Secondary Organic Aerosols Derived from Intermediate Volatility n-Alkanes Adopt Low Viscous Phase State

Tommaso Galeazzo[1], Bernard Aumont[2], Marie Camredon[2], Richard Valorso[2], Yong B. Lim[3], Paul J. Ziemann[4,5], and Manabu Shiraiwa[1,*]

1. Department of Chemistry, University of California, Irvine, CA92625, USA
2. Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France
3. California Air Resources Board, Riverside, CA92507, USA
4. Department of Chemistry, University of Colorado, Boulder, Colorado, USA
5. Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado, USA

* Correspondence to: m.shiraiwa@uci.edu

Abstract.

Secondary organic aerosol (SOA) derived from n-alkanes, as emitted from vehicles and volatile chemical products, is a major component of anthropogenic particulate matter, yet its chemical composition and phase state are poorly understood and hardly constrained in aerosol models. Here we provide a comprehensive analysis of n-alkane SOA by explicit gas-phase chemistry modeling, machine learning, and laboratory experiments to show that n-alkane SOA adopt low viscous semisolid or liquid states. Our study underlines the complex interplay of molecular composition and SOA viscosity: n-alkane SOA with higher carbon number mostly consists of less functionalized first-generation products with lower viscosity, while the lower carbon number SOA contains more functionalized multigeneration products with higher viscosity. This study opens up a new avenue for analysis of SOA processes and the results indicate little kinetic limitations of mass accommodation in SOA formation, supporting the application of equilibrium partitioning for simulating n-alkane SOA formation in large-scale atmospheric models.

Introduction

Secondary organic aerosols (SOA) are ubiquitous in the atmosphere, affecting climate, air quality and public health (Pöschl and Shiraiwa, 2015; Jimenez et al., 2009). They are generally formed by multigenerational oxidation of volatile organic compounds (VOCs) emitted by both anthropogenic and biogenic sources followed by condensation of semi-volatile oxidation products into the particle phase (Ziemann and Atkinson, 2012; Kroll and Seinfeld, 2008). As an important class of SOA precursors, there is a growing attention to intermediate volatile organic compounds (IVOCs), which can partition to the gas phase upon dilution of primary organic aerosols after fresh emission sources such as vehicle tailpipes, combustion of fossil and fuel oils, and volatile chemical products (Robinson et al., 2007; McDonald et al., 2018). The inclusion of IVOCs in the model simulations helps to reduce the gap between model simulation and field observation of SOA (de Gouw et al., 2011; Li et al., 2022; Zhao et al., 2016).

SOA can adopt different particle phase states (liquid, amorphous semisolid, and glassy solid), depending on their chemical composition, relative humidity and temperature (Virtanen et al., 2010; Petters et al., 2019; Reid et al., 2018; Renbaum-Wolff et al., 2013) and also evolving upon chemical aging and photochemistry (Baboomian et al., 2022). SOA phase state plays an important role in a number of atmospheric multiphase processes (Shiraiwa et al., 2017). The occurrence of glassy SOA in the free troposphere can impact activation pathways of ice crystals and cloud droplets (Knopf and Alpert, 2023). Slow diffusion in viscous particles induces kinetic limitations in heterogeneous and multiphase reactions (Zhang et al., 2018; Zhou et al., 2019; Shiraiwa et al., 2011), affecting long-range transport (Shrivastava et al., 2017; Mu et al., 2018). The timescale of SOA partitioning can be prolonged in viscous particles (Schervish and Shiraiwa, 2023), retarding uptake of semi-volatile compounds and mixing of different particle populations (Ye et al., 2016). Particle phase state also modulates SOA growth to cloud condensation nuclei sizes, affecting cloud life cycle (Zaveri et al., 2022). While the phase states of SOA generated by biogenic VOCs such as terpenes and isoprene have been extensively studied (Virtanen et al., 2010; Petters et al., 2019; Renbaum-Wolff et al., 2013; Baboomian et al., 2022; Zhang et al., 2018), those derived from IVOCs are hardly investigated and remain poorly constrained.

Viscosity (η) is a dynamic property that characterizes the particle phase state, which can be derived from the glass transition temperature (T_g) of the constituting species (Koop et al., 2011). Several structure-activity relationships models have been developed to predict the T_g of an organic compound using various molecular properties including molar mass, atomic O:C ratio (Shiraiwa et al., 2017), elemental composition (DeRieux et al., 2018), and volatility (Li et al., 2020; Zhang et al., 2019). A method was developed to predict SOA viscosity from the T_g -scaled Arrhenius plot of fragility by considering Gordon-Taylor mixing rule and hygroscopic growth of SOA particles (DeRieux et al., 2018; Shiraiwa et al., 2017). The T_g compositional parameterizations (CP) and the viscosity prediction method have been applied to high resolution mass spectrometry data of various types of SOA including toluene SOA (DeRieux et al., 2018), SOA generated by diesel fuels (Song et al., 2019), β-caryophyllene SOA (Maclean et al., 2021), and SOA generated by surrogate VOC mixtures by healthy and stressed plants (Smith et al., 2021), agreeing well with viscosity measurements. However, CP substantially overestimated viscosity measurements of indoor surface films which are mostly composed of unsaturated high molar mass compounds such as triglycerides (O'Brien et al., 2021). CP does not consider molecular structure nor functionality explicitly, representing a limitation of this method. Galeazzo and Shiraiwa (2022) overcame this limitation by developing a machine learning-based model, tgBoost, with an application of cheminformatics "molecular embeddings" that retains detailed information on atomic composition, molecular structure and connectivity. The main novel feature introduced by tgBoost is model capability to predict different T_g for structural isomers and high sensitivity of T_g to various functional groups, consistent with viscosity measurements for functionalized compounds (Rothfuss and Petters, 2017; Grayson et al., 2017).

Long-chain linear alkanes (n-alkanes) are representative IVOCs and account for a substantial fraction of non-methane hydrocarbons in urban air as mainly emitted from anthropogenic activities such as vehicle exhausts and incomplete fuel combustion (Li et al., 2022). Gas-phase oxidation of n-alkanes by OH radicals can trigger the formation of SOA with high yields, as observed in laboratory experiments (Aimanant and Ziemann, 2013a; Lim and Ziemann, 2009b; Srivastava et al., 2022) and field observations (Gentner et al., 2012; Li et al., 2022). Gas-phase oxidation pathways of n-alkanes are relatively well understood and successfully simulated by detailed gas-phase chemistry modeling (Aumont et al., 2012; La et al., 2016), but the chemical composition of n-alkane SOA has only been characterized well for the C_{16} n-alkane (Ranney et al., 2023) and the phase state and viscosity of alkane SOA are unknown. Therefore, the n-alkane SOA system provides an ideal benchmark for the investigation of the interplay of chemical composition, particle phase state and kinetic limitations influencing SOA growth and evolution.

In this study, we implemented tgBoost in an explicit gas-phase chemistry model GECKO-A to investigate the complex interplay of chemical composition, kinetic partitioning, and phase state of n-alkane SOA generated under dry and high NOx conditions. The GECKO-A model is one of the most comprehensive generators of gas-phase chemical schemes to date, as it automatically generates detailed gas-phase chemical mechanisms involving thousands to millions of oxidation products from a given VOC precursor based on established reaction pathways and structure–activity relationships (Aumont et al., 2012; La et al., 2016). The simulations were conducted with variable effective mass accommodation coefficient to consider potential kinetic limitations in amorphous semisolid particles (Shiraiwa and Pöschl, 2021). The simulated results were compared with chamber experimental data on SOA yields (Lim and Ziemann, 2009b) as well as new measurements on thermal desorption temperatures and functional group distributions.

Methods:

Model simulations.

We applied the Generator for Explicit Chemistry and Kinetics of the Organics in the Atmosphere (GECKO-A) (Aumont et al., 2012; La et al., 2016) to obtain detailed reaction schemes of gas-phase OH oxidation of n-alkanes along with rate constants. The GECKO-A generator used for the oxidation of linear n-alkanes treats chemistry of peroxy (RO_2) and alkoxy (RO) radicals. Under high NOx conditions, RO_2 radicals mainly react with NO and NO_2, to form closed-shell compounds or RO radicals, which undergo reaction with O_2, unimolecular decomposition (i.e. C-C bond breaking) or isomerization, generating stable compounds and/or to new RO_2 radicals. The detailed protocol for such mechanism generation is available in previous studies (Aumont et al., 2013; Aumont et al., 2005; Aumont et al., 2012; La et al., 2016). In this study, the generated chemical schemes include the description of the formation of organic species up to four generations. Species with vapor pressure below 10^{-13} atm are assumed to be of low enough volatility to completely partition to the condensed phase and their gas phase chemistry is then not generated in the mechanism to reduce the mechanism (La et al., 2016). The number of species treated in the model was ~10^4 species for dodecane (C_8H_{18}) that increases to ~10^5 species for heptadecane ($C_{17}H_{36}$).

The latest structure-activity relationships are treated for the chemistry of organic compounds with OH radical (Jenkin et al., 2018b, a; Jenkin et al., 2019), the bimolecular reactions of peroxy radicals (Jenkin et al., 2019), as well as alkoxy radical decomposition and H migration reaction rates (Vereecken and Peeters, 2009; La et al., 2016). The vapor pressures of semi-volatile species were estimated by using Nannoolal's group contribution method (Nannoolal et al., 2008) implemented in GECKO-A, as described in detail in Valorso et al. (2011). The model treats unimolecular particle-phase reactions including cyclization of hydroxyketones and dehydration of cyclic hemiacetals to form dihydrofurans (La et al., 2016). The model does not treat autoxidation and dimerization in the gas phase, but these processes should be minor pathways during n-alkane oxidation in the presence of high NOx as the reaction of peroxy radicals with NOx should be dominant (Praske et al., 2018; Pye et al., 2019); thus, their absence from GECKO-A chemical schemes should not have major impacts on the simulated results.

These explicit chemical mechanisms were implemented into a box model to simulate the multigenerational oxidation of n-alkanes, partitioning of oxidation products into the particle phase based on their vapor pressures, and vapor wall loss to mimic chamber experiments (La et al., 2016). We replicated the experimental conditions used in Lim and Ziemann (2009b) to generate SOA from OH oxidation of C_8-C_{17} n-alkanes at high NO_x conditions in the presence of non-volatile dioctyl sebacate (DOS) seed particles with particle radius of 150 nm and mass loading of 200 μg m^{-3}. Temperature was held constant at 295.15 K, pressure was set at 1 atm and RH was fixed at 0.5%. Photolysis frequencies were calculated based on the cross sections, quantum yields as described in Aumont et al. (2005) and the photonic flux of blacklight lamps. Each simulation ran for 1 hour and the time evolution of species concentration were computed through a two-step method that solves stiff ordinary differential equations (Verwer, 1994; Verwer et al., 1996). To investigate effects of mass concentrations, we also simulated experiments of n-alkane photooxidation under high NO_x conditions with low mass loadings by Presto et al. (2010). The number concentration of seed particles with particle diameter of 200 nm was ~5000 cm^{-3}, corresponding to the mass concentration of ~20 μg m^{-3}. Initial mixing ratios of n-alkane and NO_x were in the range of 3 – 99 ppb and 1 – 5 ppm, respectively, as reported in Presto et al. (2010) and these conditions were applied in the model.

The box model accounts for mass transfer kinetics of organic species between gas and particle phases. Partitioning follows Raoult's law at equilibrium and partitioning kinetics is described by the gas-particle mass transfer coefficient with the Fuchs-Sutugin approach (Seinfeld and Pandis, 2016). For the base case scenario, we fixed the mass accommodation coefficient (α) to be 1 based on molecular dynamics simulations (Julin et al., 2014), assuming particles being low viscous liquids without kinetic limitations of bulk diffusion. To account for potential kinetic limitations in viscous particles, we applied an effective mass accommodation coefficient (α_{eff}) that is a function of volatility and bulk diffusivity (Shiraiwa and Pöschl, 2021):

$$\alpha_{\mathrm{eff}} = \alpha_{\mathrm{s}} \frac{1}{1+\frac{\alpha_{\mathrm{s}}\,\omega\, C^0}{4\,D_{\mathrm{b}}\,\rho_{\mathrm{p}}}\frac{r_{\mathrm{p}}}{5}\cdot 10^{-12}\frac{\mathrm{g\ cm^{-3}}}{\mathrm{\mu g\ m^{-3}}}} \quad (1)$$

where α_s is the surface accommodation coefficient assumed to be 1, ω (cm s^{-1}) is the mean thermal velocity of the organic compound in the gas phase, r_P (cm) is the particle radius, ρ_p (g cm^{-3}) is the particle density, and C^0 (μg m^{-3}) is the pure compound saturation mass concentration. D_b (cm^2 s^{-1}) is bulk diffusivity as simulated by conversion of viscosity as detailed below. α_{eff} values are shown as a function of D_b and vapor pressure p^o in Fig A3a. We accounted for a reversible gas-to-chamber wall partitioning of gases and assumed a fixed first-order deposition rate constant of 5×10^{-4} s^{-1} based on experimental observations and previous modeling studies (Krechmer et al., 2016; La et al., 2016; Lim and Ziemann, 2009b). A desorption rate constant from wall to the gas phase was derived by using a parameter of $C_w/M_w\gamma_w$ of 9 μmole m^{-3} for n-alkanes and 120 μmole m^{-3} for oxidation products based on chamber observations (Matsunaga and Ziemann, 2010), as discussed in La et al. (2016). Potential concentration gradients in the particle phase are not resolved explicitly and SOA particles are assumed to be homogeneously well-mixed implicitly.

The glass transition temperatures (T_g) of organic compounds were predicted by the machine learning-based model tgBoost (Galeazzo and Shiraiwa, 2022) and the parameterization based on elemental composition (DeRieux et al., 2018; Li et al., 2020). The implementation of the compositional parametrization into the GECKO-A box model was done in Galeazzo et al. (2021) with a thorough description of all the equations, assumptions and steps adopted for the implementation of this viscosity estimation method. In this study, we implemented tgBoost, a newly developed machine learning model for better predictions of T_g. tgBoost is a powerful model that can discern compositional isomers by functionality and predict the glass transition temperature of an organic compound *i* ($T_{g,i}$) with an uncertainty of ± 18.3 K using the canonical SMILES notation of a molecule (Galeazzo and Shiraiwa, 2022). We have implemented a pipeline (i.e., gecko2vec) into GECKO-A to predict T_g of compounds from the chemical mechanism in a fast and computationally efficient manner. Gecko2vec executes three main steps: first, it translates the IDs of the compounds of interest of the GECKO-A mechanism into the respective canonical SMILES notations (translation step); second, it transforms the canonical SMILES notations into the respective molecular embeddings (i.e., unique 300-dimensional numerical representations of molecules; embedding step); and finally, the pretrained tgBoost model and its weights are loaded and used to predict T_g of each species (prediction step). Within the box model, the T_g of total SOA particles ($T_{g,org}$) resulting from the combination of its organic component and water mixture is computed using the Gordon–Taylor equation (Dette et al., 2014; Koop et al., 2011; Zobrist et al., 2008). $T_{g,org}$ can be converted to viscosity based on the Vogel-Tammann-Fulcher approach assuming the fragility parameter of 10 (DeRieux et al., 2018). Viscosity is further converted into bulk diffusivity using the fractional Stokes-Einstein equation with a fractional parameter of 0.93 and an effective molecular radius of 0.5 nm (Evoy et al., 2019). For both model simulations with CP and tgBoost, the particle number concentration is assumed to remain constant (coagulation is not treated), while the particle radius evolves following the partitioning of organic compounds.

Laboratory experiments.

SOA particles were generated from OH oxidation of C_8-C_{17} n-alkanes in a 5.9 m^3 Teflon environmental chamber filled with clean air under high NO_x conditions in the presence of non-volatile dioctyl sebacate (DOS) seed particles, as described in detail elsewhere (Lim and Ziemann, 2009b). Briefly, 1 ppm of n-alkane, 10 ppm of methyl nitrite, and 10 ppm of NO were added to the chamber from a glass bulb, and ~200–400 μg m^{-3} of seed particles were added from an evaporation-condensation apparatus. Relatively high mass concentrations of seed particles were used so that semi-volatile compounds would condense to particles, minimizing vapor deposition to chamber walls (Zhang et al., 2014; Matsunaga and Ziemann, 2010). Blacklights covering two of the chamber walls were then turned on for 60 min to form OH radicals by methyl nitrite photolysis (Atkinson et al., 1981). The amount of n-alkane reacted was measured by collecting Tenax® samples before and after the experiment and analyzing by gas chromatography with flame ionization detection (GC-FID). Aerosol volume concentrations were measured using a scanning mobility particle sizer (Docherty et al., 2005) and converted to an SOA mass formed using a density of 1.06 g cm^{-3}. SOA mass yields (mass of SOA formed/mass of n-alkane reacted) were calculated from the measured SMPS mass (corrected for particle wall loss using the ~20% h^{-1} decay in mass after the lights were turned off) and the GC-FID analyses. The final SOA mass concentrations were in the range of ~300 – 6000 μg m^{-3} depending on precursors (Lim and Ziemann, 2009b). The SOA yields measured in these experiments were reported previously (Lim and Ziemann, 2009b), but in light of a recent comparison of the accuracy of our SMPS measurements with filter sampling the values reported here are higher by a factor of 1.24 (Bakker-Arkema and Ziemann, 2021).

A temperature-programmed thermal desorption (TPTD) method was also used to measure thermal desorption temperatures of DOS that was present as seed particles in n-alkane SOA. Particles were sampled directly from the chamber into a thermal desorption particle beam mass spectrometer (Tobias et al., 2000), where they were formed into a beam inside an aerodynamic lens, transported into a high vacuum chamber, and impacted on a copper rod vaporizer that was coated with a non-stick polymer and cooled to –40°C. Note that compounds with vapor pressure <10^{-5} Torr is estimated to undergo negligible evaporation with the residence time of ~0.2 s in the aerodynamic lens (Tobias et al., 2000). After sampling for 30 min, the vaporizer was warmed by room air to –5°C and then heated at 2°C min^{-1} to 200°C. Compounds desorbed according to volatility and entered a quadrupole mass spectrometer, where they were ionized by 70 eV electrons prior to mass analysis. In one recent n-hexadecane experiment, the composition of nitrate, hydroxyl, carbonyl (ketone + aldehyde), carboxylic acid, ester, and peroxide functional groups in SOA was measured using derivatization-spectrophotometric methods, with the amount of -CH_2- groups calculated by difference (Ranney et al., 2023). We note that in that experiment the SOA yield measured by filter sampling was nearly identical to the one we measured previously after applying the above correction.

Results and discussion

SOA yields and viscosity.

Figure 1 shows comparisons of measurements and modeling for (a) SOA yields, (b) functional group distributions, (c) N:C ratios, and (d) O:C ratios. Figure 1(a) shows the measured yields of SOA generated from the oxidation of n-alkanes (C_nH_{2n+2}; n = 8 - 17) (Lim and Ziemann, 2009b). The model base case (black line) with mass accommodation coefficient of 1 for all species represents no kinetic limitations in the particle phase and the results are similar to previous simulations performed by La et al. (2016). Vapor wall loss was considered based on experimental observations and previous modeling studies (Krechmer et al., 2016; La et al., 2016; Lim and Ziemann, 2009b), which is important to account for as no wall loss would lead to a significant overestimation of SOA yields, as shown in the black dotted line and was discussed in detail in La et al. (2016). Both experimental and simulated SOA yields increase with an increase of *n*, reflecting the decrease in volatility of the precursor and its oxidation products (Shiraiwa et al., 2014). The observed SOA yield trend is consistent with measurements by a thermal desorption particle beam mass spectrometer, showing that n-alkane SOA are composed of less oxidized products with lower volatility for precursors with higher *n* (Lim and Ziemann, 2009b, a).

The overall good agreement suggests that multigenerational chemistry in the gas phase and partitioning of semi- and low-volatile products, as explicitly treated by GECKO-A box modeling, are the dominant pathway of n-alkane SOA formation under these conditions. It also suggests that peroxy radicals ($RO_2^{\cdot}$) mainly react with NOx, minimizing auto-oxidation and gas-phase dimerization by $RO_2^{\cdot} + RO_2^{\cdot}$ reactions. Good model agreement also suggests that particle-phase oligomerization chemistry is not a dominant process, while particle-phase unimolecular reactions including cyclization of hydroxyketones and dehydration of cyclic hemiacetals forming dihydrofurans are treated in the model as they are important for the further oxidation due to the presence of a double bound in the dihydrofurans (Lim and Ziemann, 2009a; La et al., 2016). Thus, the GECKO-A model seemingly treats all essential processes for simulations of n-alkane SOA formation under high NOx conditions. Note that a very recent study suggested that cyclic hemiacetals form acetal dimers in the particle phase for SOA formed from the reaction of n-hexadecane SOA and OH/NOx (Ranney et al., 2023). In addition, particle-phase chemistry was shown to be substantial in n-alkane SOA formation under low NOx conditions through peroxyhemiacetal and oligomer formation (Shiraiwa et al., 2013; Ziemann and Atkinson, 2012). The impact of such particle-phase chemistry may warrant further investigations by future model development and experimental studies.

To explore the potential impacts of particle phase state on SOA formation and partitioning, we implemented an effective mass accommodation coefficient (α_{eff}) which can effectively consider kinetic limitations of bulk diffusion and also account for the effect of vapor pressure on partitioning kinetics for species with various volatilities (Shiraiwa and Pöschl, 2021). Bulk diffusivity evolves upon SOA formation, which can be derived by viscosity and T_g as predicted from the machine learning-based tgBoost model (dashed green line in Fig. 1a) and the compositional parametrization (CP, dashed orange line in Fig. 1a). The simulated SOA yields with tgBoost are very similar to the base case scenario with $\alpha = 1$, while the application of the CP leads to smaller SOA yields for n = 15-17. These results indicate that α_{eff} is close to 1 with little kinetic limitations of bulk diffusion for most cases, except some limitations are predicted by CP for large precursors. Deviations of tgBoost and CP stem from the difference in phase state and viscosity predicted by the two methods.

Figure 2(a) shows the simulated viscosity and corresponding bulk diffusivity of n-alkane SOA. Remarkably, the two models predict contrasting trends. The simulated glass transition temperature ($T_{g,org}$) of SOA is presented in Fig. A1. The CP predicts a decrease in $T_{g,org}$ for C_{8-12} with the lowest $T_{g,org}$ of ~250 K, which is likely due to a decrease of O:C ratio (Fig. 1d) as lower O:C ratio can lead to a decrease of T_g (DeRieux et al., 2018; Shiraiwa et al., 2017), followed by an increase of $T_{g,org}$ with n to reach ~270 K with C_{17}. These values correspond to viscosity of 10^4 - 10^6 Pa s, indicating that n-alkane SOA adopts viscous semisolid phase state. The increase of viscosity for larger precursors is apparently reasonable, as their oxidation products would have higher molar mass which would generally correspond to higher $T_{g,org}$ (Koop et al., 2011; Shiraiwa et al., 2017). Based on the Stokes-Einstein relation, bulk diffusivity would be in the range of 3×10^{-15} - 10^{-12} cm^2 s^{-1}. The characteristic timescale of bulk diffusion in an average particle diameter of 300 nm can be as low as ~2 hours (Shiraiwa et al., 2011), which is longer than experimental timescale of one hour. These low diffusivities and long diffusion timescale can induce concentration gradients in the particle bulk, reducing α_{eff} to cause significant kinetic limitations to retard SOA growth, which is not consistent with the measured SOA yields.

tgBoost predicts the opposite trend, predicting a monotonic decrease of $T_{g,org}$ and viscosity with an increase of n, suggesting that SOA phase state shifts from an amorphous semisolid state ($10^2 < \eta < 10^5$ Pa s) towards a liquid-like phase state ($\eta < 10^2$ Pa s). These results are counter-intuitive as T_g values of n-alkanes increases with an increase of n, which can be reproduced with great precision by tgBoost (Galeazzo and Shiraiwa, 2022). The determinants explaining this unexpected trend are chemical composition and molecular structure of the oxidation products as discussed below. The characteristic timescale of bulk diffusion is less than one second in a low viscous state and high bulk diffusivity (Shiraiwa et al., 2011) and SOA particles are expected be homogeneously well-mixed. Hence, α_{eff} remains very close to 1 with little kinetic limitation of bulk diffusion.

Unfortunately, no direct viscosity measurements of n-alkane SOA generated under high NO_x conditions are available to date, while there are two studies for n-alkane SOA generated under NOx-free conditions. Saukko et al. (2012) (Saukko et al., 2012) observed that n-heptadecane ($C_{17}H_{36}$) SOA with low O:C ratio did not bounce from an impactor plate. It indicates that these particles adopted a liquid-like state, as indicated by the violet shading in Fig. 2(a), which is consistent with the tgBoost prediction. Shiraiwa et al. (2013) estimated bulk diffusivity of n-dodecane ($C_{12}H_{26}$) SOA generated without NO_x to be 10^{-12} cm^2 s^{-1} using a kinetic multilayer model to simulate evolution of particle size distribution. While these two data points cannot be directly compared with the viscosity predictions of high NOx n-alkane SOA, they serve as reference data points for now and direct viscosity or bulk diffusivity measurements of high NO_x n-alkane SOA are warranted in future studies.

Figure 2(b) shows the thermal desorption profiles of DOS that was present as seed particles within the SOA formed from oxidation of the n-alkanes. Since DOS desorption involved diffusion through the SOA prior to escape into vacuum, these profiles provided a means for probing the SOA viscosity. The peaks in the DOS profiles for the C_{8-13} and C_{14-17} n-alkanes are closely grouped, with vaporizer temperature at ~80 °C and ~65 °C, respectively, with the peak for pure DOS occurring in between at ~72°C. The observed decrease in desorption temperatures from low to high carbon numbers suggests an increase in effective volatility of DOS in SOA generated from larger n-alkanes. In addition, Lim and Ziemann (2009) have observed that C_{10} n-alkane SOA generated under high NOx conditions evaporate at higher temperatures compared to C_{12} and C_{15} n-alkane SOA based on total ion thermal desorption measurements (Lim and Ziemann, 2009b). Volatility and T_g were shown to exhibit clear anticorrelation (Li et al., 2020); hence, these results strongly indicate that C_{8-13} SOA have higher T_g and viscosity compared to C_{13-17} SOA. It is remarkable to note that the C_{13} profile is bimodal with peaks at ~80 °C and ~65 °C (Fig. 2b), which is in line with tgBoost prediction that the viscosity of C_{13} alkane SOA is at the edge of amorphous semi-solid and liquid phase states (Fig. 2a). These results indicate that n-alkane SOA generated by larger precursors adopt low viscous liquid-like states, while n-alkane SOA generated by smaller precursors adopt viscous semisolid states, in agreement with tgBoost predictions. The major strength of tgBoost is that it considers molecular structure and functionality for T_g predictions, while the compositional parameterization does not account for this effect, leading to intuitive but erroneous predictions.

Chemical composition of SOA.

Figure 1 also shows the simulated (c) N:C and (d) O:C ratios of SOA with $\alpha = 1$ (black line) and $\alpha = \alpha_{eff}$ with T_g determined with tgBoost (green line) or the compositional parameterization (orange line). The N:C ratio is very similar among all simulations being ~0.2 for C_8 and decreasing progressively to ~0.03 with each addition of a carbon atom in the precursor. O:C ratios were calculated in two different ways by treating a nitrate ($-ONO_2$) group to contain either three (solid lines) or one (dashed lines) oxygen atoms. One oxygen atom is also considered because O:C ratios reported from aerosol mass spectrometer measurements generally treat a nitrate group the same as a hydroxyl group, since they have the same effect on oxidation state (Farmer et al., 2010). Similar to the N:C ratio, there is a constant decrease in O:C of SOA with increasing *n*, which is consistent with previous measurements for n-pentadecane ($C_{15}H_{32}$) SOA (Aimanant and Ziemann, 2013a) and n-hexadecane ($C_{16}H_{34}$) SOA in this study, even though the simulated values are ~45% and 15% lower than the measured N:C and O:C ratios, respectively. The discrepancies are likely due to errors on modeling gas-wall partitioning and gas-particle partitioning. The difference may also be caused by missing processes in the model such as reactive uptake of oxidants and particle-phase chemistry.

We measured functional group distributions in n-hexadecane SOA using derivatization-spectrophotometric methods described in Aimanant and Ziemann (2013b), as shown in Fig. 1(b) and summarized in Table A1. Experimental measurements report high presence of $-CH_2-$ (13.81) and $-ONO_2$ (0.91), followed by ROH (0.41), RC(=O) (0.38), and RC(=O)OR (0.28), with the average measured number of groups per C_{16} molecule in parenthesis. Figure 1(b) includes simulation results by GECKO-A with CP and tgBoost, showing overall satisfactory agreement. The simulated results with tgBoost show excellent agreement for hydroxyl and methylene groups, while the simulated nitrates and carbonyls (ketones + aldehydes) are lower than the measurements. The simulation by CP has also a similar trend, but with significantly lower presence of nitrates, carbonyls, and esters.

Figure 3(a) shows the top 15 oxidation products in the particle phase formed by the oxidation of n-hexadecane simulated by GECKO-A box model with tgBoost. Note that positional isomers are lumped into one species and that the five species in the first row constitute majority (~86%) of SOA mass. The simulated SOA is composed mostly by 1st generation products including alkyl nitrates, hydroxynitrates, and hydroxyketones. There is also a significant presence of 2nd and 3rd generation products such as esters and dinitrates. We also found multi-functionalized decomposition products including smaller chain hydroxy nitrates and alkyl lactones as well as particle-phase products from cyclization of hydroxyketones and dehydration of cyclic hemiacetals to form dihydrofurans. A very recent study by Ranney et al. (2023) measured n-hexadecane oxidation products under high NOx, finding that alkyl nitrates, hydroxyl nitrates, hydroxyl carbonyls, cyclic hemiacetals, and cyclic hemiacetal nitrates are major products. These compounds are indeed major products as shown in Fig. 3a, confirming that GECKO-A simulated n-alkane oxidation very well. There are notable differences in molecular composition for SOA simulated by CP (Fig. A2): the major compounds are 1st generation single and multi-functionalized products, followed by some 2nd and 3rd generation products, without decomposition products in the top species.

The simulated T_g by both methods for each compound are listed in Fig. 3. Overall tgBoost predicts T_g to be 157 – 221 K which are much lower compared to CP, especially with significant differences for organic nitrates and multi-functionalized species. As tgBoost considers the molecular structure, functional group and atomic interconnectivity of a molecule, it should make better predictions for multi-functionalized compounds based on the presence of different functional groups. CP is based on elemental composition and it predicts high T_g for compounds with high molar mass, predicting same T_g for isomers. In addition, the CP for CHON compounds was developed based on T_g values mainly estimated from their melting points, as there are limited number of CHON compounds with measured T_g available. T_g of organic nitrates are especially scarce and future T_g measurements for organic nitrates are desired to improve T_g parameterizations. For these reasons, CP overestimates T_g for oxidation products of n-alkane with long chain on average by ~66 K compared to tgBoost, overpredicting SOA viscosity as shown in Fig. 2(a).

Figure 3 also lists α_{eff} values, showing that they are very close to 1 for tgBoost, with SOA to be low viscous liquid with little kinetic limitations in mass accommodation. Additional oxidation products with lower concentrations are listed in Fig. A3 and their α_{eff} remain also close to 1. In contrast, as CP predicts the SOA phase state to be viscous amorphous semisolid, α_{eff} values for semi-volatile compounds become significantly smaller to kinetically limit mass accommodation. This decrease of α_{eff} is larger for compounds with higher volatility, as such compounds have higher re-evaporation rate on viscous particles with lower rate of bulk diffusion (Shiraiwa and Pöschl, 2021) (Fig. A3). α_{eff} for lower volatility compounds remain high, as they exhibit much lower desorption rates and are less likely to re-evaporate, even if their diffusion into the bulk is slow. Consequently, SOA simulated with CP mainly consists of later generation products with higher functionalization and molar masses.

Figure 3(b) shows top 15 oxidation products of n-decane ($C_{10}H_{26}$) as predicted by GECKO-A with tgBoost. SOA is mostly composed of 2nd and 3rd generation products with multiple functional groups including nitrates, ketones, and alcohols. These highly oxidized products have T_g in the range of 225 – 304 K, with similar predictions by CP and tgBoost. This is consistent with previous studies that demonstrated successful applications of CP to predict the measured viscosity of SOA derived from biogenic and other relatively small precursors (DeRieux et al., 2018; Smith et al., 2021; Baboomian et al., 2022). These results are consistent with total ion thermal desorption profiles of n-alkane SOA formed in the presence of NOx (Lim and Ziemann, 2009b): C_{10} SOA was observed to have a broad single peak around ~75 °C, indicating the presence of low volatility multigenerational products; in contrast, C_{12} and C_{15} SOA exhibited two peaks with one larger peak at lower temperature, corresponding to 1st generation products and another smaller peak for multigenerational products. The phase state of n-decane SOA is predicted to be semisolid, but kinetic limitations are not strong as α_{eff} values for most compounds are only slightly reduced from 1.

Effects of mass loadings on viscosity.

The use of higher mass loadings in chamber experiments than ambient conditions assured that the condensation of semi-volatile vapors to suspended particles is a dominant process over vapor wall deposition (Zhang et al., 2014; Matsunaga and Ziemann, 2010). Chamber experiments of n-alkane photooxidation at high NO_x were also conducted with lower mass loading by Presto et al. (2010), who measured temporal evolution of SOA yields as shown in Fig. 4(a). SOA yields are increased with an increase of SOA mass concentrations, which is consistent with SOA absorptive partitioning theory (Pankow, 1994). The oxidation of larger precursors leads to higher SOA yields, in agreement with Lim and Ziemann (2009b) as presented in Fig. 1a. As shown with solid lines, the GECKO-A box model simulated experimental observations of SOA yields very well.

Figure 4(b) depicts the simulated SOA viscosity. We observed the same trend as Fig. 2(a) with lowering of viscosity upon an increase of carbon number *n*. SOA phase state is predicted to be semisolid for low carbon *n*, while it is expected to be liquid for high *n*. The predicted viscosity is about one order of magnitude higher compared to Fig. 2(a). Lower mass loadings suppress partitioning of higher volatility compounds, resulting in higher viscosity as condensation would be dominated by lower volatility compounds with higher T_g (Jain et al., 2018; Champion et al., 2019; Grayson et al., 2016; DeRieux et al., 2018).

Atmospheric Implications.

The phase state and viscosity of SOA formed by IVOCs have been largely unknown and unexplored. We demonstrated in this study that SOA derived from small and middle size n-alkane (C_{12} and smaller) mostly consists of multigenerational oxidation products to adopt an amorphous semisolid state, while larger n-alkane SOA are mainly composed of first generation lightly oxidized products to adopt a low viscous liquid state. This result is counter-intuitive, as it has been established that higher molar mass would lead to higher glass transition temperature, and hence, higher viscosity (Koop et al., 2011; Shiraiwa et al., 2017). In fact, the viscosity of biogenic SOA follows this trend: the viscosity of isoprene (C_5H_8) SOA is reported to be lower than monoterpene ($C_{10}H_{16}$, such as α-pinene and limonene) SOA (Renbaum-Wolff et al., 2013; Zhang et al., 2019), while oxidation products of sesquiterpene ($C_{15}H_{24}$) increase viscosity of SOA (Smith et al., 2021), which is captured by empirical parameterizations based on elemental composition (DeRieux et al., 2018; Li et al., 2020). In contrast, n-alkane SOA exhibits an opposite trend, as indicated by thermal desorption measurements that show that DOS in SOA formed by oxidation of large n-alkanes has higher volatility. Hence, the SOA has lower viscosity, due to the enhanced presence of less functionalized first-generation products (Li et al., 2020; Zhang et al., 2019). This trend is successfully predicted by GECKO-A combined with machine learning-based model tgBoost, which emphasizes the importance of consideration of functionality and molecular structure in accurate predictions of T_g. The relationship between viscosity and composition is also reflected in the atomic O:C and N:C ratios of n-alkane SOA, which decrease monotonically upon an increase of carbon number of the n-alkane, since higher oxidation state and functionalization can increase T_g (DeRieux et al., 2018; Koop et al., 2011; Shiraiwa et al., 2017; Saukko et al., 2012).

IVOCs have gained growing attention for better characterization of urban air quality, as they represent an important source of SOA as shown by chamber experiments (Aimanant and Ziemann, 2013a; Lim and Ziemann, 2009b) and as observed in field observations (Gentner et al., 2012; Li et al., 2022; Robinson et al., 2007; McDonald et al., 2018). While a few large-scale aerosol models treat IVOC SOA to achieve better agreement with ambient measurements (de Gouw et al., 2011; Li et al., 2022; Zhao et al., 2016), IVOC SOA is still highly uncertain in terms of chemical composition and particle phase state and model parameters and treatments for SOA formation and partitioning are poorly constrained. Our study provides critical insights for these aspects, showing that n-alkane SOA formation under high NOx conditions (as usually the case for ambient urban air) is dominated by gas-phase chemistry followed by partitioning. As the generated SOA particles adopt a low viscous state, there is little kinetic limitations of mass accommodation and bulk diffusion, which supports the application of equilibrium SOA partitioning in the boundary layer. While the experiments and modeling were conducted for dry conditions in this study, the phase state and viscosity of ambient n-alkane SOA would be expected to be even lower under humid conditions due to hygroscopic growth and water acting as plasticizer. Note that further experiments and model simulations are required for different conditions for middle and upper free troposphere, as viscosity is expected to become higher under low temperatures.

It is highly remarkable that the combination of tgBoost and GECKO-A box model accurately simulates SOA yields, functional group distributions and phase state. This new model represents a unique and comprehensive tool for simulating formation, partitioning and chemical evolution of SOA, opening up a new avenue for analyzing complex interplay of gas-phase chemistry and particle-phase processes and composition in SOA for detailed analysis and interpretation of laboratory experiments and field observations. In addition, we propose to pursue the application of this model as a basis for the development of a detailed master mechanism of multiphase aerosol chemistry as well as for the derivation of simplified but realistic parameterizations for air quality and climate models. In regional and global air quality models, it is challenging and computationally very expensive to treat complex SOA multiphase processes. Thus, such processes should be treated in efficient but effective way and the new model shall serve as benchmark for the development of simplified SOA descriptions.

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Authors contributions. TG and MS designed the study. TG conducted model simulations and data analysis. RV, MC, and BA developed the GECKO-A model. YL and PZ conducted experimental measurements. All authors discussed the results. TG and MS wrote the manuscript with contributions from all coauthors.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

Code/Data availability. The simulation data may be obtained from the corresponding author upon request. The model tgBoost is available in Github (https://github.com/U0M0Z/tgpipe) and in the homepage (https://azothai.ps.uci.edu/).

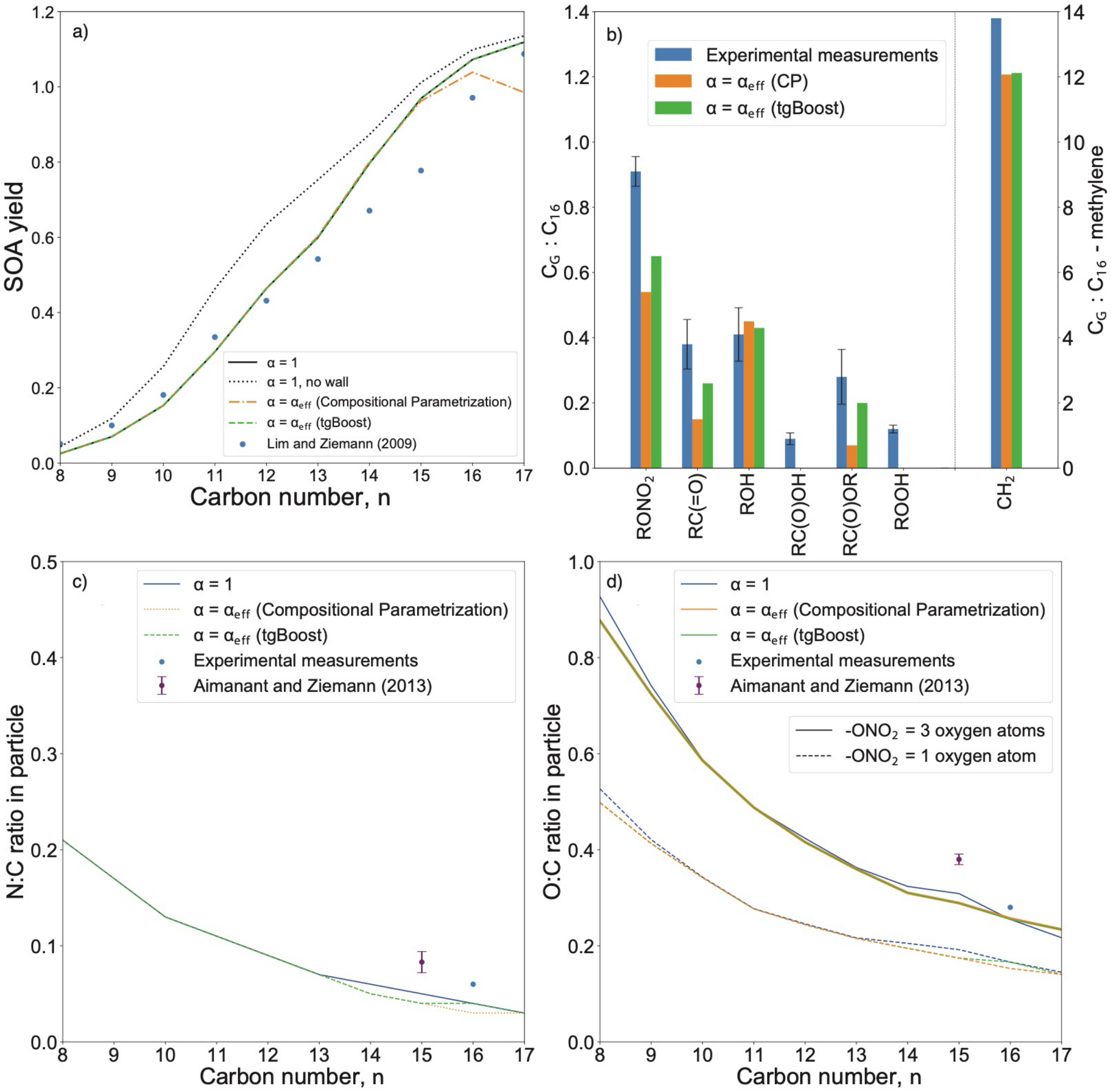

Figure 1: (a) Yields of SOA generated from OH oxidation of linear n-alkanes as measured by Lim and Ziemann (2009) (markers) (Lim and Ziemann, 2009b) and modeled by the GECKO-A box model (lines). The black line represents the base case with mass accommodation coefficient (α) of 1. The dashed lines represent simulations with effective mass accommodation coefficient (α_{eff}) as a function of bulk diffusivity from tgBoost (green) and the compositional parameterization (orange). (b) Simulated functional group distributions of n-hexadecane ($C_{16}H_{34}$) oxidation products in the particle phase. The blue bars represent experimental measurements. The green and orange bars represent GECKO-A box model simulations with α_{eff} with tgBoost and the compositional parameterization, respectively. (c) N:C and (d) O:C ratios in SOA formed by n-alkane oxidation simulated by the GECKO-A box model. The black line represents the base case with α of 1. The dashed lines represent simulations with α_{eff} with tgBoost (green) and the compositional parameterization (orange).

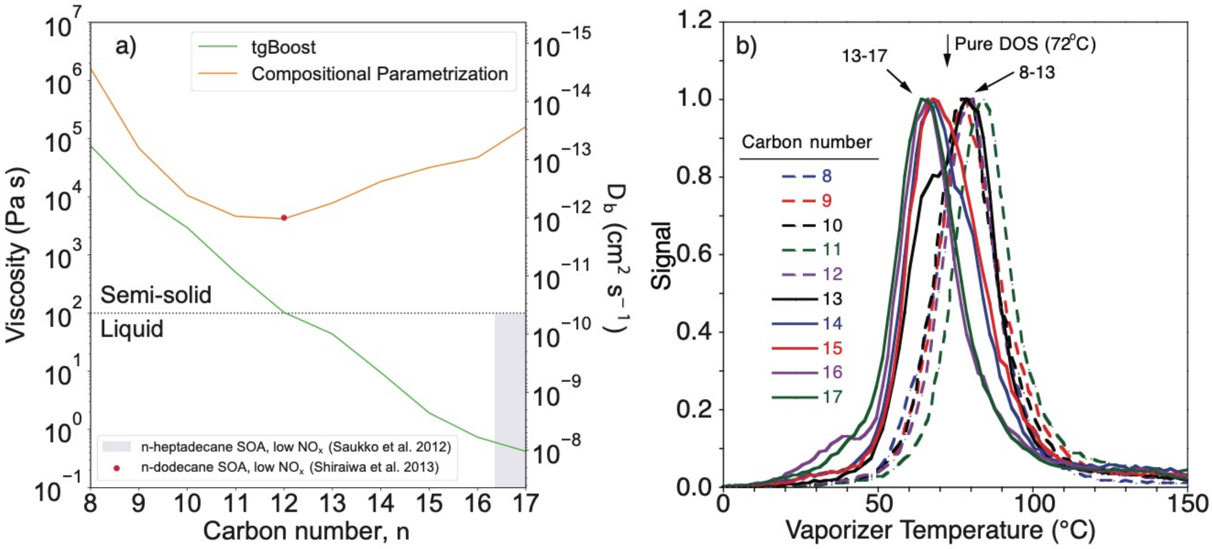

Figure 2: Phase state of n-alkane SOA. (a) Predicted viscosity of SOA generated from n-alkanes as computed by the GECKO-A box model with the T_g compositional parametrization (orange line) and tgBoost (green line) at the last step of the simulations (t = 3600 s). (b) Thermal desorption temperatures of dioctyl sebacate (DOS) that was present as seed particles in n-alkane SOA.

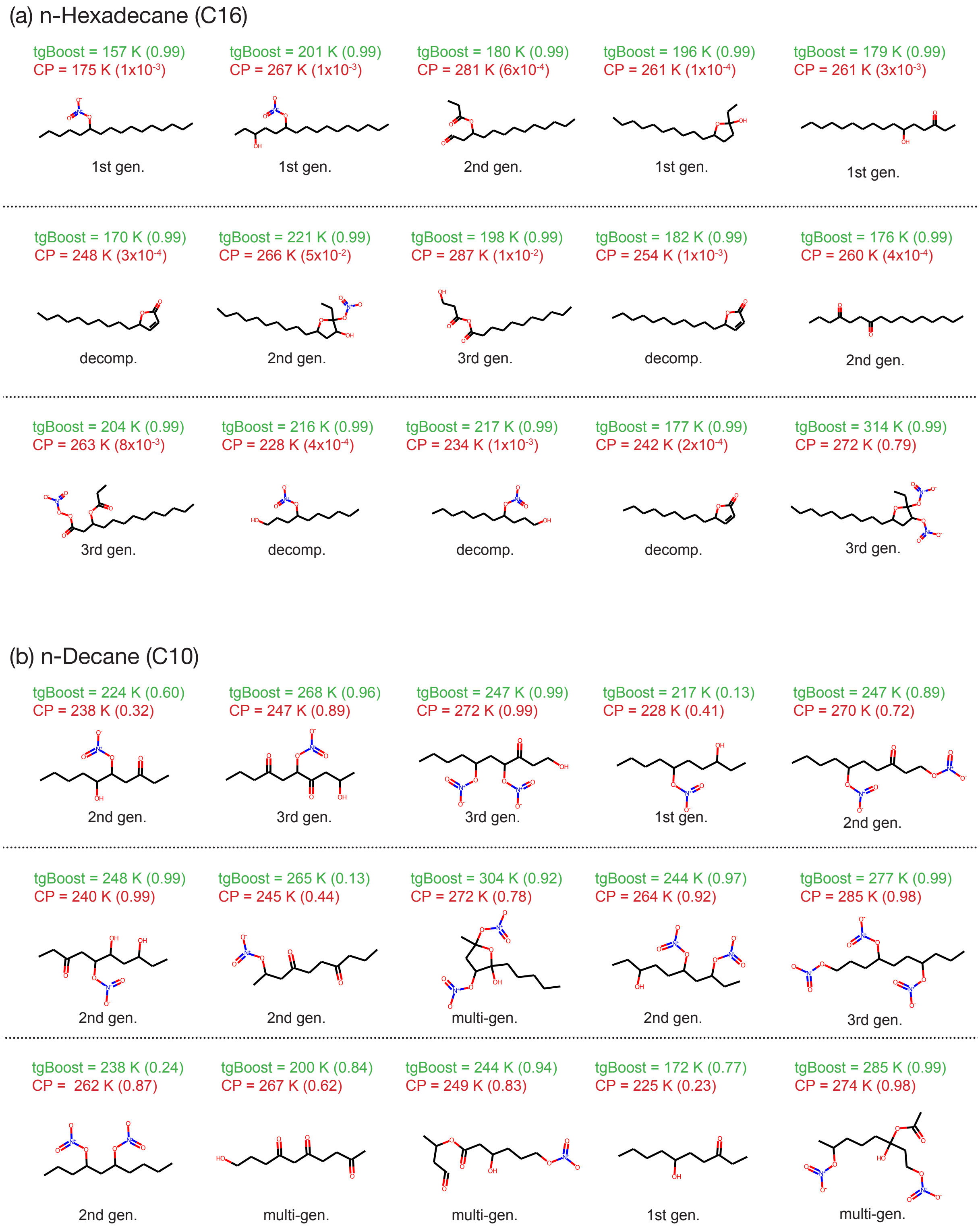

Figure 3: Molecular composition of oxidation products of n-alkanes under high NOx conditions in the particle phase. Top 15 SOA contributors with highest concentrations in (a) n-Hexadecane ($C_{16}H_{34}$) SOA and (b) n-Decane ($C_{10}H_{32}$) simulated by GECKO-A with effective mass accommodation coefficient (α_{eff}) with tgBoost. The species are reported in descending concentrations from left to right and from top to bottom. Positional isomers are lumped into one species. Listed values are T_g as calculated by tgBoost and CP and α_{eff} values at the end of simulation (3600 s) in brackets. Types of compounds are also noted (1st, 2nd, and 3rd generation products, decomposition products).

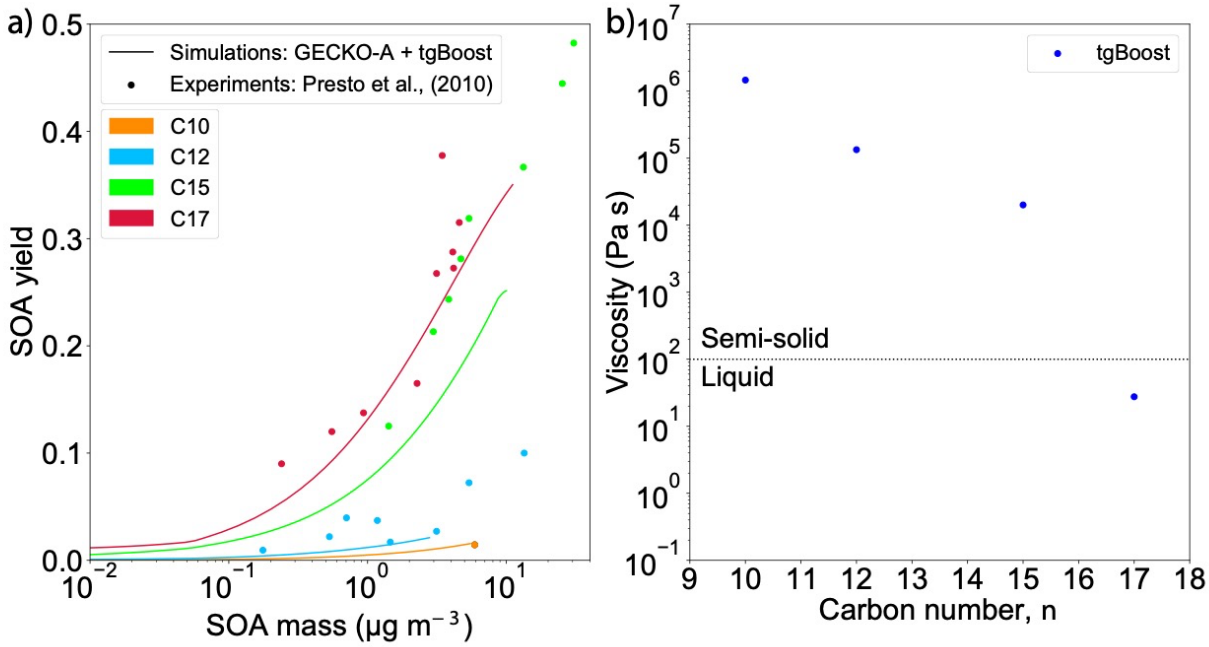

Figure 4: Effects of mass loadings on SOA yields and viscosity. (a) SOA yields from photo-oxidation of n-decane (C10), n-dodecane (C12), n-pentadecane (C15), and n-heptadecane (C17) at high NOx as a function of SOA mass concentration, as measured in Presto et al. (2010) (markers) and as modeled by the GECKO-A box model combined with tgBoost (lines). (b) SOA viscosity as modeled by the GECKO-A box model combined with tgBoost.

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Appendix.

Table A1: Experimental and simulated functional group distributions, O:C and N:C ratios of SOA generated from C16 oxidation by OH in presence of high NO_x.

FG/C16 molecule	Experimental	Simulated (tgBoost)	Simulated (CP)
Nitrate	0.91	0.65	0.54
Carbonyl	0.38	0.26	0.15
Hydroxyl	0.41	0.43	0.45
Carboxyl	0.09	0.0	0.0
Ester	0.28	0.2	0.07
Peroxide	0.12	0.01	0.0
Methylene	13.81	12.12	12.07
O:C	0.28	0.25	0.25
N:C	0.06	0.04	0.03
H:C	1.85	/	/
MW	294	/	/
Density (g cm^{-3})	1.10	1.06	1.06

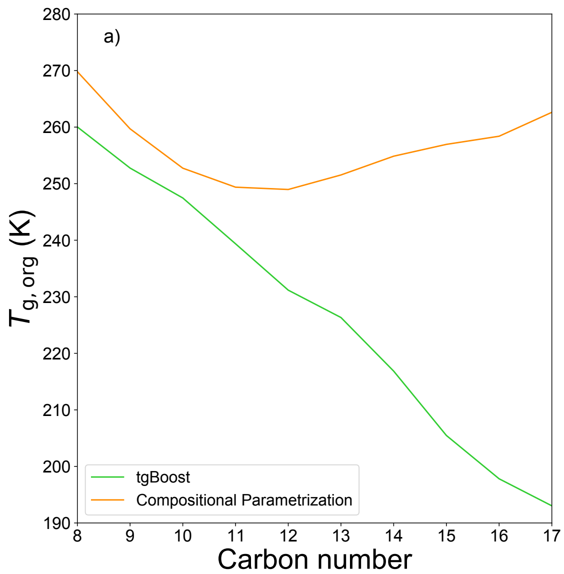

Figure A1: Predicted $T_{g,org}$ of SOA generated from n-alkanes as computed by the GECKO-A box model with the T_g compositional parametrization (orange line) and tgBoost (green line) at the last step of the simulations (t = 3600 s).

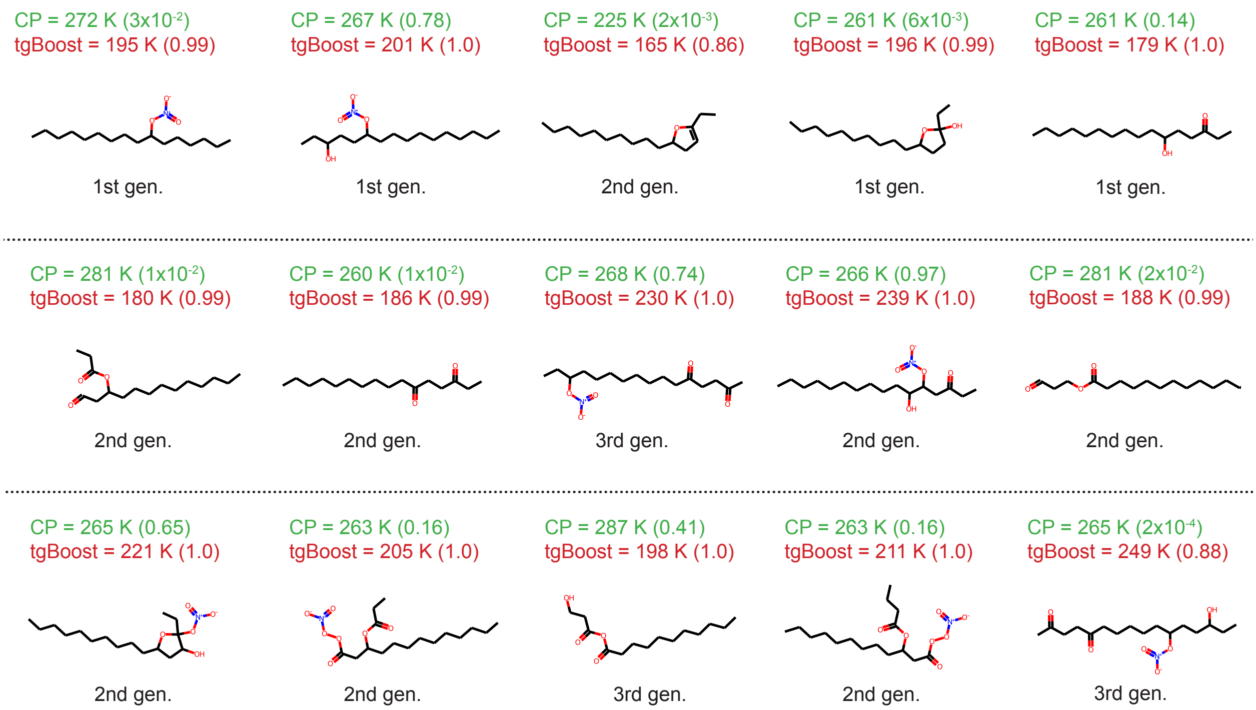

Figure A2. Top 15 species with highest concentrations in oxidation products of n-hexadecane ($C_{16}H_{34}$) under high NOx conditions simulated by GECKO-A with effective mass accommodation coefficient (α_{eff}) with the compositional parameterization. The species are reported in descending concentrations from left to right and from top to bottom. Listed values are T_g as calculated by tgBoost and CP and α_{eff} values at the end of simulation (3600 s) in brackets. Types of compounds are also noted (1st, 2nd, and 3rd generation products, decomposition products).

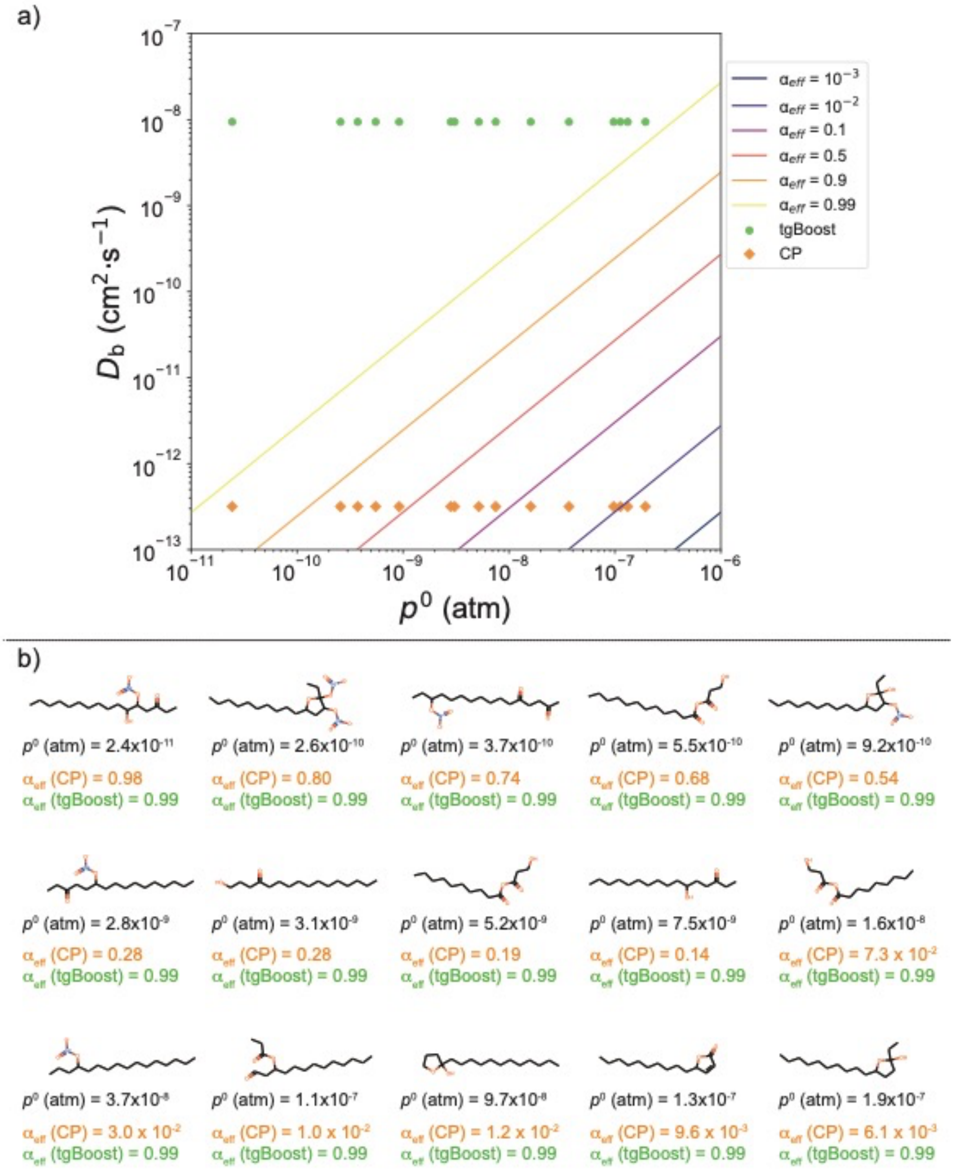

Figure A3. a) α_{eff} isolines as a function of bulk diffusivity D_b and saturation vapor pressure p^o of semi-volatile species. b) Selection of various representative SOA contributors produced during the oxidation of n-hexadecane. The species are ordered by decreasing vapor pressure. The reported α_{eff} values for each SOA contributor are calculated for D_b estimated with tgBoost ($D_b = 1\times10^{-8}$ cm^2 s^{-1}) and CP ($D_b = 3\times10^{-13}$ cm^2 s^{-1}). The values of α_{eff} for the selected species are reported as points in the top panel. It shows that for the liquid-like state estimated with the tgBoost configuration, α_{eff} tend towards 1 for all species. This behavior is not observed in the amorphous semi-solid state estimated using the CP model configuration for species with p^o above 10^{-9} atm. For the simulated conditions, species with p^o between 10^{-8} and 10^{-6} atm are of enough low volatility to partition between the particle and gas phases at equilibrium. For species in that volatility range, no mass transfer limitation is observed with the tgBoost configuration, unlike the CP configuration. Using the CP configuration, the most volatile SOA contributors are subjected to substantial mass transfer limitation and are therefore mainly eliminated by gas-phase oxidation or wall deposition.