

Constraining condensed-phase formation kinetics of IEPOX-SOA

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Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols

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et al., 2015). The rate of IEPOX injection into the chamber is simulated in the model by an exponential decay of IEPOX in the injection manifold. The decay constant (λ) was varied between 1×10^{-3} – $2 \times 10^{-3} \text{ s}^{-1}$ as a fitting parameter to better match the timescale of observed SOA growth. However, over the 2 h duration of the experiment, the value of the decay constant had a negligible effect on the final model-predicted SOA growth.

The complete set of differential equations used to track each individual species in the model is provided in Eqs. (2)–(12).

$$\frac{d[\text{IEPOX}_{(g)}]}{dt} = \lambda[\text{IEPOX}_{(\text{manifold})}] - k_{\text{het}}[\text{IEPOX}_{(g)}] - k_{\text{wall}}[\text{IEPOX}_{(g)}] \quad (2)$$

$$\begin{aligned} \frac{d[\text{IEPOX}_{(aq)}]}{dt} = & k_{\text{het}}[\text{IEPOX}_{(g)}] - k_{R1}[\text{IEPOX}_{(aq)}][\text{H}_2\text{O}][\text{H}^+] \\ & - k_{R2}[\text{IEPOX}_{(aq)}] \left[\text{SO}_4^{2-} \right] [\text{H}^+] - k_{R3}[\text{IEPOX}_{(aq)}][\text{H}^+] \\ & - k_{R4}[\text{IEPOX}_{(aq)}][\text{H}^+] - k_{R5}[\text{IEPOX}_{(aq)}][\text{H}^+][\text{tetrol}] \\ & - k_{R6}[\text{IEPOX}_{(aq)}][\text{H}^+][\text{IEPOX-OS}] - k_{R7}[\text{IEPOX}_{(aq)}][\text{H}^+][\text{IEPOX-OS}] \\ & - k_{R8}[\text{IEPOX}_{(aq)}] - k_{\text{wall-aerosol}}[\text{IEPOX}_{(aq)}] \end{aligned} \quad (3)$$

$$\frac{d[\text{tetrol}]}{dt} = k_{R1}[\text{IEPOX}_{(aq)}][\text{H}_2\text{O}][\text{H}^+] - k_{\text{wall-aerosol}}[\text{tetrol}] \quad (4)$$

$$\frac{d[\text{IEPOX-OS}]}{dt} = k_{R2}[\text{IEPOX}_{(aq)}] \left[\text{SO}_4^{2-} \right] [\text{H}^+] - k_{\text{wall-aerosol}}[\text{IEPOX-OS}] \quad (5)$$

$$\frac{d[\text{triol}]}{dt} = k_{R3}[\text{IEPOX}_{(aq)}][\text{H}^+] - k_{\text{wall-aerosol}}[\text{triol}] \quad (6)$$

$$\frac{d[\text{diolTHF}]}{dt} = k_{R4}[\text{IEPOX}_{(aq)}][\text{H}^+] - k_{\text{wall-aerosol}}[\text{diolTHF}] \quad (7)$$

$$\frac{d[\text{dimer}]}{dt} = k_{R5}[\text{IEPOX}_{(aq)}][\text{H}^+][\text{tetrol}] - k_{\text{wall-aerosol}}[\text{dimer}] \quad (8)$$

$$\frac{d[\text{dimerOS}]}{dt} = k_{R6}[\text{IEPOX}_{(\text{aq})}][\text{H}^+][\text{IEPOX-OS}] - k_{\text{wall-aerosol}}[\text{dimerOS}] \quad (9)$$

$$\frac{d[\text{other}]}{dt} = k_{R7}[\text{IEPOX}_{(\text{aq})}][\text{H}^+][\text{IEPOX-OS}] - k_{\text{wall-aerosol}}[\text{other}] \quad (10)$$

$$\frac{d[\text{HSO}_4^-]}{dt} = -k_{R2}[\text{IEPOX}_{(\text{aq})}][\text{H}^+][\text{HSO}_4^-] R_{\text{SO}_4} - k_{\text{wall-aerosol}}[\text{HSO}_4^-] \quad (11)$$

$$\begin{aligned} \frac{d[\text{SO}_4^{2-}]}{dt} = & k_{R2}[\text{IEPOX}_{(\text{aq})}][\text{H}^+][\text{HSO}_4^-] R_{\text{SO}_4} \\ & - k_{R2}[\text{IEPOX}_{(\text{aq})}][\text{H}^+][\text{SO}_4^{2-}] - k_{\text{wall-aerosol}}[\text{SO}_4^{2-}] \end{aligned} \quad (12)$$

Rate constants (k) for Reactions (R1)–(R8) were systemically varied until model output closely matched the offline tracer measurements. Initial values were assigned to k_{R1} – k_{R8} , and the model run in a continuous loop, varying each rate constant to minimize the sum of the squares of the differences between the filter measurements and model output, under the constraint that all $k > 0$. Implicitly, this approach assumes that tracer quantitations are robust, a correct representation of IEPOX-derived SOA speciation and mass loading, and that the filter collection and extraction efficiency are 100 %.

3 Results and discussion

3.1 Model output and comparison to chamber data

Five chamber experiments were performed with the low RH $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ seed aerosol system. Table 1 lists initial chamber conditions, including seed aerosol surface area and mass loading and the mass of IEPOX placed in the injection manifold. Figure 1 shows aerosol mass data and the corresponding model simulation for one experiment (Exp. No. 1). The initial seed aerosol mass loading is $113 \mu\text{g m}^{-3}$, and IEPOX injection is initiated at experiment time (t) = 0. SOA mass growth is most rapid for 30 min

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the relationship between 2-methyl-2,3-epoxybutane and 2,3-epoxybutane reaction rate constants to estimate those for 2-methyl-2,3-epoxybutane-1,4-diol (β -IEPOX). For 2-methyltetrol formation, Pye et al. (2013) used the value estimated by Eddingsaas et al. (2010) and assumed a water concentration of 55 M in order to derive a third-order rate constant with an explicit water dependence. The resulting rate constants are $9 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ for formation of 2-methyltetrol (Reaction R1) and $2 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ for formation of IEPOX-OS (Reaction R2). A similar treatment can be applied to the pseudo second-order hydrolysis rate constant (2-methyltetrol formation) for a mixture of *cis*- and *trans*- β -IEPOX from Cole-Filipiak et al. (2010) to obtain a rate constant of $6.5 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$. Purely computational estimates of 5.3×10^{-2} and $5.2 \times 10^{-1} \text{ M}^{-2} \text{ s}^{-1}$ for 2-methyltetrol and IEPOX-OS, respectively, are also available for comparison (Piletic et al., 2013). Apart from the computational study, these rate constants are of the same order as those predicted by the model, $3.4 \pm 3.2 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ for 2-methyltetrols and $4.8 \pm 3.4 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ for IEPOX-OS, indicating that the model gives a reasonable representation of the kinetics of the multiphase process in light of the low RH, non-ideal conditions in the highly concentrated chamber aerosols.

Epoxide ring-opening reactions by general acids (i.e., bisulfate) have not been explicitly included in the model. The contribution is expected to be negligible as the branching ratio between the bisulfate and H^+ -catalyzed reaction channels is likely to heavily favor the H^+ channel. For example, in Exp. No. 1, $\sim 98\%$ of the epoxide ring-opening is predicted to proceed through the H^+ -catalyzed channel compared to that of bisulfate.

Aerosol surface area was held constant at initial seed aerosol levels over the course of a model run, and thus k_{het} is insensitive to additional surface area resulting from IEPOX-derived SOA (Riedel et al., 2015). However, the presence of organics such as polyethylene glycol have been shown to lower γ and therefore k_{het} (Gaston et al., 2014), and it is unclear whether the presence of IEPOX-derived SOA components would have a similar effect. A consequence of the constant surface area is that the model does not account for any possible slowing of the uptake rate resulting from increased aerosol

organic content. Measurements of γ on mixed and pure IEPOX-SOA would be required to resolve this question.

Given the estimates of the tracer formation rate constants, the calculated k_{het} , and the model output, φ_{SOA} can be estimated as the ratio of the sum of the tracer production rates over the IEPOX_(g) heterogeneous loss rate (Riedel et al., 2015). Averaged over the five experiments, $\varphi_{\text{SOA}} = 0.078 \pm 0.025$ (1σ), with the largest φ_{SOA} from the 5 mg IEPOX injections and the smallest φ_{SOA} from the 30 mg injections. The drop in φ_{SOA} with increased IEPOX injection mass is a function of the increased amount of “other SOA” measured in these experiments. The higher molecular weight assumed for the oligomeric products relative to the molecular weight of the tracers requires less IEPOX to be reacted in order to match the total SOA mass loadings, thus driving down φ_{SOA} . $\varphi_{\text{SOA}} = 0.078$ is similar to that predicted from an independent modeling approach which estimated the φ_{SOA} for this aerosol system at 0.1–0.12 (Riedel et al., 2015). These results indicate that the molar yield of SOA from IEPOX heterogeneous reactions is likely to be significantly < 1 for the majority of atmospheric conditions where aerosols are likely to contain more water and be less acidic than in this study.

3.3 Atmospheric implications

Figure 5 shows the model output after 6 h processing time, using as inputs the rate constants from Table 3 and initial atmospheric conditions which might be representative of a daytime summer urban/rural mixed air mass: 50 % RH, ~ 500 pptv gas-phase IEPOX, and $250 \mu\text{m}^2 \text{cm}^{-3}$ of ammonium bisulfate aerosol surface area, corresponding to an aerosol mass loading of $\sim 10 \mu\text{g m}^{-3}$. The model predicts $0.37 \mu\text{g m}^{-3}$ of total SOA with the bulk (77 %) being 2-methyltetrols, and minor amounts of IEPOX-OS (14 %), C₅-alkene triols (7 %), and 3-MeTHF-3,4-diols (2 %). The remaining tracers – IEPOX-dimer, IEPOX-dimerOS, and “other SOA” – are predicted to form in small amounts ($< 0.6 \text{ ng m}^{-3}$). Additionally, this simulation predicted no appreciable titration of total aqueous inorganic sulfate, suggesting that titration is unlikely to occur in atmo-

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would likely represent an upper limit to the formation of such SOA species under the assumption that more than one tracer could potentially be formed from the degradation of these products. However, in the absence of evidence to the contrary, there is general agreement that tracers constitute a large fraction of IEPOX-SOA, and additional investigations are required prior to the proposal that certain SOA tracers represent decomposition products.

In summary, this study is a first approach at placing kinetic constraints on the formation of species that have been quantified in laboratory and field measurements but lack directly measured experimental rate constraints. While bulk solution rate constant estimates are desirable, such measurements pose a challenge when authentic standards are unavailable or when surrogates do not adequately represent the true compounds. Additionally, it is unclear that bulk-phase kinetics can approximate aerosol-phase reactions where non-ideal conditions likely play a role. The flexible approach described here may readily be extended to other SOA production systems known to have atmospheric importance.

This study approximates tracer branching ratios for the currently proposed SOA tracers resulting from IEPOX uptake, a necessary step to predict isoprene-derived SOA production in regional models that guide policy decisions. Additional laboratory studies to identify SOA products and elucidate formation mechanisms are important to ensure that both chamber and field measurements accurately reflect atmospheric processes. Modeling developed on the basis of such experimental systems can then be extended to large-scale models.

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**Constraining
condensed-phase
formation kinetics of
IEPOX-SOA**

T. P. Riedel et al.

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Table 1. Summary of conditions for each chamber SOA experiment.

| Exp. No. | IEPOX injected (mg) | Seed surface area ($\mu\text{m}^2 \text{cm}^{-3}$) | Seed mass ($\mu\text{g m}^{-3}$) |
|----------|---------------------|--|------------------------------------|
| 1 | 30 | 1480 | 113 |
| 2 | 30 | 1660 | 125 |
| 3 | 15 | 1200 | 76 |
| 4 | 5 | 800 | 59 |
| 5 | 5 | 800 | 57 |

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Table 3. Model-predicted formation reaction rate constants for IEPOX-SOA tracers.

| SOA tracer formed | k | Reaction |
|-------------------------------|--|----------|
| 2-methyltetrols | $3.4 \pm 3.2 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ | (R1) |
| IEPOX-OS | $4.8 \pm 3.4 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ | (R2) |
| C ₅ -alkene triols | $8.8 \pm 3.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ | (R3) |
| 3-MeTHF-3,4-diols | $2.6 \pm 3.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ | (R4) |
| IEPOX-dimer | $1.3 \pm 0.7 \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$ | (R5) |
| IEPOX-dimerOS | $6.8 \pm 4.6 \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$ | (R6) |
| other SOA | $5.7 \pm 6.9 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ | (R7) |

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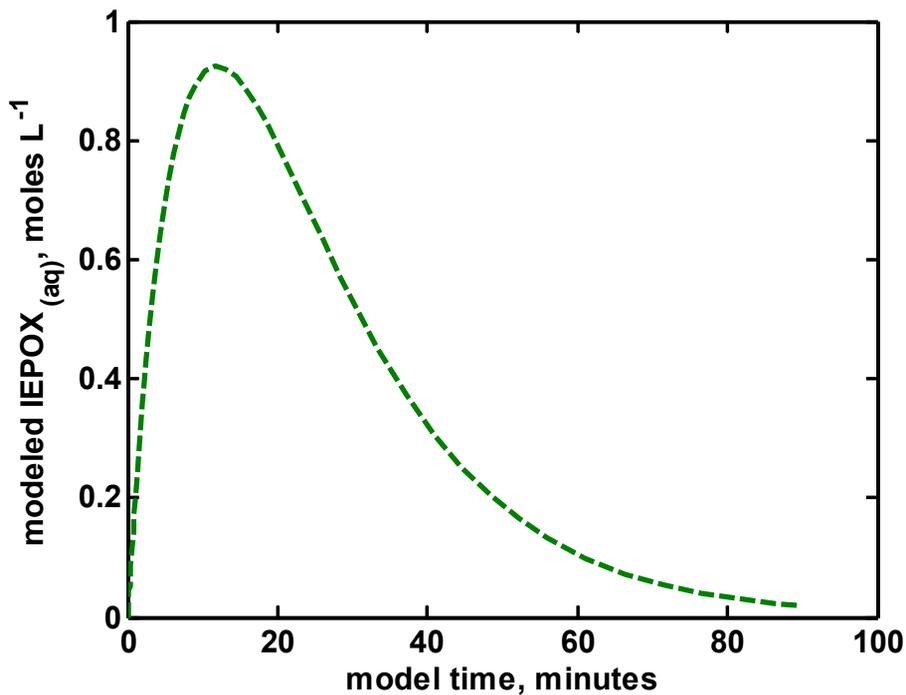


Figure 2. Model output of aqueous-phase IEPOX concentrations during Exp. No. 1 simulation.

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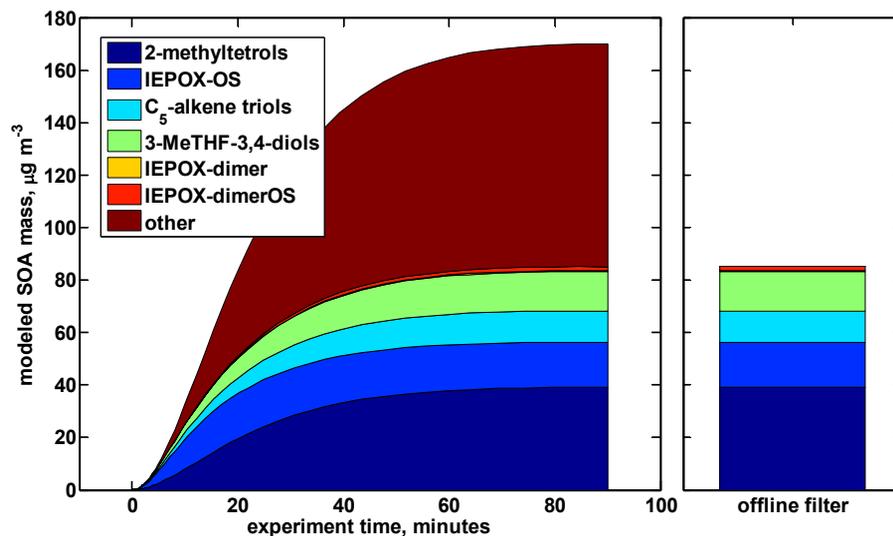


Figure 3. Model output of IEPOX-SOA tracers (left panel) and the associated filter-based tracer measurements (right panel) for Exp. No. 1. The “other SOA” is calculated as the difference between the chamber-measured aerosol mass loadings and the sum of the filter-based tracer loadings.

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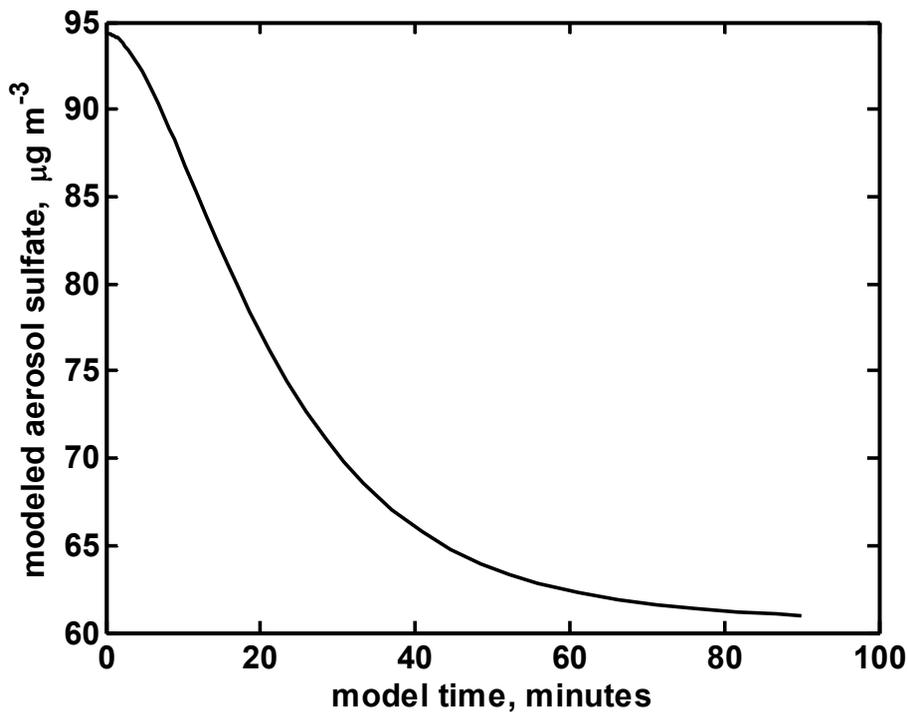


Figure 4. Model output of predicted titration of total inorganic aerosol sulfate ($[\text{SO}_4^{2-}] + [\text{HSO}_4^-]$) due to sulfated tracer formation during Exp. No. 1 simulation.

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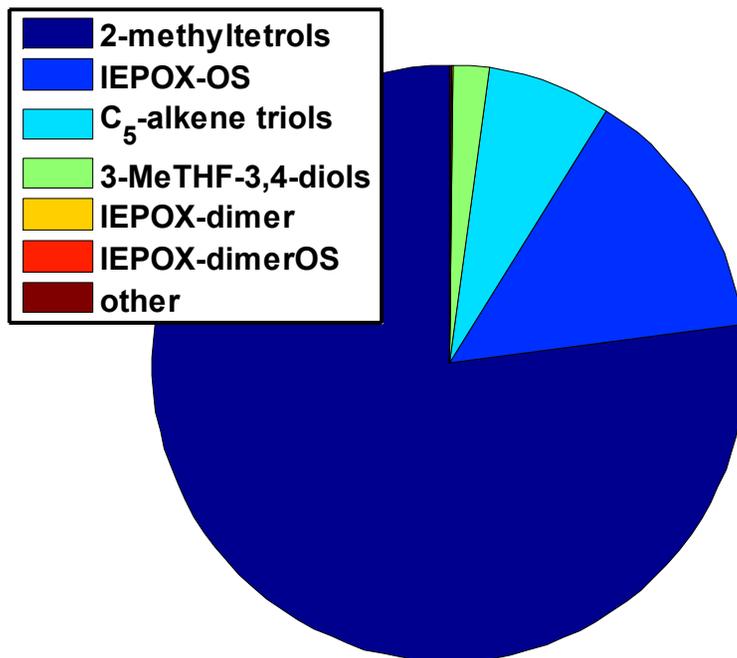
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Total predicted SOA mass = 0.37 $\mu\text{g m}^{-3}$

Figure 5. Model-predicted IEPOX-SOA tracer distribution and loadings for atmospherically relevant initial conditions.

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