



Model–measurement comparison of functional group abundance in α -pinene and 1,3,5-trimethylbenzene secondary organic aerosol formation

Giulia Ruggeri¹, Fabian A. Bernhard¹, Barron H. Henderson², and Satoshi Takahama¹

¹ENAC/IIIE Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland

²Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL, USA

Correspondence to: Satoshi Takahama (satoshi.takahama@epfl.ch)

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Abstract. Secondary organic aerosol (SOA) formed by α -pinene and 1,3,5-trimethylbenzene photooxidation under different NO_x regimes is simulated using the Master Chemical Mechanism v3.2 (MCM) coupled with an absorptive gas–particle partitioning module. Vapor pressures for individual compounds are estimated with the SIMPOL.1 group contribution model for determining apportionment of reaction products to each phase. We apply chemoinformatic tools to harvest functional group (FG) composition from the simulations and estimate their contributions to the overall oxygen to carbon ratio. Furthermore, we compare FG abundances in simulated SOA to measurements of FGs reported in previous chamber studies using Fourier transform infrared spectroscopy. These simulations qualitatively capture the dynamics of FG composition of SOA formed from both α -pinene and 1,3,5-trimethylbenzene in low- NO_x conditions, especially in the first hours after start of photooxidation. Higher discrepancies are found after several hours of simulation; the nature of these discrepancies indicates sources of uncertainty or types of reactions in the condensed or gas phase missing from current model implementation. Higher discrepancies are found in the case of α -pinene photooxidation under different NO_x concentration regimes, which are reasoned through the domination by a few polyfunctional compounds that disproportionately impact the simulated FG abundance in the aerosol phase. This manuscript illustrates the usefulness of FG analysis to complement existing methods for model–measurement evaluation.

1 Introduction

Atmospheric aerosols are complex mixtures that can contain a multitude of chemical species (Seinfeld and Pandis, 2006). While the inorganic fraction comprises a relatively small number of compounds, the organic fraction (or organic aerosol, OA) includes thousands of compounds with diverse molecular structures (Hamilton et al., 2004). These compounds take part in multitude of gas phase, aerosol phase, and heterogeneous transformation processes (e.g., Kroll and Seinfeld, 2008; Hallquist et al., 2009; Ziemann and Atkinson, 2012) that must be modeled with sufficient fidelity to predict atmospheric concentrations and impacts from various emission scenarios.

A mechanism central to these processes is the formation of semivolatile organic compounds (SVOCs) through gas-phase oxidation of volatile organic compound (VOC) precursors and their reaction products. α -pinene (APIN) and 1,3,5-trimethylbenzene (TMB) are examples of biogenic and anthropogenic VOC precursors, respectively, which have been studied for their chemical reaction mechanisms and aerosol yields in environmentally controlled chamber experiments and numerical simulation. APIN is a monoterpene compound primarily emitted from coniferous vegetation (Fuentes et al., 2000; Tanaka et al., 2012) with high emission rate, reactivity, and secondary organic aerosol (SOA) generation potential (e.g., Fehsenfeld et al., 1992; Lamb et al., 1993; Chameides et al., 1988; Jenkin, 2004; Tolocka et al., 2004; Sindelarova et al., 2014). TMB is an aromatic compound emitted from vehicular emissions and a major contributor to urban organic aerosol (e.g., Kalberer et al., 2004); its degradation mechanism has also been subject of collective eval-

uation (Metzger et al., 2008; Wyche et al., 2009; Rickard et al., 2010; Im et al., 2014). Gas-phase oxidation reactions are modeled with chemically explicit or semi-explicit treatment, or alternatively using a basis set approach based on simplified molecular or property descriptors; SOA formation is commonly modeled by coupling these reactions with partitioning of oxidation products to an absorptive organic phase (e.g., Jenkin et al., 1997; Pun et al., 2002; Griffin et al., 2003; Aumont et al., 2005; Capouet et al., 2008; McFiggans et al., 2010; Barley et al., 2011; Chen et al., 2011; Murphy et al., 2011; Aumont et al., 2012; Jathar et al., 2015; McVay et al., 2016). SVOCs produced by such reactions can in reality partition among multiple phases (vapor, organic liquid, aqueous, solid), and participate in additional functionalization, accretion, or fragmentation reactions in one of many phases (Kroll et al., 2011; Cappa and Wilson, 2012; Im et al., 2014; Zhang and Seinfeld, 2013; Zhang et al., 2015). These processes are represented in models with varying degrees of detail; simplifying or wholly omitting various mechanisms out of concerns for computational feasibility or lack of sufficient knowledge. For instance, in a work we follow closely in this manuscript, Chen et al. (2011) used a fully explicit gas-phase reaction mechanism with absorptive organic partitioning and evaluated the potential importance of missing heterogeneous and condensed-phase mechanisms based on discrepancy of model simulation and experiments.

Our capability to simulate SOA formation is often evaluated against aerosol mass yield, O:C, carbon oxidation state, mean carbon number, volatility, and specific species or compound classes when available (e.g., Robinson et al., 2007; Kroll et al., 2011; Donahue et al., 2012; Nozière et al., 2015). These properties can be measured using various forms of mass spectrometry (e.g., Jayne et al., 2000; Jimenez et al., 2009; Nizkorodov et al., 2011) or through monitoring changes in size distribution in combination with isothermal dilution or thermal heating (e.g., Grieshop et al., 2009; Cappa, 2010; Epstein and Donahue, 2010; Donahue et al., 2012). Functional group (FG) composition is a complementary representation of organic molecules and complex organic mixtures that offers a balance between parsimony and chemical fidelity for measurement and interpretation.

FGs represent structural units of molecules that play a central role in chemical transformations and provide insight into evolution of complex organic mixtures without monitoring all species explicitly (Holes et al., 1997; Sax et al., 2005; Presto et al., 2005; Lee and Chan, 2007; Chhabra et al., 2011; Zeng et al., 2013). FG abundances have also been associated with volatility (e.g., Pankow and Asher, 2008), hygroscopicity (e.g., Hemming and Seinfeld, 2001; Suda et al., 2014), and magnitude of nonideal interactions in the condensed phase (e.g., Ming and Russell, 2002; Griffin et al., 2003; Zuend et al., 2011). However, two impediments have been the likely cause of slow adoption of this representation. Building quantitative calibration models of FG abundance have posed analytical challenges, but

rapid progress has been made over the past decade with Fourier transform infrared spectroscopy (FTIR) (e.g., Sax et al., 2005; Reff et al., 2007; Coury and Dillner, 2008; Day et al., 2010; Takahama et al., 2013; Ruthenburg et al., 2014; Takahama and Dillner, 2015), nuclear magnetic resonance (Decesari et al., 2007; Cleveland et al., 2012), spectrophotometry (Aimanant and Ziemann, 2013; Ranney and Ziemann, 2016), and gas chromatography–mass spectrometry with derivatization (Dron et al., 2010). The second challenge is computationally harvesting FG abundance from a large set of known molecular structures. To this end, Ruggeri and Takahama (2016) developed a set of substructure definitions corresponding to FGs that can be queried against arbitrary molecules specified by their molecular graphs.

In this work, we apply these new substructure definitions to describe the FG composition of products simulated by gas-phase reactions prescribed with the Master Chemical Mechanism (MCMv3.2) (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003; Bloss et al., 2005) and SOA constituents formed by their dynamic absorptive partitioning (Chen et al., 2011). Three instances of APIN photooxidation under varying initial concentrations of oxides of nitrogen (NO_x), and TMB oxidation in the presence of NO_x are studied in accordance with aerosol FG composition characterized by Sax et al. (2005) and Chhabra et al. (2011) in chamber studies using FTIR. The model results are analyzed through a suite of FG abundances and model–measurement comparisons of measured FGs are presented to hypothesize reasons (including unimplemented mechanisms) for discrepancies where they occur.

2 Methods

We target our model simulations to mimic SOA formation in environmentally controlled chambers for which FG measurements are available.

2.1 Systems studied

Photooxidation of APIN under “low- NO_x ” (NO_x/APIN of 0.8), “high- NO_x ” (NO_x/APIN of 18), and no- NO_x conditions (designated as l NO_x , h NO_x , and n NO_x , respectively), and TMB under “low- NO_x ” (NO_x/TMB ratio of 0.24; designated as l NO_x) conditions were simulated in this study to compare with available measurements of aerosol FG composition in environmental chamber experiments. Simulations were run at 298 K and with conditions closely following experimental descriptions summarized in Table 1, with a few exceptions. In the case of APIN degradation in high- NO_x conditions, the H_2O_2 was used as the OH radical initiator as CH_3ONO is not available in the MCMv3.2 degradation scheme. When the reacted instead of initial precursor concentration is reported, this value is used as the initial concentration for the simulations. This decision is supported by the

Table 1. Summary of the experimental conditions studied in this work. For simplification, an ID has been given to each system.

ID	Publication	Precursor	Measurement conditions
APIN-INO _x	Sax et al. (2005)	α -pinene: 300 ppb	low NO _x : 240 ppb RH: 61 % seed: none radical initiator: propene, 300 ppb
APIN-hNO _x	Chhabra et al. (2011)	α -pinene: 47 ppb reacted	high NO _x : 847 ppb RH: 5 % seed: ammonium sulfate, 27 $\mu\text{g m}^{-3}$ radical initiator: CH ₃ ONO, 200–400 ppb
APIN-nNO _x	Chhabra et al. (2011)	α -pinene: 46 ppb reacted	no NO _x RH: 4 % seed: ammonium sulfate, 24 $\mu\text{g m}^{-3}$ radical initiator: H ₂ O ₂ ,
TMB-INO _x	Sax et al. (2005)	1,3,5-trimethylbenzene: 1312 ppb	low NO _x : 320 ppb RH: 60 % seed: none radical initiator: propene, 300 ppb

virtual observation that 99 % of the precursor is reacted after 4.5–6.5 h in these cases (Fig. S1 in the Supplement) and specification of higher initial concentrations leads to reacted quantities inconsistent with experimental specifications.

2.2 Model formulation

While differing in implementation, the model specification resembles the MCM-SIMPOL framework described by Chen et al. (2011). The chemical mechanism prescribed by MCMv3.2 (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003; Bloss et al., 2005) was used to simulate the gas-phase oxidation of volatile organic compounds (VOCs). The Kinetic Pre-Processor (KPP; Damian et al., 2002; Sandu and Sander, 2006; Henderson, 2016) was used to generate the gas-phase chemistry code in Fortran 90. A separate dynamic absorptive partitioning (Pankow, 1994) module was added via sequential operator splitting (Yanenko, 1971; Orland and Boris, 2000; Vayenas et al., 2005) to simulate gas-particle (G-P) partitioning after the reaction operator. Pure component vapor pressures of organic compounds in the MCMv3.2 degradation schemes were calculated using SIMPOL.1 (Pankow and Asher, 2008), and non-ideal interactions were neglected in these simulations (i.e., activity coefficients were set to unity for all species). Vapor pressures are converted to equivalent mass concentrations C^0 (Sect. S1 in the Supplement), and normalized by a reference value for presentation in logarithmic units (Seinfeld and Pandis, 2006) such that the notation $\log C^0$ implies $\log_{10}(C^0/1 \mu\text{g m}^{-3})$. LSODE (Livermore Solver for Ordinary Differential Equations; Radhakrishnan and Hindmarsh, 1993) was used as the numerical solver for each operation (reaction and G-P partitioning). A time step of 60 s is used in this study, as it is in

the order of magnitude of the timescale of gas-phase oxidation and condensation/evaporation under chamber conditions (Cocker et al., 2001) and leads to stable solutions. Radiation intensities were fixed at their maximum throughout the simulations to mimic conditions used in the chamber studies, with values corresponding to clear-sky conditions at an altitude of 0.5 km, 1° solar zenith angle in July, and a latitude of 45° N (Derwent et al., 1996; Hayman, 1997; Derwent et al., 1998; Saunders et al., 2003).

Absorptive partitioning to a purely organic phase is considered in this model (Sect. S1). The relative humidity (RH) specified in the experiments are converted to equivalent concentrations of H₂O for participation in the HO₂ radical self reaction to form hydrogen peroxide (Mozurkewich and Benson, 1985), but water uptake by the aerosol and its influence on G-P partitioning of organic compounds (Seinfeld et al., 2001; Chang and Pankow, 2010) is not considered. As aerosol growth following homogeneous and heterogeneous nucleation processes of the condensed organic phase in the chamber experiments are not included in the model, we use a seed $C_{\text{OA,init}}$ of 1 $\mu\text{g m}^{-3}$ to initiate G-P partitioning (Sect. S2). We specify the bulk of $C_{\text{OA,init}}$ to be a generic, non-volatile organic solvent that does not participate in reactions or partitioning and is in equilibrium with the initial composition of the gas phase (Sect. S2). The relative composition reported in this study is insensitive to this value after 1 h of simulation (Figs. S3 and S4). To differentiate between the SOA formed in the simulation and the total organic aerosol phase involved in partitioning, we denote the former quantity as C_{SOA} and the latter as $C_{\text{OA}} = C_{\text{OA,init}} + C_{\text{SOA}}$. No condensed-phase reactions are included; as with Chen et al. (2011) we consider them a potential source of model-

measurement discrepancies. While the particle diameter of the monodisperse population is allowed to grow according to the organic aerosol condensed (Sect. S2 in the Supplement), the number concentration of particles is kept fixed during the simulation; losses of both particles and gases to chamber walls (e.g., Loza et al., 2010; Matsunaga and Ziemann, 2010; Zhang et al., 2014a) are neglected. These assumptions will affect calculations of total yield and rate of change in aerosol mass; however, aerosol mass yields are in the range of physical expectation (Fig. S5; mass concentrations represented in the volatility basis set convention are also shown in Fig. S6 for reference). Relative abundances of functional groups are robust with respect to many of these assumptions and will be the primary focus of our presentation and model–measurement comparisons. However, the impact of vapor losses to chamber walls may require investigation in future work. An assumption of a common wall loss parameter for all species (e.g., Zhang et al., 2014b) would mostly reduce the overall yield from simulation, but compound-dependent wall losses (Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2015) may preferentially reduce the concentration of the most condensable substances in the system and lead to a different relative particle composition (Cappa et al., 2016; La et al., 2016). The magnitude of this effect also depends on the number of condensable species formed, the range of saturation concentrations spanned, and their absolute abundance.

2.3 Simulation analysis

A chemoinformatic tool (APRL-SSP; Takahama, 2015) described by Ruggeri and Takahama (2016) is used to harvest FG abundances (enumeration of the FG fragments) from each molecule in the simulations. This tool consists of scripts invoking OpenBabel and Pybel (O’Boyle et al., 2008, 2011) and SMARTS patterns (DAYLIGHT Chemical Information Systems, 2015) formulated and validated for these chemical systems. Using this tool, molecular structure is mapped to input parameters for SIMPOL.1, and FG abundances of the organic aerosol mixture are obtained from molecular concentrations. Most importantly, we extract two arrays with elements ϕ_{ip} , the number of times FG p occurs in molecule i , and ϕ_{ipa}^* , the number of times atom type a occurs in FG p in molecule i . We combine these two coefficients with the molecular or molar concentrations C of compound i in phase α generated by our simulations to estimate several useful mixture properties for time t_j :

$$\sum_{i \in \mathcal{M}} C_i^\alpha(t_j) \phi_{ip} = \text{abundance of FG } p$$

$$C_i^\alpha(t_j) \phi_{ip} / \left(\sum_{i \in \mathcal{M}} C_i^\alpha(t_j) \phi_{ip} \right) = \text{fractional contribution of molecule } i \text{ to abundance of FG } p$$

$$\sum_{i \in \mathcal{M}} C_i^\alpha(t_j) \phi_{ipa}^* = \text{apportionment of atoms of type } a \text{ to FG } p.$$

The summation is taken for the set of all compounds (or molecule types) \mathcal{M} . The last quantity is used to separate the contributions of O:C and N:C from various FGs. The set of patterns were constructed to meet conditions of completeness and specificity (each atom is matched by one and only one group) such that the sum of oxygen and nitrogen atoms in each FG sums to the total number of atoms in the system (Ruggeri and Takahama, 2016). Polyfunctional carbon atoms are not considered in the condition for specificity (matches by multiple groups lead to overestimation of counts in ϕ_{ipa}^*); therefore, the total number of carbon used in the denominator of these atomic ratios is estimated using the SMARTS pattern [#6].

We additionally estimate integrated reaction rates (IRRs; Jeffries and Tonnesen, 1994) to examine degradation rates relative to rates of production in the gas phase (g) for selected systems. The IRR for reaction r affecting compound i at time t_j is calculated from the rate constant k and the product of concentrations C :

$$\begin{aligned} \text{IRR}_{ri}(t_j) &= C_i^{(g)}(t_j) - C_i^{(g)}(t_j - \Delta t) \\ &= \int_{t_j - \Delta t}^{t_j} dt \left(k_r \prod_{i' \in \mathcal{M}_r} C_{i'}^{(g)}(t) \right) \\ &\approx \Delta t \left(k_r \prod_{i' \in \mathcal{M}_r} C_{i'}^{(g)}(t_j) \right). \end{aligned}$$

\mathcal{M}_r is the set of compounds involved in reaction r . The expression in parentheses is the conventional rate equation for reaction r . To obtain the IRR for functional group p , we multiply by the factor ϕ_{ip} described above:

$$\text{IRR}_{rp}(t_j) = \sum_{i \in \mathcal{M}_r} \text{IRR}_{ri}(t_j) \phi_{ip}.$$

IRR estimates were harvested from the LSODE solver, and the PERMM package (Henderson, 2015) was used to associate compounds and FGs with each reaction.

2.4 Measurements

FTIR analysis reported by Sax et al. (2005) and Chhabra et al. (2011) quantified the molar abundance of alkane CH (aCH), carboxylic acid (COOH), non-acid (ketone and aldehyde) carbonyl (naCO), alcohol OH (aCOH), and organonitrate (CONO₂) FGs. Uncertainties in the FG quantification have been reported to be between 5 and 30 % (Russell, 2003; Takahama et al., 2013). Sax et al. (2005) collect particles in the range of 86–343 nm onto zinc selenide substrates by impaction, while Chhabra et al. (2011) sample generated aerosol onto polytetrafluoroethylene (PTFE) filters for FTIR analysis. Measurement artifacts can arise during time-integrated collection of aerosol samples and can differ according to duration of sampling (Subramanian et al., 2004) or method of collection (Zhang and McMurry, 1987). The

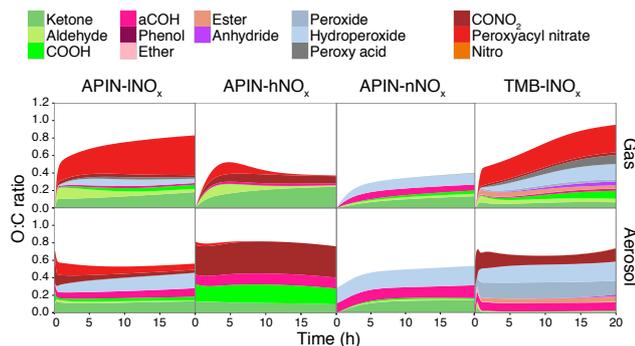


Figure 1. Time series of the relative molar contribution of different FGs to the O : C in the gas phase (top panels) and aerosol phase (bottom panels) simulated in this work for APIN-INO_x, APIN-hNO_x, APIN-nNO_x, and TMB-INO_x. The contribution of each FG to the O : C ratio accounts for the number of oxygen atoms per FG.

primary driver for absorptive and evaporative artifacts which may impact bulk mass estimation is the difference between the changing gas-phase composition and equilibrium vapor composition with respect to the aerosol phase, but model simulations suggest the relative gas-phase composition stabilizes after the first few hours. Changes in particle composition due to condensed-phase chemistry may perturb the equilibrium, but this phenomenon may be interpreted together with condensed-phase processes not included in the model. In the analysis of Chhabra et al. (2011), samples transported off-site for analysis were frozen to minimize evaporation and reaction artifacts during storage. Additionally, evaporative losses in the analysis chamber of the FTIR (during purging of headspace with dry nitrogen gas) were minimized by rapid scanning, and Sax et al. (2005) report that the spectrum was stable even when repetitive measurements are performed.

In this work, we limit our discussion to results based on molar rather than mass concentrations of FG abundances. While mass concentrations are commonly reported for FTIR measurements of ambient samples (e.g., Russell et al., 2009), estimates are based on fixed assumptions regarding the apportionment of polyfunctional carbon atoms to associated FGs (e.g., Allen et al., 1994; Russell, 2003; Reff et al., 2007; Takahama et al., 2013; Ruthenburg et al., 2014). These assumptions can affect both mass estimation and atomic ratios (e.g., O : C). Chhabra et al. (2011) proposed a modification based on assumed molecular structures in their chamber experiments, and mass estimates using these values are shown in Fig. S7. Constraining the mapping of measured bonds to atoms for estimation of these quantities in various mixtures are planned for future work. For model–measurement comparison, we select the subset of FGs that are reported by measurement and use relative metrics normalized only by measured fractions of OA.

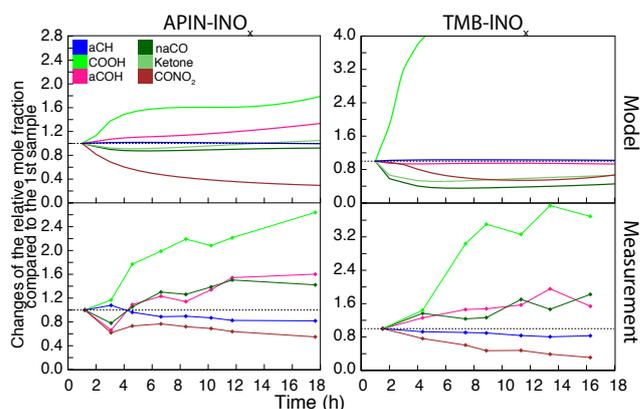


Figure 2. Comparison of the changes of the relative mole fraction compared to the first sample for COOH, COH, CO, aCH, and CONO₂ of the aerosol phase measured by Sax et al. (2005) and modeled in this work for APIN-INO_x and TMB-INO_x. For a chosen FG, the changes of the relative mole fraction compared to the first sample are calculated as the ratio between the relative mole fraction at the chosen time and the relative mole fraction at 1 h. naCO includes ketone and aldehyde FGs, but the change in relative ketone FG abundance is also shown separately for illustration. The contribution of ketone and aldehyde to CO have been reported separately in the model results. The x axis refers to the hours after the lights were turned on in the chamber for the bottom panel (Measurement) and the time after the start of the simulation in the top panel (Model). The dashed line corresponds to $y = 1$ and has been added for visual reference.

3 Results and discussion

In each of the following sections, we begin by describing the simulated evolution of FGs primarily in terms of their contribution to the O : C ratio (Fig. 1) and then discuss comparisons of mole fractions with observations for a subset of measured FGs (Figs. 2 and 3).

3.1 APIN-INO_x

3.1.1 Simulation results

Initially, only the most oxygenated species condense to the aerosol phase, but oxygenated products continue to be formed in the gas phase and the O : C values exceed the aerosol-phase O : C after 4 h. The O : C ratios approach 0.75 and 0.6 for the gas and aerosol phases, respectively, after 20 h of simulation (Fig. 1). The O : C ratio of the simulated aerosol phase is comparable to the O : C ratio measured by Chen et al. (2011) and Zhang et al. (2015) in ozonolysis and photooxidation experiments without NO_x (~ 0.5 in both cases).

The FG that contributes the most to the aerosol O : C ratio after 20 h is hydroperoxide (31 %), while in the gas phase peroxyacyl nitrate is the major contributor (carrying five oxygen atoms per peroxyacyl nitrate FG) with 55 % of the O : C ratio of the gas-phase mixture. Some peroxyacyl nitrates are

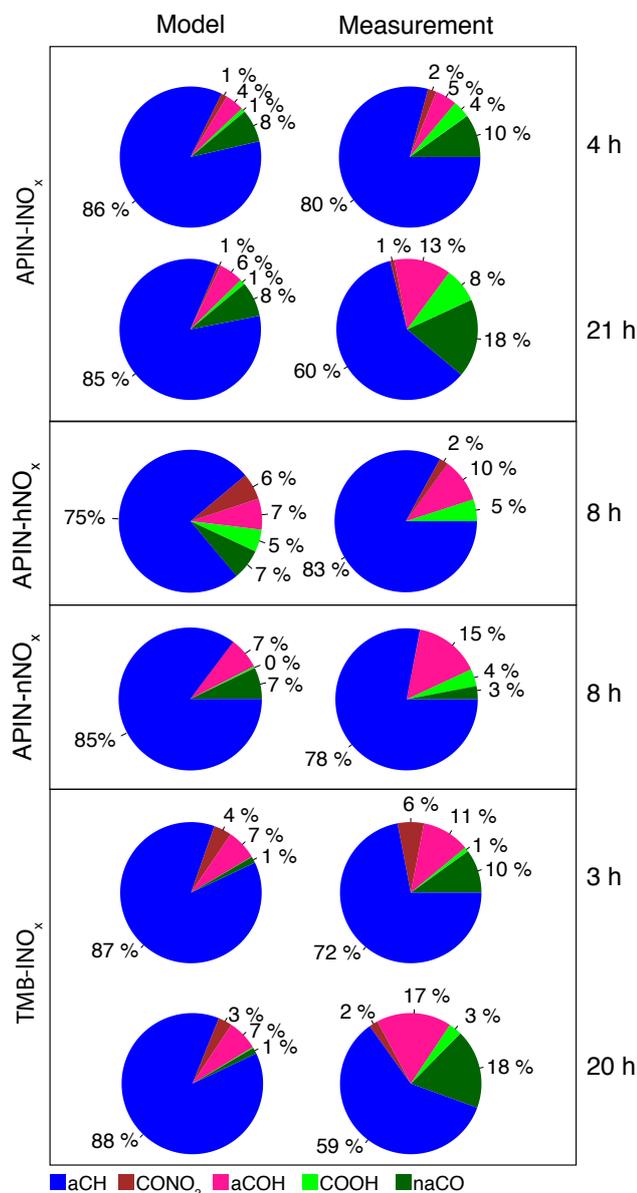


Figure 3. Pie charts illustrating the time-integrated relative aerosol mole fraction of aCH, CO, COOH, CONO₂, and aCOH in model simulations and experiments. The mole fractions reported in simulations are summed with respect to the subset of FGs that are reported by measurement to facilitate direct comparison. The time reported refers to the hours after the lights were turned on in the chamber (Measurements), and the time after the start of the simulation (Model). In the pie charts reporting the measurement conducted by Chhabra et al. (2011) (APIN-hNO_x and APIN-nNO_x) the CNH₂ fraction has been omitted in order to obtain a direct comparison between model and experiments. The sum of percentages combines to 100 ± 1%, as individual values were rounded to the nearest whole number for labeling.

also partitioned to the aerosol phase as reported in laboratory measurements (Jang and Kamens, 2001), but make a smaller contribution (12%) to the aerosol O:C. aCOH and CONO₂ FGs are found in higher abundance in the aerosol phase than many other FGs (Sect. S4) and contribute to the aerosol-phase O:C, while contributing negligibly to the gas-phase O:C. The large contribution of hydroperoxide FG to the aerosol-phase O:C is consistent with their large contributions to SOA mass suggested in previous studies (Bonn et al., 2004; Wang et al., 2011; Mertes et al., 2012).

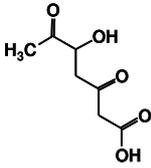
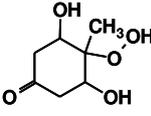
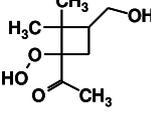
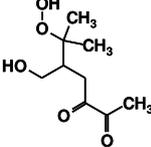
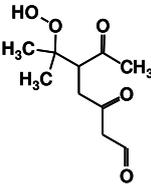
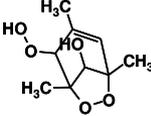
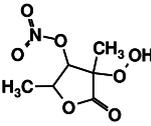
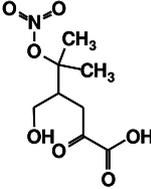
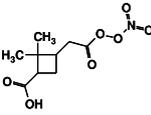
Addition of COOH lowers the pure component vapor pressure of a given molecule by 4 orders of magnitude (Kroll and Seinfeld, 2008; Pankow and Asher, 2008), but contributions to gas- and aerosol-phase O:C are approximately equal. In the gas phase, CH₃CO₂H (formed from degradation of the peroxyacid radical compound CH₃CO₃) constitutes 60% of the COOH fraction (Fig. 4) at maximum C_{SOA} (9.3 h). The aldehyde and ketone CO lower the pure component vapor pressure by around 1 order of magnitude (Kroll and Seinfeld, 2008), but their contribution to O:C is greater than COOH in the aerosol phase on account of the higher abundance of carbonyl-containing compounds. More than 80% of the moles of carbonyl in both the gas and aerosol phases are associated with ketone rather than aldehyde CO (Fig. S8).

We note the prevalence of several large polyfunctional compounds contributing to the aerosol phase. Their cumulative contributions to the total abundance varies over time (Figs. S9 and S10); their contributions at peak C_{SOA} are shown in Fig. 4. Four compounds (C97OOH, C98OOH, C106OOH, and C719OOH) comprise 70% of the ketone and 80% of the hydroperoxide abundance. C811PAN contributes 50% of the peroxyacyl nitrate and also 45% of the COOH. Illustrations for these compounds are provided in Table 2. Pinonic acid is the second largest contributor to COOH FG, which is consistent with previous reports of pinonic acid being a major contributor to SOA in APIN photooxidation over a range of NO_x conditions (Eddingsaas et al., 2012).

3.1.2 Model–measurement comparison of FG mole fractions

Qualitative changes in the mole fractions of COOH, aCOH, and CONO₂ FGs over the initial values reported by Sax et al. (2005) are well captured by the model (Fig. 2). The magnitude of increase in COOH is higher in the measurements than in the model: an increase of 2.6 times compared to 1.5 times can be seen between the beginning and the end of the measurements and the simulation, respectively. For aCOH the discrepancy is smaller; an increase of 1.5 times from the beginning to the end of the experiments compared to 1.3 in the simulation is found. For CONO₂, the relative mole fraction decreases from 1 to 0.6 during the experiment, while the model predicts a decrease to 0.3. For carbonyl (CO), the model is able to capture the general trend of initial decrease followed by an increase after 4 h. The trend in modeled naCO

Table 2. Illustration of several polyfunctional molecules discussed in Sect. 3.

MCM name	Molecular weight	$\log C^0$ (298 K)	Structure
H3C25CCO2H	174.1513	1.16	
C719OOH	176.1672	0.97	
C97OOH	188.2209	2.33	
C98OOH	204.2203	1.45	
C106OOH	216.2310	1.92	
TM135BPOOH	202.2045	2.78	
NMXYFUOOH	207.1382	3.40	
C813NO3	235.1913	-0.38	
C811PAN	247.2020	2.17	

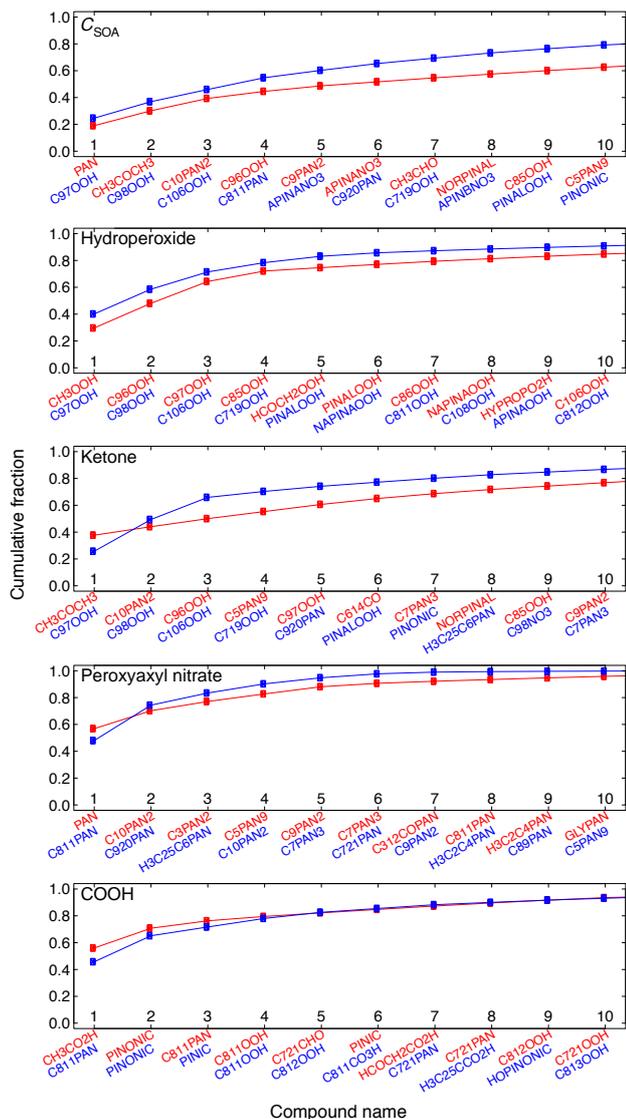


Figure 4. Cumulative contribution (as a fraction of total) of each compound to the overall C_{SOA} mass and abundance of different FG fragments for the APIN-INO_x simulation. Compounds are arranged in order of decreasing contribution in each phase (i.e., first molecule contributes the greatest amount). Contributions to the aerosol phase are shown in blue and the gas phase in red.

is largely contributed by ketone, as it comprises more than 80 % of the naCO (Fig. S8). The magnitude of decrease in relative mole fraction of aCH observed by Sax et al. (2005) is not captured by the model. The measured relative mole fraction compared to the first sample decreases from 1 to 0.8, while its change is not detectable in the simulation (Fig. 2).

The evolving differences in mole fractions between measurement and model are better viewed in Fig. 3. The oxidized fraction in the simulation is consistently lower than in the measurements, as it remains below 16 % in the model but increases to 40 % after 20 h in the reported measurements.

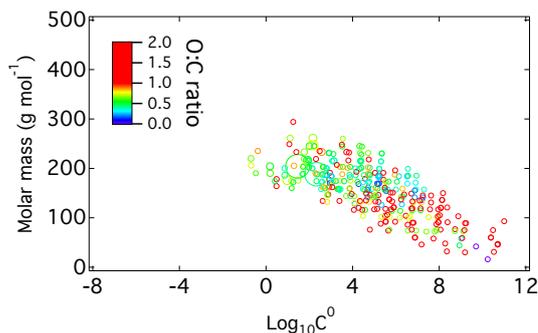


Figure 5. Molar mass vs. the logarithm of the pure components saturation concentration for the compounds included in the APIN and propene MCMv3.2 degradation scheme. The size of the circles is proportional to the compound mass in the aerosol phase found in APIN-INO_x simulation.

We consider two condensed-phase reaction mechanisms that may lead to such differences. Viewing the distribution of the compounds present in the MCM APIN-INO_x degradation scheme on $\log C^0$ vs. molar mass space (Fig. 5), we see that the model does not include lower-volatility compounds with molecular masses higher than 300 g mol^{-1} observed in experiments (Shiraiwa et al., 2014). This high-molecular-mass fraction cannot entirely explain the missing COOH, aCOH, and naCO, however, as accretion reactions do not significantly increase the O : C of the mixture (Shiraiwa et al., 2014; Zhang et al., 2015). In the analysis by Shiraiwa et al. (2014), these compounds with high molecular mass and low volatility have an O : C ratio between 0.3 and 0.6. Furthermore, Zhang et al. (2015) report that around 60 % of the APIN SOA mass generated in environmentally controlled chamber experiments for loadings up to $60 \mu\text{g m}^{-3}$ is constituted by SVOCs. This observation suggests that the role played by the gas-phase production of polyfunctional, extremely low volatility compounds (ELVOCs) observed in greater abundance (Ehn et al., 2014) at lower aerosol C_{OA} loadings and condensed-phase dimerization reactions can only partly be responsible for the discrepancies between simulations and experiments that we report in this study. Proposed dimerization reactions do not contribute to depletion of aCH bonds, and dimers produced in the aerosol phase have been found to have a similar O : C ratio to the monomer (Zhang et al., 2015). Photolysis of hydroperoxides has been suggested as a condensed-phase mechanism that leads to increase in naCO (Epstein et al., 2014), but an estimate based on the 6-day lifetime molar conversion of hydroperoxide groups to naCO only increases the latter fraction from 8 to 9 % of the FG mole fraction after 21 h (though naCO increases by 9 % over the case of no conversion) and does not fully explain the discrepancy between model and measurements for this FG. However, further oxidation due to dissolved oxidants, such as the OH radical, may reduce the proportion of aCH relative to oxidized groups, though this rate is also dependent on

Table 3. Comparison of pure component vapor pressures (atm) estimated (at 298 K) for the most abundant CONO₂ compounds in the aerosol phase for the APIN-hNO_x simulation. Calculations were accessed using the UManSysProp tool (Topping et al., 2016).

Compound	SIMPOL.1 ¹	EVAPORATION ²	Nannoolal ³	Myrdal & Yalkowsky ⁴
C813NO3	4.33×10^{-11}	4.04×10^{-11}	1.70×10^{-11}	7.05×10^{-9}
C98NO3	6.12×10^{-9}	2.07×10^{-8}	8.15×10^{-9}	1.01×10^{-7}
C719NO3	2.33×10^{-9}	3.34×10^{-10}	5.96×10^{-9}	3.45×10^{-7}
APINANO3	1.55×10^{-7}	2.38×10^{-6}	9.47×10^{-7}	5.53×10^{-6}
APINBNO3	1.55×10^{-7}	8.19×10^{-6}	1.45×10^{-6}	7.39×10^{-6}
TM135BPOOH	7.22×10^{-8}	5.46×10^{-9}	8.42×10^{-11}	6.24×10^{-9}
NMXYFUOOH	2.96×10^{-7}	4.56×10^{-8}	3.41×10^{-9}	5.09×10^{-8}

¹ Pankow and Asher (2008); ² Compennolle et al. (2011); ³ Nannoolal et al. (2008); ⁴ Myrdal and Yalkowsky (1997).

diffusion and uptake of these radicals by the SOA (Donahue et al., 2013).

3.2 APIN-hNO_x

3.2.1 Simulation results

While the FGs present in APIN-hNO_x system are identical to the APIN-INO_x system, we find they occur in different proportions on account of both the lower ratio of VOC precursor to NO_x concentrations and lower absolute precursor concentrations. The predicted aerosol O : C ratio in this simulated system is approximately 0.75, while Chhabra et al. (2011) reports experimental values around 0.4 according to AMS measurements. CONO₂ accounts for 47 % of the simulated aerosol O : C after 20 h (Fig. 1). Both aldehyde and ketone CO contribute to O : C in the gas phase more than in the aerosol phase, while CONO₂, aCOH, and COOH contribute primarily to O : C in the aerosol phase. The predicted aerosol N : C ratio is also overestimated (~ 0.1 in the simulated aerosol, Fig. S11) compared to the measured value of 0.03, on account of the large contribution from CONO₂.

Lower precursor concentrations in the Caltech chamber experiments (Table 1) lead to lower concentration of condensable products in these corresponding simulations (Fig. S1), enabling only a few compounds to partition to the aerosol phase in significant quantities (Figs. S6, S9, and S10). The aerosol fraction of COOH exceeds 10 %, but the rest remains below 5 % of the gas phase, in contrast to the APIN-INO_x system, where the aerosol fraction of six FGs exceed 10 % (Fig. S12). The aerosol mass yields on the order of a few percent (Fig. S5) are consistent with C_{SOA} produced in the presence of high NO_x concentrations (e.g., Ng et al., 2007), where NO can compete for reaction with peroxy radicals that may otherwise produce lower-volatility products. However, overall C_{SOA} formed is an order of magnitude lower than the $54 \mu\text{g m}^{-3}$ reported in the experiments (Chhabra et al., 2011), which is surprising given that chamber experiments without wall loss corrections tend to underestimate true yields (e.g.,

Zhang et al., 2014a). This underprediction may suggest the increasing importance of oligomer formation (e.g., Gao et al., 2004; Tolocka et al., 2004; Kalberer et al., 2006; Kroll and Seinfeld, 2008; Chen et al., 2011; Chhabra et al., 2011; Hall and Johnston, 2011) relative to the absorptive partitioning pathway at low C_{OA} concentrations (Presto and Donahue, 2006). While production of large, polyfunctional ELVOCs might be a prime candidate for explaining the mass discrepancy at these low C_{OA} loadings (comprising up to two-thirds for mass concentrations less than $10 \mu\text{g m}^{-3}$), reactions with NO with peroxy radicals may inhibit formation of ELVOCs through the hypothesized mechanism of H abstraction and O₂ addition to peroxy radicals (Ehn et al., 2014). Sensitivity analyses conducted to increase the rate of condensation and overall C_{SOA} formed had little impact on relative abundances estimated for FGs (Sect. S2), so the interpretations presented are robust for the gas-phase reaction mechanisms included and vapor pressures prescribed in our simulations.

In Fig. 6, we see that C813NO3 is a polyfunctional compound that comprises 75 % of CONO₂, 95 % of COOH, and 70 % ketone CO abundance, and 75 % of the C_{SOA} mass in the simulated aerosol at peak C_{SOA} (3.2 h). As for APIN-INO_x, pinonic acid is the second largest contributor to COOH FG, consistent with observations in similar experiments (Eddingsaas et al., 2012). Polyfunctionality may introduce challenges in vapor pressure for linear group contribution methods such as SIMPOL.1, so we evaluate the uncertainty in vapor pressure prediction of the top five contributors (C813NO3, C98NO3, C719NO3, APINANO3, and APINBNO3) to the CONO₂ abundance and C_{SOA} mass by comparing to other methods (Table 3). SIMPOL.1 has been found to generally predict lower vapor pressures compared to other estimation methods like EVAPORATION (Compennolle et al., 2011) and the method of Nannoolal (Nannoolal et al., 2008), but in the case of mononitrates Compennolle et al. (2011) report that differences with EVAPORATION and the Myrdal–Yalkowsky method (Myrdal and Yalkowsky, 1997) are negligible. For these critical compounds, the vapor pressures estimated by SIMPOL.1 are in the range of other

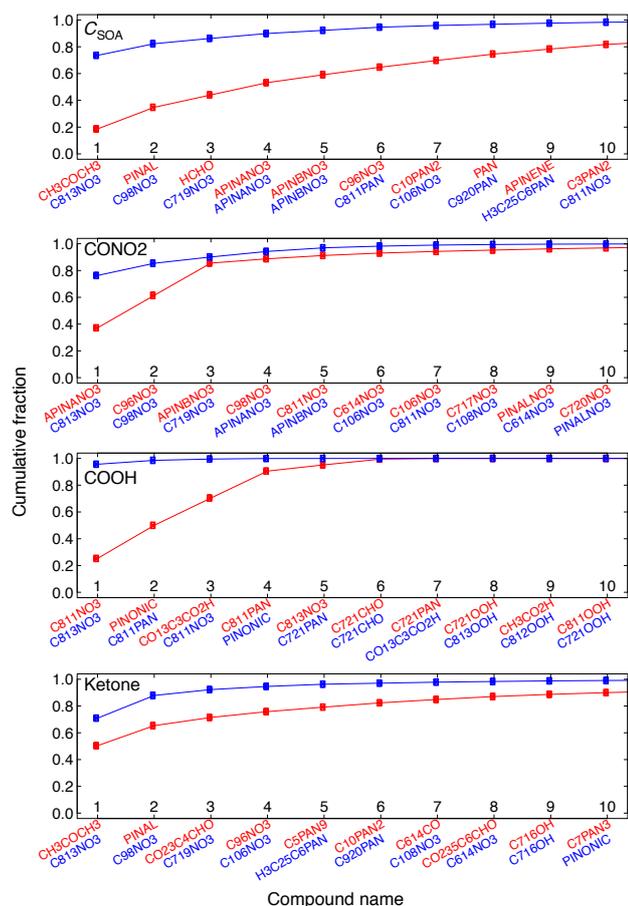


Figure 6. Cumulative contribution (as a fraction of total) of each compound to the overall C_{SOA} mass and abundance of different FG fragments for the APIN-h NO_x simulation. Compounds are arranged in order of decreasing contribution (i.e., the first compound contributes most) for each phase. Contributions to the aerosol phase are shown in blue and the gas phase in red.

estimates except for APINBNO₃ (the fifth most abundant species in the aerosol phase), where it is an order of magnitude lower than the next highest estimate. Therefore, systematic underestimation of vapor pressure is not the obvious cause of overabundance of this product in our simulation.

3.2.2 Model–measurement comparison of FG mole fractions

Compared with observations, discrepancies in the proportions of CONO₂ and naCO are higher than in the APIN-INO_x case. CONO₂ mole fraction is overestimated by the model as it accounts for 6 % of the relative mole fraction after 20 h, while in the measurements it accounts for only 2 % of the relative mole fraction (Fig. 3). The model also over predicts the relative mole fraction of naCO (7 % compared to less than 1 % in the measurements).

The low relative humidity conditions of the experiments (RH < 5 %) exclude organonitrate hydrolysis (Liu et al., 2012), not included in the model, as a possible condensed-phase pathway that explains the model–measurement discrepancy for CONO₂. Organonitrate compounds are formed from the addition of NO to a peroxy radical (e.g., C813NO₃ is formed from the addition of NO to C813O₂). Yields are affected by the rate of HO₂ or NO₃ addition to the peroxy radical and the branching ratio of the reaction to produce organonitrate or alkoxy radical and NO₂ (Noziere et al., 1999; Ruppert et al., 1999; Aschmann et al., 2002; Pinho et al., 2007). High uncertainty in CONO₂ production rates by lumped chemical reaction schemes has also been reported (Henderson et al., 2011), but uncertainties may also be present in explicit mechanisms for the reasons described. A smaller number of components condensing to the aerosol phase may lead to greater sensitivity of simulation results to individual values of such rate constants or vapor pressures (which may otherwise be compensated across a larger suite of compounds or reactions), resulting in higher likelihood of discrepancies between model predictions and observations.

3.3 APIN-nNO_x

3.3.1 Simulation results

The apportionment of O:C in the APIN-nNO_x system is qualitatively similar to APIN-INO_x, without contributions from nitrogenated groups. The FG composition of gas and aerosol O:C ratios are very similar, though the value is higher in the latter phase (Fig. 1). The aerosol-phase O:C ratio increases in the simulation to arrive to 0.53 after 20 h, while the observed O:C ratio by Chhabra et al. (2011) is between 0.3 and 0.4. We can see that in the very beginning of the simulations the only compounds contributing to the O:C ratio that are able to partition to the aerosol phase have aCOH and hydroperoxide moieties. The ketone FG starts contributing to O:C in the aerosol phase only after this initial phase. The hydroperoxide FG accounts for 42 % of the total SOA O:C ratio after 20 h of simulation.

As for APIN-hNO_x, the C_{SOA} formed in these simulations is an order of magnitude less than the 64 $\mu\text{g m}^{-3}$ reported for the corresponding experiment. Sensitivity analysis with respect to C_{SOA} (by varying the amount of absorptive mass) indicates that relative proportions analyzed are again representative of aerosol formed according to the chemical mechanism and vapor pressure estimation method in our simulation framework (Sect. S2), which excludes accretion reactions in the condensed phase. The same four carbonyl compounds that make up 70 % of the ketone CO comprise over 90 % of the naCO, 80 % of hydroperoxide, and 80 % of the C_{SOA} in this system (Fig. 7) at peak C_{SOA} (12.1 h). In contrast to APIN-INO_x and APIN-hNO_x, multifunctional organonitrate compounds do not contribute to the COOH abundance; it is effectively accounted for by only two

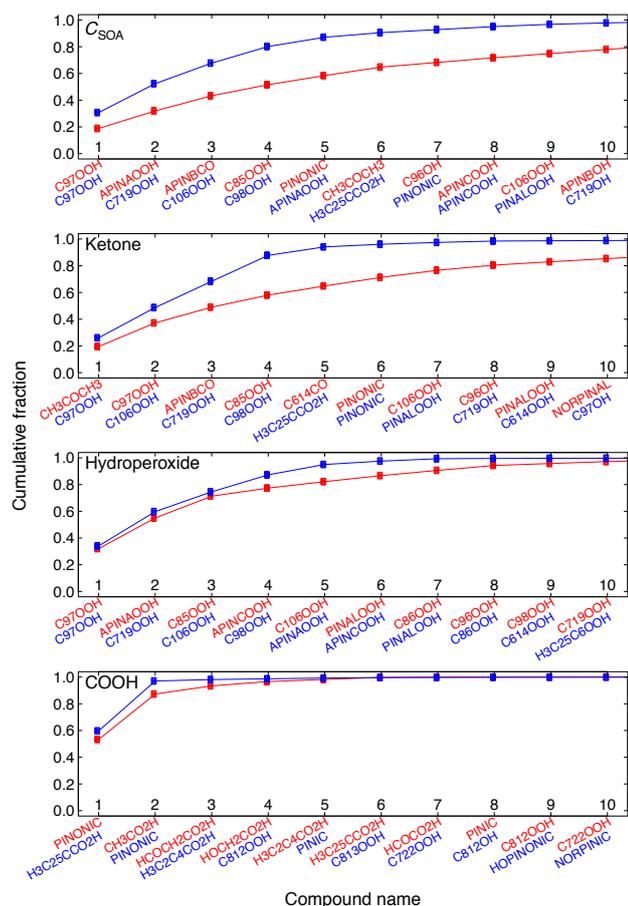


Figure 7. Cumulative contribution (as a fraction of total) of each compound to the overall C_{SOA} mass and abundance of different FGs for the APIN- $n\text{NO}_x$ simulation. Compounds are arranged in order of decreasing contribution (i.e., the first compound contributes most) for each phase. Contributions to the aerosol phase are shown in blue and the gas phase in red.

compounds: H3C25CCO2H (Table 2) contributing 60 % and PINONIC (pinonic acid) contributing 40 %. The reason for the large contribution of H3C25CCO2H is its saturation concentration of $\log C^0$ of 1.2, while PINONIC has a $\log C^0$ of 3.0 but its total (gas+aerosol) concentration is almost an order of magnitude more than H3C25CCO2H (Fig. S13). As with the APIN- $h\text{NO}_x$ simulations, the dominance of so few polyfunctional compounds in the aerosol phase is surprising; past studies have identified more than five smaller compounds comprising observed APIN (and other precursor) ozonolysis aerosol yields under dry conditions (Yu et al., 1999; Pankow, 2001). These compounds are primarily composed of COOH, aCOH, and aldehyde CO groups, which are present in low abundance in our simulations.

3.3.2 Model–measurement comparison of FG mole fractions

In Fig. 3 we can observe that the highest discrepancies in the FG relative mole fraction between experimental observations and simulations are found in the oxygenated FGs (COOH, aCOH, and naCO). While the naCO mass fraction is overestimated by the model (7 % in the model compared to 3 % in the experiment), the COOH and aCOH are underestimated (less than 1 % in the model compared to 3 % in the experiment for COOH and 7 % compared to 15 % for aCOH). Reactions of aldehydes with hydroperoxides can form peroxyhemiacetals (Jang and Kamens, 2001; Docherty et al., 2005), leading to a reduction in naCO. However, if the condensed-phase naCO is mostly ketone as predicted by the model (Figs. 1 and S8), this is not likely to improve model–measurement agreement of the relative mole fractions of naCO.

Simulation of COOH production by gas-phase oxidation has also been reported to underestimate its abundance in OA in other studies (e.g., Aumont et al., 2012). In particular, there is a question whether the gas-phase production rate is low or production and degradation rates are both high. To examine this question, IRR contributions to production and loss of COOH from semi-volatile compounds that can condense to the aerosol phase in appreciable proportions ($\log C^0 \leq 2.5$) are shown in Fig. 8. The net change in moles of COOH due to degradation is 83 % of the production for these compounds. There are more compounds contributing to the aerosol-phase COOH in the APIN- INO_x simulation and the net degradation is only 13 % of the net production. One known mechanism for production of COOH by heterogeneous reactions not included in the model involves the transformation of hydroxy carbonyls (formed from alkoxy radicals) to dihydrofurans (Ziemann and Atkinson, 2012), which are further oxidized in the gas phase primarily by O_3 . However, as there is no NO_x in the APIN- $n\text{NO}_x$ system, the O_3 production rate is small (concentrations are less than 0.6 ppb in our simulations, Fig. S14). The model–measurement discrepancy may again be partially due to the low concentrations of condensable products and small number of products partitioning to the aerosol phase in this simulation. Production and condensation of ELVOCs or additional oxidation mechanisms in the condensed phase not implemented in our model may also contribute to this discrepancy.

3.4 TMB- INO_x

3.4.1 Simulation results

In the TMB- INO_x simulations, continued oxidation in the gas phase proceeds for the entire duration of simulation and the O:C ratio approaches unity, while the aerosol-phase O:C and FG composition largely stabilizes in magnitude after the first several hours. In this mechanism, we note the presence of esters, ethers, organic peroxides ($\text{ROOR}' + \text{ROOH}$), and

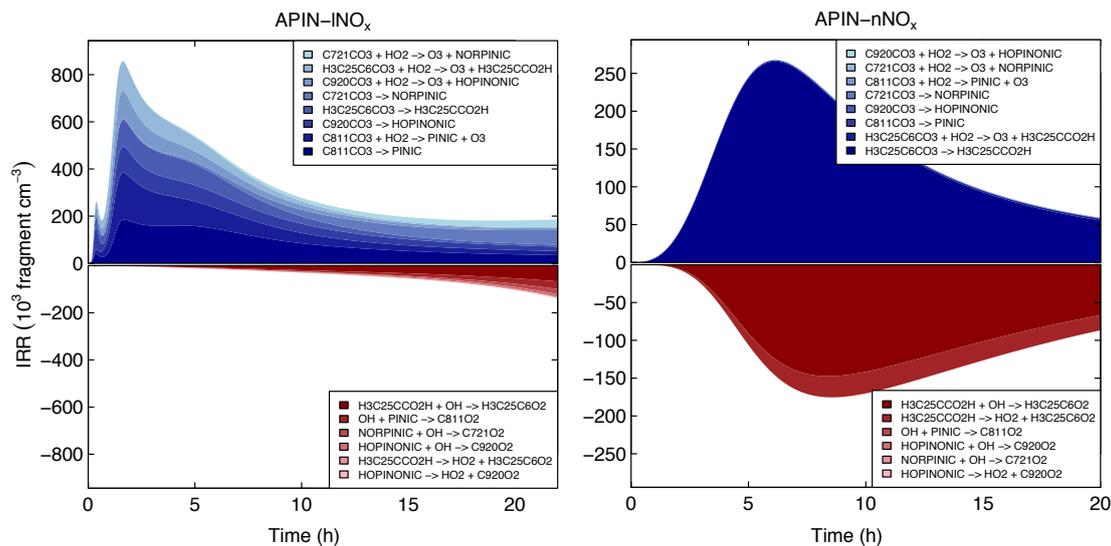


Figure 8. Integrated Reaction Rates for the COOH group (denoted in units of fragments per molecule).

anhydrides which were not present in the APIN photooxidation schemes. The O : C ratio of the simulated SOA is (~ 0.7). While overall O : C in experiments of Sax et al. (2005) were not reported, Sato et al. (2012) report values in the range of 0.25–0.47 for similar TMB photooxidation experiments with NO_x and methyl nitrate as OH source, with no seed and lower RH ($< 1\%$).

The peroxyacyl nitrate is the FG that contributes the most to the gas-phase O : C ratio (around 30 %), as in the APIN- INO_x case. Peroxide, hydroperoxide, and CONO_2 are major contributors to the aerosol O : C ratio and ester and aCOH are also present in the aerosol phase. COOH, anhydrides, peroxy acid, peroxyacyl nitrate, and naCO contribute to the gas phase. The high peroxide and hydroperoxide contribution to the aerosol phase in this simulation agrees with their reported role in SOA formation from TMB photooxidation in low- NO_x conditions (Wyche et al., 2009). However, the C_{SOA} mass fraction of compounds containing organic peroxide is 96 % in our simulations, which is higher than what has been experimentally determined by Sato et al. (2012) in similar conditions ($12 \pm 8\%$).

While higher precursor concentrations lead to high concentrations of condensable products in the gas phase, two compounds (TM135BPOOH and NMXYFUOOH) make up over 70 % of C_{SOA} at its peak (11.9 h). While formation and condensation of ELVOCs in the experimental system cannot be ruled out, it is likely that their contribution would be much smaller than the SVOC fraction on account of the high mass loadings (Fig. S1) (Zhang et al., 2015). TM135BPOOH is found to contribute 60 % to the aCH and 65 % of hydroperoxide FGs in the aerosol phase at peak C_{SOA} (Fig. 9). TM135BPOOH is a hydroxy hydroperoxide bicyclic peroxide (Table 2) that is formed after many oxidation steps that follow the first addition of OH to the aromatic ring (Rickard

et al., 2010). This compound has been also indicated by Rickard et al. (2010) as a potential SOA forming compound from TMB photooxidation and was found to be the most abundant hydroperoxide compound in the beginning of the photooxidation simulation they conducted. In our estimation, vapor pressures for these compounds predicted by SIMPOL.1 are at the upper end of estimates by three other methods (Table 3), so it is less plausible that the high abundance of these species in the condensed phase can be attributed to underestimation of vapor pressures.

3.4.2 Model–measurement comparison of FG mole fractions

The model is able to capture the general trends in COOH and CONO_2 relative to the first sample but the difference in magnitude is higher than APIN- INO_x case (Fig. 2). The measured changes in COOH indicate an increase by a factor of 4, while predicted COOH increases by as much as a factor of eight during the same time. The CONO_2 mole fraction at the end of our simulation is around 0.7, while it arrives at 0.4 in the experimental observations. The increase in naCO and aCOH that are captured by simulation for APIN- INO_x are not captured for TMB- INO_x . As for APIN- INO_x , the degradation of the aCH fraction and the appearance of naCO and aCOH are slower in the model than in the experiments carried by Sax et al. (2005). From the molar fractions shown at different simulation times in Fig. 3 we find better agreement in the beginning of the simulation and the differences in the FG molar fraction is higher compared to APIN- INO_x .

The low proportion of naCO compared to simulations described in preceding sections is due to the lack of multifunctional ketone compounds. The ester CO abundance is on the same order as ketone CO (Fig. S8) in our simu-

CO and hydroperoxide FGs. The relative abundance of ketone CO is overestimated compared to observations; the O : C is also overestimated, possibly on account of the large (42 %) contribution from the hydroperoxide FG which originates from the same set of molecules. For the TMB-INO_x photooxidation simulations, general trends in the changes in relative mole fractions compared to the first sample for COOH, aCOH, naCO, aCH, and CONO₂ also qualitatively follow observations, but their magnitudes have more discrepancies with experiments than in the case of APIN-INO_x. These discrepancies have also been hypothesized as a sensitivity to reaction rates and vapor pressures of a few dominant products that contribute significantly to the aCH mole fraction and peroxide fraction of the aerosol O : C ratio. As for the APIN-INO_x simulations, the agreement in abundances of aCH relative to the measured set of oxidized FGs may also be explained by additional condensed-phase oxidation chemistry not included in the model.

This work illustrates that concurrent measurement of FGs alongside common techniques for atomic and molecular characterization of OA can provide an opportunity for complementary evaluation and further guide detailed understanding of chemical and physical transformations. Analysis of FG abundance can supplement tracking of individual tracers and evaluate the importance of mechanisms that lead to production of a class of compounds in the overall molar (or mass) budget. FG abundances can also provide structural interpretation to variations in elemental ratios (e.g., O : C, H : C, and N : C). Looking forward, systematic model-measurement comparison of FGs under controlled conditions may be able to provide constraints and aid development of chemical mechanism generators (e.g., Gao et al., 2016; Aumont et al., 2005). While we have uncovered only a fraction of the analysis capabilities that a FG perspective provides, we anticipate that the tools and approaches introduced in this work can encourage further comparisons between model simulations of both gas- and aerosol-phase chemistry in conjunction with emerging methods for FG quantification.

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