Constraints on the role of Laplace pressure in multiphase reactions and viscosity of organic aerosols

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Abstract

Aerosol chemistry has broad relevance for climate and global public health. The role of interfacial phenomena in condensed-phase aerosol reactions remains poorly understood. In this work, liquid drop formalisms are coupled with high-pressure transition state theory to formulate an expression for predicting the size-dependence of aerosol reaction rates and viscosity. Insights from high-pressure synthesis studies suggest that accretion and cyclization reactions are accelerated in 3-10-nm particles smaller than 10 nm. Reactions of peroxide, epoxide, furanoid, aldol, and carbonyl functional groups are accelerated by up to tenfold. Effective rate enhancements are ranked as: cycloadditions >> aldol reactions > epoxide reactions > Baeyer-Villiger oxidation >> imidazole formation (which is inhibited). Some reactions are enabled by the elevated pressure in particles. Viscosity increases for organic liquids but decreases for viscous or solid particles. Results suggest that internal pressure is an important consideration in studies of the physics and chemical evolution of nanoparticles.

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Key Points:

- An expression is formulated describing size-dependent aerosol reaction rates and viscosity by linking Köhler theory with organic chemistry
- Reactions of peroxides, epoxides, furans, aldols, carbonyls, and others are predicted to be up to tenfold faster in 3–10-nm particles
- Aerosol viscosity at the nanoscale varies as a function of the thermal properties, compressibility, and surface tension of the material

Abstract

Aerosol chemistry has broad relevance for climate and global public health. The role of interfacial phenomena in condensed-phase aerosol reactions remains poorly understood. In this work, liquid drop formalisms are coupled with high-pressure transition state theory to formulate an expression for predicting the size-dependence of aerosol reaction rates and viscosity. Insights from high-pressure synthesis studies suggest that accretion and cyclization reactions are accelerated in 3–10-nm particles smaller than 10 nm. Reactions of peroxide, epoxide, furanoid, aldol, and carbonyl functional groups are accelerated by up to tenfold. Effective rate enhancements are ranked as: cycloadditions » aldol reactions > epoxide reactions > Baeyer-Villiger oxidation » imidazole formation (which is inhibited). Some reactions are enabled by the elevated pressure in particles. Viscosity increases for organic liquids but decreases for viscous or solid particles. Results suggest that internal pressure is an important consideration in studies of the physics and chemical evolution of nanoparticles.

Plain Language Summary

Airborne particles (aerosols) are ubiquitous and have broad relevance to climate and public health. Chemical reactions in particles can alter their volatility, light absorption, toxicity, and hygroscopicity. These reactions are difficult to characterize due to the difficulty of detecting interfacial phenomena and molecules in nanoparticles. This work derives an expression to predict changes in reaction rates and viscosity of nanoparticles; the expression is then used in conjunction with a survey of data from organic synthesis studies to make predictions relevant to atmospheric chemistry. Viscosity and reaction rates change due to constriction by the force of surface tension, which raises internal pressure. Concerted cyclization and accretion reaction rates were predicted to be enhanced; the net effect on multi-step reactions is inhibition. Incorporation of these insights into atmospheric chemistry changes the way we interpret activity and reactivity in the aerosol phase.

1 Introduction

Aerosols have far-reaching impacts including adverse health effects, reduction in visibility, modification of clouds, and alteration of the Earth's climate. Aerosols affect climate by absorbing or scattering solar radiation, regulating condensation and evaporation of atmospheric trace gases including water, and affecting cloud properties by serving as cloud condensation nuclei (CCN). The substantial role of aerosols in the hydrological cycle is a significant source of uncertainty in climate projections (Forster et al., 2021).

Nucleation and growth of new particles is the major contributor to both particle number and CCN-active particles in the atmosphere (H. Gordon et al., 2017; Kulmala et al., 2004; Pierce et al., 2011). The role of organic molecules in the nucleation mechanism is not precisely known (Kürten et al., 2016a,b). Nucleation occurs when a nascent molecular cluster achieves a diameter exceeding ~ 0.7 to 1.7 nm and condensation of additional molecules becomes energetically favorable (Sipilä et al., 2010). New particle formation has been observed in various environments and occurs through different chemical pathways (Kerminen et al., 2018; Kulmala et al., 2004). Although nucleation is driven by the condensation of low-volatility inorganic species such as sulfuric acid, amines, iodic acid, and nitric acid (Baccarini et al., 2020; Kurtén et al., 2008; O'Dowd et al., 2002; Sipilä et al., 2016; Wang et al., 2020; Yao et al., 2018; Zhao et al., 2011), organic molecules can also contribute (Brean et al., 2020; Fang et al., 2020; Kirkby et al., 2016). Further, condensation of organics is necessary for particle growth from ~ 3 nm towards 50–100 nm, where they may serve as CCN (Donahue et al., 2011; Mohr et al., 2019; Tröstl et al., 2016). Despite their ubiquity, the composition and volatility of organic molecules involved in particle formation and growth remain difficult to characterize (Bianchi et al., 2019; Glasius & Goldstein, 2016).

Though condensed-phase reactions have a substantial influence on atmospheric organic chemistry (Herrmann et al., 2015; Su et al., 2020), these reactions remain largely unexplored. The aerosol matrix is partly to blame. Aerosol phases can include, e.g., liquids, phase-separated liquids (Rastak et al., 2017; Renbaum-Wolff et al., 2016), viscous semisolids (S. Petters et al., 2019; Renbaum-Wolff et al., 2013; Virtanen et al., 2010), crystalline solids, and the surface phase (Enami et al., 2017; Eugene et al., 2018; Wei et al., 2018). Water is generally present in atmospheric particles and controls aerosol pH and heterogeneous reaction rates (Ervens et al., 2011; T.K.V. Nguyen et al., 2014; Pye et al., 2020). Aerosol viscosity is thought to play a critical role in determining nucleation and growth rates, but the processes involved are not yet fully understood (Reid et al., 2018). Careful application of experimental, observational, and modeling insights is needed to understand how nanoscale phase controls heterogeneous reactions.

The size-dependent aerosol surface-to-volume ratio and Laplace pressure become especially important at the nanoscale. M. Petters and Kasparoglu (2020) and Cheng et al. (2015) explore the size-dependence changes to aerosol viscosity induced by surface tension (Kaptay, 2012). Riva et al. (2021) explore the pressure dependence of imidazole formation in aerosols. The present work fills gaps in (1) the development of thermodynamic formalisms describing the pressure-induced diameter dependence of particle-phase (a) reaction rates, and (b) viscosity; and (2) evidence and application of interdisciplinary high-pressure sciences to atmospheric organic chemistry.

2 Theoretical Development

Surface tension raises the vapor pressure adjacent to a curved liquid surface relative to its Clausius-Clapeyron or Arrhenius temperature dependence; this effect is described by the Kelvin equation for pure liquids and by Köhler theory for mixtures, e.g., (Bilde et al., 2015; Kreidenweis et al., 2005):

$$S_i = a_i \exp\left(\frac{4\sigma v_i}{\text{RTD}}\right), (1)$$

where subscript *i* denotes the *i*th component, S_i is the vapor pressure outside the interface, a_i is activity, σ is surface tension, v_i is molar volume, R is the universal gas constant, T is temperature, and D is diameter; this is the Köhler equation where i = water. Laplace pressure, Δp_L , is the pressure inside a droplet resulting from intermolecular forces and the interfacial curvature: $\Delta p_L = 2\frac{\sigma}{r} + \frac{d}{dr}$, where r is the droplet radius. A volumeless surface interface is assumed and is defined by the radius-of-tension, r_t , for which $\frac{d}{dr} = 0$, yielding (Laaksonen et al., 1999; Pruppacher & Klett, 2010; Rowlinson & Widom, 1982):

 $\Delta p_L = 2 \frac{\sigma}{r_t}$. (2)

Laplace pressure keeps the condensate in mechanical equilibrium with the gas and is equivalent to $4\sigma/D$ in Köhler theory.

Figure 1 (panel A) estimates Laplace pressure in 3–500 nm particles using Eq. (2) for surface tensions corresponding to highly-concentrated aqueous salt slurries (0.080 N m⁻¹; S. Petters & M. Petters, 2016; Su et al., 2020), water (0.072 N m⁻¹), and pure organic liquid or concentrated aqueous surfactant (0.030 N m⁻¹; Hritz et al., 2016; Korosi & Kovats, 1981; S. Petters & M. Petters, 2016). For 3–10 nm particles, Δp_L is ~100–10 MPa. For 50–100 nm particles, Δp_L is ~6–1 MPa. Reduced atmospheric pressure aloft alters these values by a negligible fraction. Laplace pressure in a 3-nm particle is 400–1000× higher than that of the same material in bulk.

Is this a remarkable pressure? Figure 1 (panels B–D) compares particle internal pressures to pressures encountered in high-pressure chemistry, analytical chemistry, oceanography, and geology. Though aerosol internal pressure is too low to inactivate pathogens (Figure 1, panel C), capillary forces in the microscale could be important to bioaerosol viability (McRae et al., 2021). Pressures in particles 3–10 nm in diameter are close to those encountered in medium- to high-



pressure synthetic organic chemistry, liquid chromatography, the ocean depths, and subsurface drilling.

Figure 1. (A) Particle internal pressure for diameters of 3–500 nm, Δp_L (Eq. 1), using surface tensions of 0.08 (aqueous salts), 0.072 (water), and 0.03 N m⁻¹ (organic). (B) Pressure ranges used in high-pressure chemistry (Benito-López et al., 2008). (C) Pressures encountered in analytical chemistry and food processing. Vera = <u>VOAG</u> (Vibrating Orifice Aerosol Generator) evaporation and residual analysis (S. Petters et al., 2020). House air = laboratory compressed air. LPG = liquified petroleum gas. HPLC = high-performance liquid chromatography. UHPLC = ultrahigh-performance liquid chromatography. HPP = high-pressure Pasteurization of foods (Demazeau & Rivalain, 2011; Grove et al., 2006; Kovač et al., 2010). (D) Pressures encountered in oceanography, geomicrobiology, and petroleum geology; the lithostatic gradient is 22.7 MPa km⁻¹ and the hydrostatic gradient is 10.5 MPa km⁻¹ (Tiab & Donaldson, 2016). Pressures are absolute; v-axes apply to all panels.

How, then, does pressure affect reaction rates? The pressure dependence of a reaction rate constant, $\partial ln \frac{(k)}{\partial} p$, is derived from the free energy change during compression (Evans & Polanyi, 1936; Van Eldik & Kelm, 1980):

$$\Delta \ln(k) = -\Delta p_{\rm rxn} \Delta \frac{V^{\ddagger}}{\rm RT} \ (3)$$

where $k = \frac{k_p}{k_0}$ is the rate enhancement factor, k_p is the rate constant at high pressure, k_0 is the rate constant at the reference pressure, $\Delta p_{\rm rxn}$ is the experimental gauge pressure, and ΔV^{\ddagger} is the change in volume of the reaction transition state. The quantity ΔV^{\ddagger} is parameterizes the pressure dependence of reaction rates in high-pressure synthesis. Reactions are accelerated under pressure if they decrease in volume during the transition state, $\Delta V^{\ddagger} < 0$; reactions with a positive ΔV^{\ddagger} proceed more slowly (Klärner & Wurche, 2000). Cyclic transition states in concerted rearrangements tend to have lower ΔV^{\ddagger} than acyclic intermediates in stepwise reactions (Van Eldik & Hubbard, 1997). Bond-breaking and neutralization reactions tend to have positive ΔV^{\ddagger} , and bond-forming and ionogenic reactions tend to have negative ΔV^{\ddagger} ; this is due to relaxation or constriction of the solvent cage (Isaacs, 1997). For this reason, the volume ΔV^{\ddagger} is often split into intrinsic and the solvent-dependent molar volumes: $\Delta V^{\ddagger} = \Delta V_{intr}^{\ddagger} + \Delta V_{solv}^{\ddagger}$. Experimentally determined ΔV^{\ddagger} ranges are compiled below.

The Laplace and Evans-Polanyi expressions are here combined. Setting Δp_L equal to $\Delta p_{\rm rxn}$ yields an expression describing the reaction rate change due to the aerosol Laplace pressure:

$$\frac{k_p}{k_0} = exp\left(\frac{-4\sigma\Delta V^{\ddagger}}{\text{RTD}}\right).$$
(4)

Equation (4) is not an extension of Köhler theory (Eq. 1); rather, the remarkable similarity between Eqs. (1) and (4) is due to their similar thermodynamics. Equation (1) is based on chemical equilibrium across phase boundaries and Eq. (3), from which Eq. (4) is derived, is based on chemical equilibrium between reactants and the transition state.

Viscosity is altered under high hydrostatic pressure, changing diffusion and vibration timescales and contributing to changes in observed reaction rates. The relationship between $\Delta \ln(k)$ and $\Delta p_{\rm rxn}$ becomes nonlinear as pressure becomes high (Chen et al., 2017). A rate constant expression accounting for viscosity is derived by Sumi (1991): $k_{p'}^{-1} = k_p^{-1} + k_v^{-1}$; k_p is given in Eq. 4 and k_v is proportional to $\eta^{-0.7}$, where η is viscosity. Incorporating viscosity into Eq. (4),

$$\frac{1}{k_{p'}} = \frac{\exp\left(\frac{4\sigma\Delta V^{\ddagger}}{\text{RTD}}\right)}{k_0} + \frac{\eta^{0.7}}{c}, (5)$$

where c is a proportionality constant.

The isothermal pressure dependence of viscosity is predicted using the isothermal compressibility ($\kappa_{T,\xi}$) and isobaric thermal expansion coefficient ($\alpha_{p,\xi}$) (Schmelzer et al., 2005):

$$\left(\frac{\partial\eta}{\partial p}\right)_{T,\xi} = -\frac{\kappa_{T,\xi}(p,T,\xi)}{\alpha_{p,\xi}(p,T,\xi)} \left(\frac{\partial\eta}{\partial T}\right)_{p,\xi} (6)$$

where p is pressure, ξ is a state variable describing the molecular-level order of the mixture (Schmelzer et al., 2011), and $\left(\frac{\partial \eta}{\partial T}\right)_{p,\xi}$ is the slope of $\eta(T)$ at constant pressure. This last term, the temperature-dependent viscosity $\eta(T)$, is predicted using the Vogel–Fulcher–Tammann (VFT) equation: $\log_{10} \eta = A + \frac{B}{(T-T_0)}$; A, B and T_0 are fitted (Fulcher, 1925). Incorporation of the VFT slope into Eq. (6) yields the pressure dependence of viscosity:

$$\left(\frac{\partial\eta}{\partial p}\right)_{T,\xi} = \frac{\kappa_{T,\xi}(p,T,\xi)}{\alpha_{p,\xi}(p,T,\xi)} \frac{B\ln(10)}{\left(T-T_0\right)^2} \ 10^{\circ} \left(A + \frac{B}{T-T_0}\right). \tag{7}$$

Eq. (7) indicates that in the absence of changes in the microstructural order

(including phase change), viscosity always increases with pressure. Equations 1-4 are used for liquid mixtures and Eqs. 5-7 become important at higher viscosities.

3 Discussion

Surface tension, the defining parameter in Eqs. 1–5, is uncertain for aerosols. Prior work on aerosol surface tension has largely been undertaken in the context of nucleation (Eq. 1). Interfacial tension determines the energetic barrier to creating additional surface area and is therefore important not only in theoretical descriptions of new particle formation (Laaksonen et al., 1999), but also in CCN activation (S. Petters & M. Petters, 2016; Wex et al., 2008a) and the properties of cloud droplets (Dufour & Defay, 1963; Pruppacher & Klett, 2010). CCN activation theory and measurements have been used to understand surface tension at the nano- and microscale (Bzdek et al., 2020; Facchini et al., 1999; Forestieri et al., 2018; Nozière et al., 2014; Ovadnevaite et al., 2017; S. Petters & M. Petters, 2016; Prisle et al., 2008; Ruehl et al., 2016; Wex et al., 2008a,b). The growing consensus suggests that the surface tension is not inherently sizedependent, but that the activity term (a_i) must be accurately known to estimate the surface tension of nanoparticles smaller than ~ 100 nm from CCN activation data (Malila & Prisle, 2018; McGraw & Wang, 2021; M. Petters & Kreidenweis, 2013; Prisle et al., 2008). The implication of these studies is that nanoparticle surface tension depends in part on the phase state of the particle bulk.

Direct measurement of particle surface tension at the nanoscale has not been possible. However, simulations and microscale measurements can shed light on the surface tension at the nanoscale. Molecular dynamics simulations of liquid water in 1–2-nm nanopores indicate that the Young-Laplace equations are accurate at that scale, though tension was reduced $(0.072 \text{ to } 0.062 \text{ N m}^{-1})$ (Liu & Cao, 2016). Molecular dynamics simulations of atmospherically-relevant organic surfactants in 5-nm droplets are in good agreement with bulk measurements (Hede et al., 2011). Bzdek et al. (2020) used aerosol optical tweezers to confirm experimentally that the surface tension of 10-µm droplets containing strong surfactants is close to that of bulk measurements. Although direct evidence is limited, it is expected that the Laplace pressure predicted by Eqs. (1–2) is valid in particles larger than ~1 nm in diameter.

Figure 2 shows rate changes for atmospheric aerosol reactions estimated using known ΔV^{\ddagger} values. Panel A summarizes ΔV^{\ddagger} for a broad range of reactions. Data sources are as follows. The majority of values were transcribed from the review of Isaacs (1997). For a more generalized review based on mechanistic features, see Chen et al. (2017). Benito-López et al. (2008) provide a ΔV^{\ddagger} range for [2,2]-cycloaddition consistent with that of Isaacs, albeit narrower; the Isaacs range of -55 to -40 cm³ mol⁻¹ is displayed. For a density of 1.4 to 1.65 g cm⁻³ representative of SOA or biomass burning SOA (Kristensen et al., 2021; Nakao et al., 2013) and a molar mass of ~250 g mol⁻¹ (Hodzic et al., 2010), every 10 cm³ mol⁻¹ of ΔV^{\ddagger} corresponds to 5.6 to 6.6% of the molar volume. Yamashita et al. (2014) report high-pressure yields for lactone polymerization;

the apparent rate constant after assuming a first-order reaction is used here with Eq. (3) to produce an effective ΔV^{\ddagger} of $-7 \text{ cm}^3 \text{ mol}^{-1}$. For ring-opening of propylene oxide, isobutylene oxide, and ethylene oxide, Koskikallio and Whalley (1959) report a ΔV^{\ddagger} range of -9.2 to -6 cm³ mol⁻¹. The ΔV^{\ddagger} range for epoxide ring-opening of Isaacs is -20 to -15 cm³ mol⁻¹, which is extended to -6 cm³ mol⁻¹ here to include the Yamashita and Koskikallio and Whalley results. The neutral aqueous Michael reaction of methyl vinyl ketone with nitromethane was conducted by Jenner (1999), who used the effective pseudo-second-order rate expression with Eq. (3) to obtain the effective ΔV^{\ddagger} range of -32 to -35 cm³ mol⁻¹. Jenner (2001) report a ΔV^{\ddagger} range of -2 to -8 cm³ mol⁻¹ for a series of Bayer-Villiger reactions of peroxy acids with ketones, concluding that the reaction is concerted. The imidazole reaction of glyoxal with ammonium sulfate at different solution ionic strengths is described by Riva et al. (2021). Eq. (3) is used here with an assumed pseudo-first-order rate of polymerization, quantified using light absorption, to calculate the effective ΔV^{\ddagger} range of 2 to 27 cm³ mol⁻¹. Due to the multi-step nature of many of the reactions presented (e.g., imidazole formation, Michael addition, ring-opening polymerization), ΔV^{\ddagger} is an observed quantity variously referred to as effective, pseudo, or semi-empirical.



Figure 2. (A) Ranges in ΔV^{\ddagger} for reactions from the high-pressure organic

synthesis literature. Data sources are described in the text. Atmosphericallyrelevant reactions are given in color (cycloaddition: blue; aldol: green; radical: magenta; epoxide: gold; Baeyer-Villiger: indigo; imidazole: purple); other reactions are gray. (B) Calculated change in reaction rate due to particle internal pressure (Eq. 4), for 3- and 10-nm particles, as a function of the transition state volume, ΔV^{\ddagger} . Surface tensions of 0.08, 0.072, and 0.03 N m⁻¹ are assumed (solid, dashed, and dotted lines). Color-shaded regions trace out the uncertainty in rate change based on uncertainty in ΔV^{\ddagger} and in surface tension (colors correspond to ΔV^{\ddagger} ranges in panel A; select ranges are reprinted below the graph in panel B).

Figure 2 (panel B) summarizes expected changes in reaction rates in particles of 3 and 10 nm diameters based on Eq. (4). Color regions trace the uncertainty for different types of reactions from panel A. For cycloadditions (blue region), the potential impact of particle internal pressure is the highest and results in the maximum rate change factor of 10 in 3-nm particles with high salt content (σ $\sim 0.08 \text{ N m}^{-1}$). The imidazole reaction (purple region) results in a rate change factor of as low as 0.3 in 3-nm particles with high salt content, e.g., a 70% reduction in rate. For diameters larger than 3 nm, reactions with smaller absolute ΔV^{\ddagger} values, or surface tensions lower than 0.08 N m⁻¹, rate change factors trend away from these extremes towards unity. For example, the magenta bar in Figure 2 (panel B) traces the uncertainty in $\frac{k_p}{k_0}$ for condensed-phase radical propagation reactions $\left(\frac{k_p}{k_0} \sim 1.1 \text{ to } 2.4\right)$. Radical propagation in atmospheric chemistry is most commonly understood as the key step in oxidation (Ehn et al., 2014; Matsunaga & Ziemann, 2010; Ziemann & Atkinson, 2012). Similar propagation reactions of peroxy radicals also occur in condensed-phase organic matrices (Ingold, 1961) and in fog and cloud droplets (Lim et al., 2010). Aldol and epoxide reactions are not shaded due to their overlap with other chart elements (Figure 2, panel B) but have a $\frac{k_p}{k_0}$ of 1.05 to 3.4 and 1.02 to 2.4, respectively. Baeyer-Villiger oxidations have a $\frac{k_p}{k_0}$ of 1.01 to 1.4.

Figure 3 shows the trend in aerosol viscosity with increasing internal pressure based physicochemical properties. Panel A compares compressibility, $\kappa_{T,\xi}$, with organic surface tension, following Richard & Rogers (1971). Data are obtained for organic liquids with the formula $C_x H_y O_z$ at 298 K from (Markus, 1998; Yaws, 2003; taken from Caleman et al., 2012). Panels B and C extend the linear surface tension dependence to $\alpha_{p,\xi}$ and $\kappa_{T,\xi}/a_{p,\xi}$. Panel D shows the range in pressuredependent viscosity predicted by Eq. 7. Ranges are calculated from predicted $\kappa_{T,\xi}/a_{p,\xi}$ values (panel C). Calculations are made for 2.5, 5, and 10% sucrose in water (regions *i*, *j*, and *k*, respectively) following the detailed model of Kasparaglu et al. (2021). This model is based on liquids far from phase transition, and $d\eta/dp$ is always positive. Analogous to water melting under pressure, atmospheric aerosols are predicted to become less viscous at ultrafine sizes (Panel E) (Cheng et al. 2015; M. Petters & Kasparaglu, 2020). Experimental $d\eta/dT$ measurements for viscous atmospherically-relevant aerosols demonstrate a wider range of values indicative of more complex mixtures (Table S1) (Marsh et al., 2018; S. Petters et al., 2019; Rothfuss & M. Petters, 2017).



Figure 3. Predicted trend in viscosity with increasing pressure for a series of organic liquids. X-axis: surface tension at 298.15 K. (A) Isothermal compressibility. (B) Isobaric coefficient of thermal expansion. (C) Ratio κ_T/α_p . Open black circle: water (Schmelzer et al., 2005). Solid lines: best fit; Dotted lines: 95% CI. (D) Predicted slope of viscosity as a function of pressure assessed at 298.15 K and atmospheric pressure for a slope $d\eta/dT$ (Pa s K⁻¹) for (i) 2.5%, (j) 5%, and (k) 10% sucrose in water (Kasparoglu et al., 2021; Rothfuss & M. Petters, 2017). Shaded regions reflect uncertainty in κ_T/α_p (panel C). (E) Predicted trend for atmospheric aerosols.

4 Implications for Multiphase Atmospheric Chemistry

This work combines the Laplace and Evans-Polyani expressions for application to atmospheric chemistry. It is predicted that all particle-phase reactions are affected by particle internal pressure as a function of particle diameter (D <~10 nm), surface tension, effective ΔV^{\ddagger} , and pressure-induced changes in aerosol phase state. The following explores the effects of Laplace pressure on known reaction systems. The estimates presented here can then serve to start the discussion of reactions of similar highly-functionalized molecules in nucleating

or evaporating nanoparticles.

Highly oxygenated molecules (HOMs) are a class of low molecular weight compounds that participate in both nucleation and subsequent particle growth (Ehn et al., 2014). HOMs (e.g., multifunctional peroxides) can serve as oxidants in condensed-phase Baeyer-Villiger reactions, in which hydroperoxides or peroxyacids oxidize aldehydes or ketones. Bayer-Villiger reactions have a slightly negative ΔV^{\ddagger} and have been observed in chamber experiments (Claffin et al., 2018) and in the field (Pospisilova et al., 2020). Because HOMs are an important early participant in new particle growth, they are likely present in 3–10-nm particles (Bianchi et al., 2019). Thus, pressure likely provide moderate enhancement of peroxide depletion rates and higher carboxylic acids yields, similar to the observations of Pospisilova et al.

Epoxides, e.g., -lactones, are important oxidation products of biogenicallyderived hydroperoxides. Isoprene-derived epoxydiols (Paulot et al., 2009; Surratt et al., 2010) and -pinene derived epoxides (Eddingsaas et al., 2012) form photochemically under low-NO conditions. Under high-NO conditions, formation of isoprene-derived hydroxymethyl-methyl--lactone (T.B. Nguyen et al., 2015; Surratt et al., 2010) and methacrylic acid epoxide (Lin et al., 2013) is observed. Epoxides undergo acid-catalyzed ring-opening reactions in the aerosol, contributing up to 14-40% of organic aerosol mass in forested regions (Budisulistiorini et al., 2015; Froyd et al., 2010; W.W. Hu et al., 2015; Schulz et al., 2018; Xu et al., 2015). Ring-opening rates and mechanisms are guided by solution pH and ionic strength (Eddingsaas et al., 2010; Lin et al., 2013; T.B. Nguyen et al., 2014; S. Petters et al., 2021). High hydrostatic pressure has been used to differentiate between the S_N1 and S_N2 reaction pathways for epoxides (Baliga & Whalley, 1964; Whalley, 1959). Structural features play an important role in both the rate and the mechanism of epoxide reactions (Eddingsaas et al., 2010; Minerath & Elrod, 2009; S. Petters et al., 2021), meaning that the effect of particle internal pressure is compound-specific. For example, the multistep ammonium-catalyzed reaction of isoprene-derived epoxydiols at high pH (Nozière et al., 2018) may proceed more slowly at elevated pressure, analogous to the result of Riva et al. (2021) for glyoxal reacting with ammonium. The five-membered lactone, -butyrolactone, undergoes acid-catalyzed ring-opening reactions exclusively under high hydrostatic pressure due to the stability of its ring structure at lower pressures (Houk et al., 2008; Yamashita et al., 2014).

Furanoic compounds are an important group of five-membered aromatic heterocyclic gases emitted during biomass burning (Hartikainen et al., 2018). New particle formation is observed in biomass burning plumes during photochemical oxidation (Hennigan et al., 2012). The uptake of furans by aerosols and hydrometeors can result in condensed-phase reactions adding to particulate mass (Liang et al., 2018; Tomaz et al., 2018). Diels-Alder cycloadditions of furans with alkenes have enhanced yields under high pressure, due in part to the prevention of thermally-accelerated reverse reactions (Dauben & Krabbenhoft, 1976; Isaacs, 1997; Oppolzer, 1991). Furanoic compounds present during the growth of these new particles can partition into the condensed phase and experience elevated pressures. Note that in-flame nucleation and soot formation results in particles greater than ~10 nm (Johansson et al., 2018); nanosphere soot and tarballs have diameters of ~50 and ~250 nm, respectively (Adachi et al., 2019). Though compaction of soot occurs by capillary forces (Bhandari et al., 2019; D. Hu et al., 2021; Leung et al., 2017; Ma et al., 2013), the pressure in these accumulation-mode particles is also outside the range for which condensed-phase reaction rates are altered (Figure 1, panel A). Given that cycloadditions including the Diels-Alder reaction are the most dramatically accelerated by increased pressure, oligomerization of furanoid compounds during the nucleation and growth of new particles in sunlit biomass burning plumes is likely affected by particle internal pressure.

Carbonyls such as pyruvic acid and glyoxal are highly water-soluble and can dimerize (Loeffler et al., 2006; Perkins et al., 2016) or undergo multi-step oligomerization in the presence of ammonium (Maxut et al., 2015). Riva et al. (2021) show that high hydrostatic pressure reduces the oligomerization rate of glyoxal in the presence of ammonium sulfate. Pyruvic acid undergoes imidazole formation and this reaction rate is likely reduced in the nucleation-mode aerosol. Hazen et al. (2002) show that pyruvic acid decarboxylates under pressure to form acetic acid and carbon dioxide and undergoes aldol condensation to form dimers and trimers; a large fraction of these decarboxylate to form methyl succinate, and some undergo Diels-Alder cyclization. Pyruvic acid dimers are important in atmospheric chemistry because they are surface-active (B. Gordon et al., 2019; Hazen et al., 2002) and cyclize in droplets (Perkins et al., 2016; S. Petters et al., 2020). Aldol reactions are a hypothesized route for reactive uptake of gases or modification of aerosol optical properties when catalyzed by inorganic salts (Nozière et al., 2010), and have been suggested for highly acidic particles and in evaporating droplets (De Haan et al., 2009; Herrmann et al., 2015; Jang et al., 2002).

Characterization of molecules and reaction mechanisms in aerosols is challenging and often informed by studies of bulk samples at standard temperature and pressure (Glasius & Goldstein, 2016). Higher pressures may enable the formation of different reaction products. For example, high pressure can prevent backwards reactions or enable otherwise-unfavorable ring-opening reactions. This work adjusts the existing assumptions of aerosol phase state, opening the door for future and retrospective studies seeking to match observations to reaction models.

Aerosol viscosity is predicted to change due to Laplace pressure. Organic solvents become more viscous under pressure (Cook et al., 1994; Herbst et al., 1993; Isaacs, 1997). In contrast, supercooled water becomes less viscous as the hydrogen bond network collapses (~300 MPa) (Singh et al., 2017). Further, melting points of various organic and inorganic substances are depressed in sub-100-nm particles (M. Petters & Kasparoglu, 2020), and secondary organic aerosols below 20 nm are predicted to liquify (Cheng et al., 2015).

5 Conclusions

This work combines thermodynamics from aerosol physics and organic physical chemistry to formulate expressions for the diameter-dependent reaction rates and viscosity in particles. Application of this equation is guided by a survey of synthetic organic chemistry and suggests that heterogeneous reaction rates are accelerated by up to tenfold in 3–10-nm particles. Elevated pressure is explored as a primary contributor to size-dependent reaction rates and mechanisms of highly oxygenated molecules (HOMs) and other peroxides, furans and furanoids, epoxides and other lactones, and carbonyls. Rate enhancements are ranked as follows: cycloadditions > aldol reactions > epoxide ring-opening reactions > Baeyer-Villiger oxidation by peroxides > imidazole oligomerization of carbonyls. High-pressure changes to aerosol viscosity depend on aerosol composition and temperature. Careful work is needed to separate the effects of particle internal pressure, viscosity, curvature, pH, phase separation, surface tension, and other factors on reactions within particles.

Data Availability

Data are being archived on Zenodo (https://zenodo.org/) and are uploaded as Supporting Information.

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Supplement: Constraints on the role of Laplace pressure in multiphase reactions and viscosity of organic aerosols

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Supporting Data

Table S1 contains Vogel-Fulcher-Tammann equation parameters to describe the temperature dependence of viscosity.

Table S2 contains the rate enhancements discussed in the main text. The rate enhancement factor, k, is calculated according to Eq. (4).

| | Α | В | T_0 | Reference |
|--|--------|--------|--------|---------------------------|
| Sucrose aerosol at 80 nm | 1.1756 | 172.01 | 324.92 | Rothfuss & MPetters, 2017 |
| α -pinene-derived SOA at 100 nm | 2.119 | 148.65 | 256.58 | Petters et al., 2019 |
| Limonene-derived SOA at 100 nm | -0.068 | 348.21 | 251.06 | Petters et al., 2019 |
| Myrcene-derived SOA at 100 nm | 0.914 | 228.38 | 243.60 | Petters et al., 2019 |
| Carene-derived SOA at 100 nm | 1.949 | 108.16 | 282.04 | Petters et al., 2019 |
| Carene-derived SOA at 100 nm | 1.465 | 96.50 | 288.63 | Petters et al., 2019 |
| Ocimene-derived SOA at 100 nm | 2.346 | 80.00 | 275.38 | Petters et al., 2019 |
| Carene-derived SOA at 100 nm | 0.000 | 265.83 | 263.42 | Petters et al., 2019 |
| Sucrose (90%) + NaNO ₃ at 80 nm | 0.72 | 160.77 | 326.33 | Marsh et al., 2018 |
| Sucrose (70%) + NaNO ₃ at 80 nm | 0.70 | 280.1 | 293.35 | Marsh et al., 2018 |
| Sucrose (60%) + NaNO ₃ at 80 nm | 0.79 | 257.96 | 291.29 | Marsh et al., 2018 |
| Sucrose (80%) + NaNO ₃ at 80 nm | 0.70 | 195.25 | 315.48 | Marsh et al., 2018 |
| Sucrose (70%) + NaNO ₃ at 80 nm | 0.84 | 242.81 | 300.33 | Marsh et al., 2018 |
| Sucrose (60%) + NaNO ₃ at 80 nm | 0.72 | 188.18 | 304.11 | Marsh et al., 2018 |
| Sucrose (55%) + NaNO ₃ at 80 nm | 1.21 | 232.62 | 284.95 | Marsh et al., 2018 |
| Sucrose (50%) + NaNO ₃ at 80 nm | 1.05 | 252.13 | 283.15 | Marsh et al., 2018 |
| Sucrose (0%) + citric acid at 80 nm | 1.07 | 230.17 | 265.17 | Marsh et al., 2018 |
| Sucrose (20%) + citric acid, 80 nm | 1.25 | 297.94 | 256.85 | Marsh et al., 2018 |
| Sucrose (40%) + citric acid, 80 nm | 0.70 | 139.78 | 294.61 | Marsh et al., 2018 |
| Sucrose (60%) + citric acid, 80 nm | 1.16 | 302.93 | 270.45 | Marsh et al., 2018 |
| Sucrose (80%) + citric acid, 80 nm | 1.24 | 232.92 | 294.79 | Marsh et al., 2018 |
| Sucrose (90%) + citric acid, 80 nm | 1.29 | 282.57 | 299.38 | Marsh et al., 2018 |

Table S1. Ranges of reaction rate enhancement factors, k, for heterogenous aerosol reactions as a function of reaction type and particle diameter.

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| | ——1.7 | nm—— | ——3 r | ım—— | 10 : | nm—— | —————————————————————————————————————— | nm—— | 50 ı | nm—— | ——100 | nm—— $\left[\Delta V_{\min}^{\ddagger}, \Delta V_{\max}^{\ddagger}\right]^{a}$ |
|---------------------------------|--------|---------|--------|---------|--------|--------|--|--------|--------|--------|--------|--|
| All reactions | 0.1286 | 65.2622 | 0.3127 | 10.6735 | 0.7056 | 2.0347 | 0.8698 | 1.3286 | 0.9326 | 1.1527 | 0.9657 | 1.0736 [-55, 27] |
| Cycloadditions – (2+2) | 3.1254 | 65.2622 | 1.9074 | 10.6735 | 1.2138 | 2.0347 | 1.0806 | 1.3286 | 1.0395 | 1.1527 | 1.0196 | $1.0736 \ [-55, -40]^{b,c}$ |
| Cycloadditions – dipolar | 3.1254 | 44.6367 | 1.9074 | 8.6065 | 1.2138 | 1.9074 | 1.0806 | 1.2947 | 1.0395 | 1.1379 | 1.0196 | 1.0667 [-50, -40]° |
| Cycloadditions – Diels–Alder | 2.3506 | 44.6367 | 1.6231 | 8.6065 | 1.1564 | 1.9074 | 1.0598 | 1.2947 | 1.0295 | 1.1379 | 1.0146 | 1.0667 [-50, -30]° |
| Cycloadditions – catalyzed | 2.0385 | 14.2819 | 1.4972 | 4.5121 | 1.1287 | 1.5715 | 1.0496 | 1.1982 | 1.0245 | 1.0946 | 1.0122 | 1.0462 [-35, -25]° |
| Cycloadditions – intramolecular | 2.0385 | 9.7682 | 1.4972 | 3.6383 | 1.1287 | 1.4732 | 1.0496 | 1.1676 | 1.0245 | 1.0806 | 1.0122 | 1.0395 [-30, -25]° |
| Baylis–Hillman reactions | 4.1556 | 44.6367 | 2.2416 | 8.6065 | 1.274 | 1.9074 | 1.1017 | 1.2947 | 1.0496 | 1.1379 | 1.0245 | 1.0667 [-50, -50]° |
| Quaternization of RX | 2.3506 | 44.6367 | 1.6231 | 8.6065 | 1.1564 | 1.9074 | 1.0598 | 1.2947 | 1.0295 | 1.1379 | 1.0146 | 1.0667 [-50, -30]° |
| Ionogenic SNAr reactions | 2.3506 | 20.8811 | 1.6231 | 5.5958 | 1.1564 | 1.6763 | 1.0598 | 1.2295 | 1.0295 | 1.1088 | 1.0146 | 1.053 [-40, -30]° |
| Neutral aqueous Michael | 2.4884 | 15.4091 | 1.6763 | 4.7106 | 1.1676 | 1.5919 | 1.064 | 1.2044 | 1.0315 | 1.0974 | 1.0156 | 1.0476 [-36, -32] ^e |
| Wittig reactions | 1.7679 | 9.7682 | 1.3811 | 3.6383 | 1.1017 | 1.4732 | 1.0395 | 1.1676 | 1.0196 | 1.0806 | 1.0097 | 1.0395 [-30, -20]° |
| Aldol reactions | 1.3296 | 9.7682 | 1.1752 | 3.6383 | 1.0496 | 1.4732 | 1.0196 | 1.1676 | 1.0097 | 1.0806 | 1.0049 | 1.0395 [-30, -10]° |
| H ₂ transfer | 2.0385 | 6.6811 | 1.4972 | 2.9337 | 1.1287 | 1.3811 | 1.0496 | 1.1379 | 1.0245 | 1.0667 | 1.0122 | 1.0328 [-25]° |
| Solvolysis of RX | 1.5332 | 6.6811 | 1.274 | 2.9337 | 1.0754 | 1.3811 | 1.0295 | 1.1379 | 1.0146 | 1.0667 | 1.0073 | 1.0328 [-25, -15]° |
| Radical propogation | 1.7679 | 4.5696 | 1.3811 | 2.3655 | 1.1017 | 1.2947 | 1.0395 | 1.1088 | 1.0196 | 1.0530 | 1.0097 | 1.0262 [-20]° |
| Epoxide ring-opening | 1.1864 | 4.5696 | 1.1017 | 2.3655 | 1.0295 | 1.2947 | 1.0117 | 1.1088 | 1.0058 | 1.0530 | 1.0029 | $1.0262 \ [-20, -6]^{c,f,i}$ |
| Hydration of alkenes | 1.7679 | 4.5696 | 1.3811 | 2.3655 | 1.1017 | 1.2947 | 1.0395 | 1.1088 | 1.0196 | 1.0530 | 1.0097 | 1.0262 [-20]° |
| Amide/ester hydrolysis | 1.2923 | 3.3721 | 1.1564 | 1.9913 | 1.0446 | 1.2295 | 1.0176 | 1.0862 | 1.0088 | 1.0422 | 1.0044 | $1.0209 \ [-16, -9]^{c,g}$ |
| Baeyer–Villiger | 1.0586 | 1.8363 | 1.0328 | 1.4111 | 1.0097 | 1.1088 | 1.0039 | 1.0422 | 1.0019 | 1.0209 | 1.0010 | $1.0104 \ [-8, -2]^{d}$ |
| Neutral S _N 2 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 [0] ^c |
| Imidazole | 0.1286 | 0.9446 | 0.3127 | 0.9682 | 0.7056 | 0.9904 | 0.8698 | 0.9961 | 0.9326 | 0.9981 | 0.9657 | $0.9990 \ [2, 27]^{h}$ |
| Homolysis | 0.2188 | 0.8672 | 0.4227 | 0.9225 | 0.7724 | 0.9761 | 0.9018 | 0.9904 | 0.9497 | 0.9952 | 0.9745 | 0.9976 [5, 20]° |

Table S1. Ranges of reaction rate enhancement factors, k, for heterogenous aerosol reactions as a function of reaction type and particle diameter.

^a Range in the volume change during the reaction transition state (cm³ mol⁻¹)

^b Benito-López, F., Egberink, R. J. M., Reinhoudt, D. N., & Verboom, W. (2008). Tetrahedron, 64(43), 10023–10040.

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^g Osborn, A. R., & Whalley, E. (1961). Can. J. Chem., 39(5), 1094–1100.

^h Riva, M., Sun, J., McNeill, V. F., Ragon, C., Perrier, S., Rudich, Y., et al. (2021). Environ. Sci. Technol.

ⁱ Yamashita, K., Yamamoto, K., & Kadokawa, J. (2014). Chem. Lett., 43(2), 213-215.