOX ($\alpha_{\text{SOA}} = 0.16$) observed on the pure ammonium sulfate aerosol. Therefore it appears that even in the absence of a substantial concentration of acid catalyst the same ultimate mass yield can be achieved provided the timescale is sufficiently long. Model outputs for IEPOX showed good agreement with the chamber observations especially considering that the characteristic leveling off of the SOA mass growth was well represented in the model output (see Figure 2a). This was not the case for the MAE experiments as seen in Figure 2b where the model outputs fail to capture any leveling off in aerosol mass. As a result α_{SOA} estimates for MAE may be less robust compared to *trans*- β -IEPOX. An underestimation of the MAE γ – and therefore an overestimation of the α_{SOA} – could result in such differences. That said, MAE γ measurements were reproducible and the modest SOA growth coupled with the low-time resolution of the mass concentration data make modeling the MAE experiments inherently more difficult.

It should be stated that the molecular weight of the SOA is assumed to be the same as *trans*- β -IEPOX or MAE, depending on which epoxide was investigated, while the majority of SOA tracers have a molecular weight larger than the parent epoxide. As a result, the α_{SOA} reported here are likely biased high. As an upper limit example, IEPOX-derived organosulfate (216 g/mole) has been shown to be a primary component of isoprene-derived SOA with a molecular weight almost twice that of IEPOX (118 g/mole). If we assume all of the SOA mass is made up of these organosulfates our reported α_{SOA} would be biased high by about 50%.

As we state above, it is not clear how γ and the α_{SOA} are affected when a significant fraction of the aerosol surface area is represented by epoxide-derived SOA. This warrants further investigation as it could be quite relevant in regions like the southeastern United States during summer where isoprene SOA can account for a substantial portion of the PM_{2.5} mass and therefore surface area. The results presented here which constrain all reactions that contribute to IEPOX- and MAE-derived SOA could be beneficial in regional and/or global models to help

constrain predictions in total IEPOX- and MAE-derived SOA, especially since current models only constrain the model with a few known aqueous phase reaction rates.

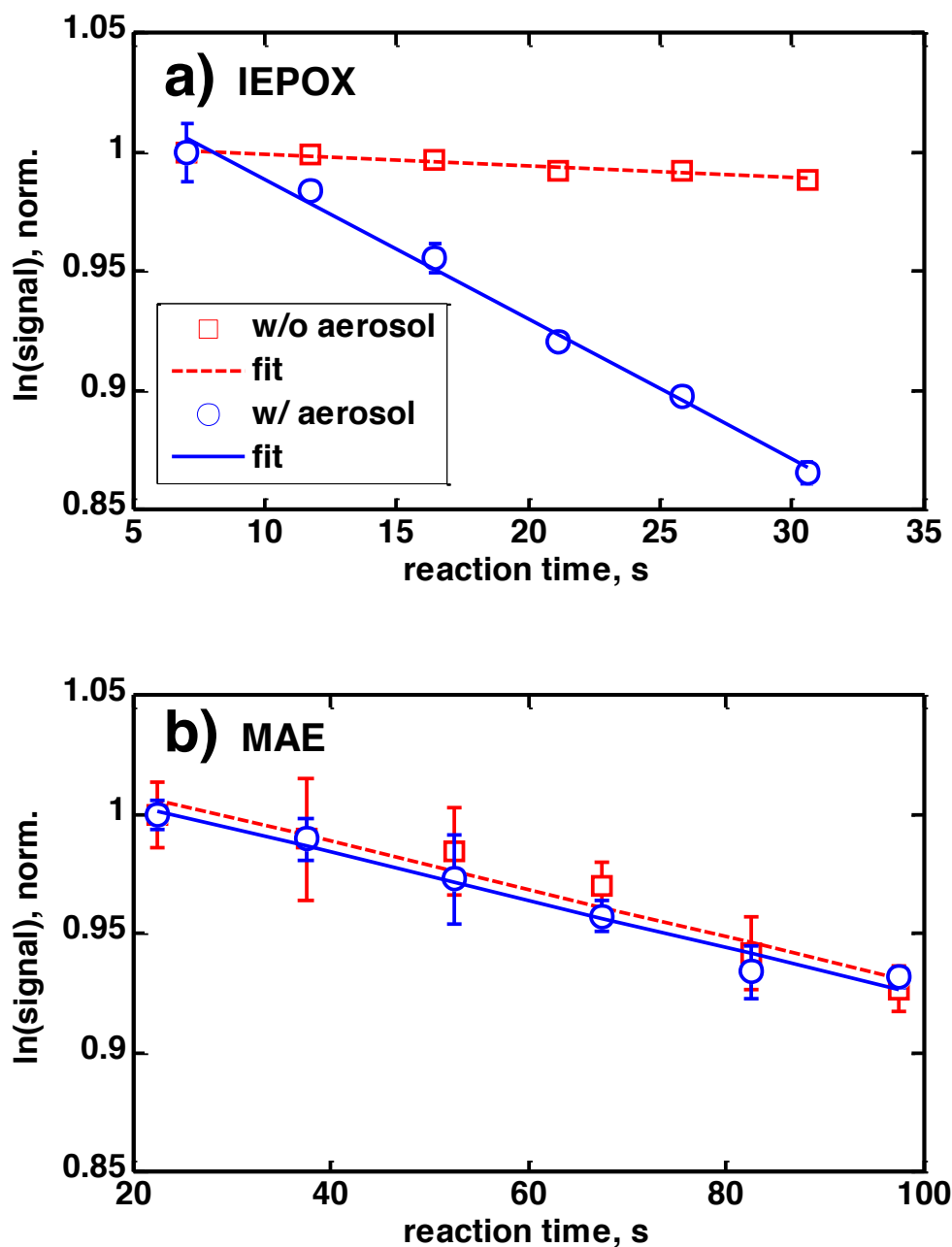


Figure 1. The average of the log of the epoxide signal versus reaction time and associated linear fit without aerosols (red squares, red dashed line is the fit) and with aerosols present in the flow reactor (blue circles, blue solid line is the fit) for (a) *trans*- β -IEPOX and (b) MAE on $(\text{NH}_4)_2\text{SO}_4$ + H_2SO_4 aerosol. Error bars represent the 2x the standard deviation of the averages. Values have been normalized to 1 for ease of comparison.

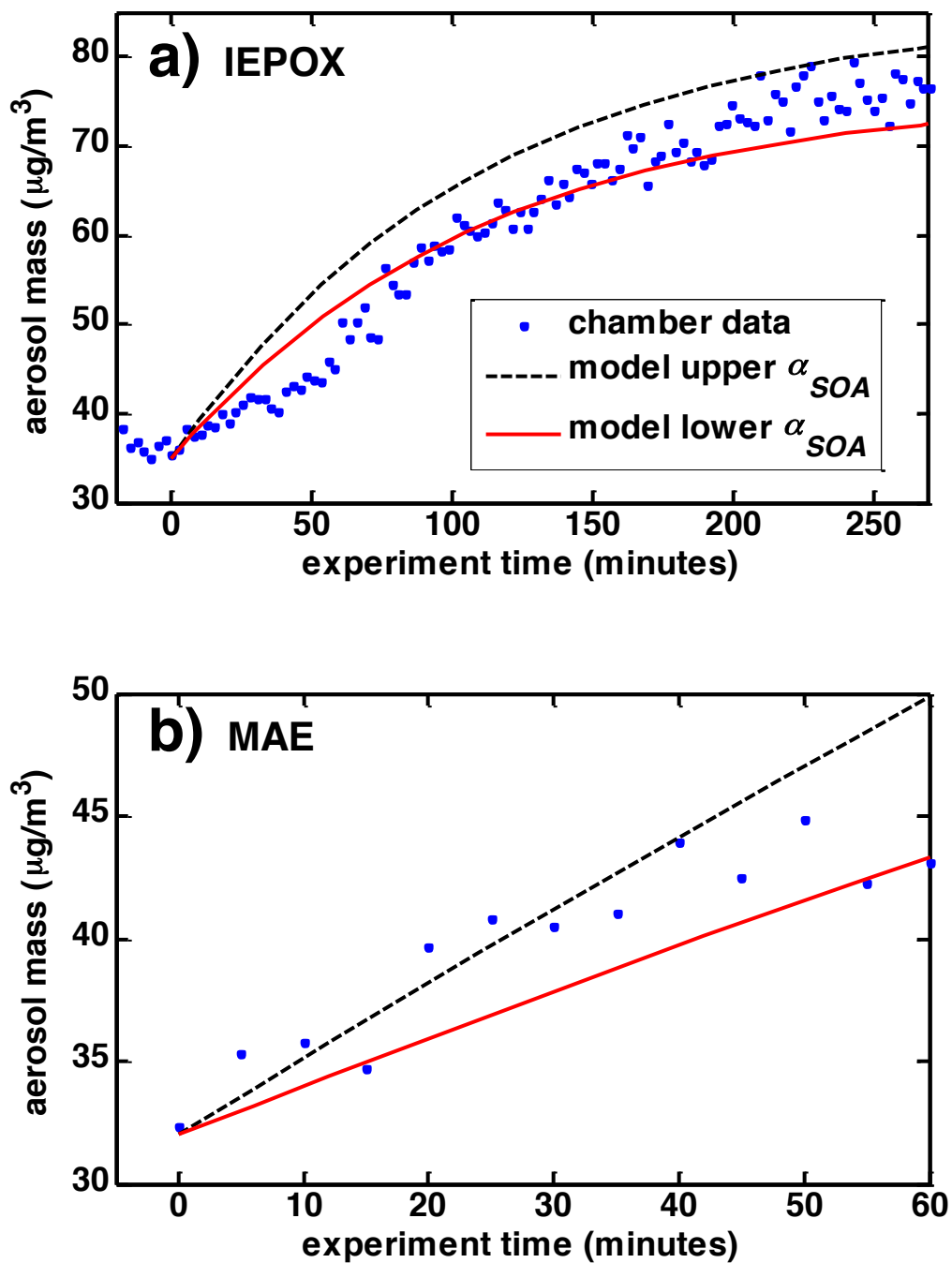


Figure 2. Chamber measured (blue dots) and modeled (black dashed line, red solid line) SOA mass loadings for (a) *trans*- β -IEPOX with $(\text{NH}_4)_2\text{SO}_4$ seed and (b) MAE with $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ seed. The black dashed lines represent the model upper estimate of molar SOA yield, and the red solid lines represent the model lower estimate.

Table 1. Summary of Experiments and Results.

epoxide	aerosol	RH	aerosol [H ⁺] (M) ^a	$\gamma \pm 1\sigma$	modeled α_{SOA} range
IEPOX	(NH ₄) ₂ SO ₄	0.50	7.74E-05	6.5e-4 ± 6.4e-4	0.13 - 0.16
IEPOX	MgSO ₄ + H ₂ SO ₄	0.08	0.04	0.011 ± 0.003	0.04 - 0.06
IEPOX	MgSO ₄ + H ₂ SO ₄	0.53	0.73	0.0094 ± 0.003	0.03 - 0.05
IEPOX	(NH ₄) ₂ SO ₄ + H ₂ SO ₄	0.05	2.78	0.021 ± 0.001	0.09 - 0.11
IEPOX	(NH ₄) ₂ SO ₄ + H ₂ SO ₄	0.59	2.01	0.019 ± 0.002	0.05 - 0.07
MAE	MgSO ₄ + H ₂ SO ₄	0.03	0.73	4.9e-4 ± 1e-4	0.05 - 0.11
MAE	(NH ₄) ₂ SO ₄ + H ₂ SO ₄	0.03	2.78	5.2e-4 ± 1.1e-4	0.14 - 0.22

^aEstimated from E-AIM model calculation of moles H⁺ and total volume of aqueous phase. E-AIM RH input must be ≥0.1, so the same [H⁺] is estimated for like aerosol compositions despite differences in experimental RH.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

N/A

Goals and Anticipated Issues for the Succeeding Reporting Period

We plan on submitting the current results as a manuscript for the peer reviewed literature. We will continue to simulate experiments as they become available from Task 3.

Detailed Analysis of the Progress of the Task Order to Date

We are currently on schedule to complete this task in time allocated.

Submitted to AQRP by:
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Principal Investigator: