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1Changes in reactivity as chemistry becomes confined
2 to an interface. The case of free radical oxidation of
3 $C_{30}H_{62}$ alkane by OH

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11ABSTRACT

12Here we examine in a simple organic aerosol the transition between heterogeneous chemistry
13under well-mixed conditions to chemistry under interfacial confinement. A single reaction
14mechanism, shown to reproduce observed OH oxidation chemistry for liquid and semisolid
15C₃₀H₆₂, is used in reaction-diffusion simulations to explore reactivity over a broad viscosity
16range. The results show that when internal mixing of the aerosol is fast and the particle interface
17is enriched in C-H groups, ketone and alcohol products, formed via peroxy radical
18disproportionation, predominate. As viscosity increases the reactions become confined to a shell
19at the gas-aerosol interface. The confinement is accompanied by emergence of acyloxy reaction
20pathways that are particularly active when the shell is 1nm or less. We quantify this trend using
21a reaction-diffusion index, allowing the parts of the mechanism that control reactivity as
22viscosity increases to be identified.

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24TOC graphic

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27INTRODUCTION

28

29 The presence of aerosols in the troposphere increases substantially the complexity of
30models for the chemical evolution of planetary atmospheres. This complexity is due in large part
31to chemistry that couples gas and condensed phase reaction mechanisms. Aerosol reactivity with
32a gas is generally measured with an uptake coefficient, γ , which is calculated from composition
33data using the expression

34
$$\gamma = \frac{2k_{rx}d_p\rho_0N_A}{3cM}(1)$$

35where k_{rx} is the apparent disappearance rate constant for the starting material in the aerosol, d_p is
36the particle diameter, ρ_0 is the aerosol density, c is the velocity of the gaseous reactant molecules,
37 M is the molecular weight of the aerosol material, and N_A is Avogadro's number. This expression
38applies if the aerosol is well mixed and the entire volume of the particle participates in the
39reaction. However, the rates of multiphase processes such as heterogeneous reactions¹⁻⁷ and
40evaporation⁸⁻¹¹ and condensation kinetics are inextricably connected to internal mixing timescales
41in aerosols. These timescales can span many orders of magnitude and are controlled by water
42content and aerosol phase state (liquid, solids and glasses).

43 Discovery of predictive elementary reaction mechanisms that take diffusion into account
44provides some insights to how transport affects reactivity. For example, Knopf *et al.*² and Davies
45*et al.*,³ observed a complex nonlinear relationship between the organic diffusion constant and OH
46reaction rate (i.e. effective reactive uptake) with levoglucosan and citric acid aerosol,
47respectively. Berkemeier *et al.*,¹² used a kinetic multilayer model to explain the complex time

48dynamics of O₃ uptake onto glassy and semi-solid shikimic acid. This complex relationship was
49used to identify more broadly how a multiphase system can evolve through limiting kinetic
50regimes represented by trajectories through a "kinetic cube".¹³ Houle *et al.*,⁴ showed how the
51uptake coefficient depends upon both the timescales for a reactive surface collision and internal
52mixing, showing that multiphase uptake should be considered an emergent property of the
53system (gas + particle), rather than a measure of the intrinsic reactivity of the interface. This
54description is consistent with results reported by Wiegel *et al.*,⁵ who showed that for OH
55reactions with semisolid alkane aerosols, there is no straightforward relationship between
56measurements of an effective uptake coefficient obtained in experiment and the inherent OH
57reactivity of triacontane.

58 These previous studies elucidate how diffusion affects consumption kinetics for specific
59cases. Here we consider broader trends, looking at how reactivity (i.e. product distribution)
60evolves with changes in the internal aerosol mixing times when the governing reaction
61mechanism is held constant. Our approach is to examine C₃₀H₆₂ aerosol + OH, whose mechanism
62has been validated for liquid and semi-solid phases,^{5, 14} and systematically vary the alkane
63diffusion coefficient (viscosity) in between these extrema to trace how the free radical chain and
64product distributions depend on viscosity. We connect reactivity to diffusion by defining a
65reaction-diffusion index that quantifies the governing kinetics, and links them to specific sections
66of the reaction mechanism.

67RESULTS AND DISCUSSION

68

69 A reaction-diffusion model framework for OH + C₃₀H₆₂ alkane aerosol has been
70 constructed from known chemistry and rate coefficients, and validated using experimental data
71 for liquid C₃₀H₆₂, squalane,^{4, 14} and its semisolid isomer, triacontane.⁵ A diagram of the reaction
72 mechanism is presented in Scheme S1 in the Supplementary Information. The free radical chain
73 reaction is initiated by H abstraction from a C-H bond located near the surface of the particle.^{4-5,}
74¹⁴⁻¹⁵ The resulting alkyl radical reacts rapidly with O₂ to form a peroxy radical. Peroxy radicals
75 disproportionate to form mainly alcohols and ketones in C-H rich environments via the Russell
76 and/or Bennet-Summers mechanisms, but also have minor channels forming alkoxy and acyloxy
77 radicals that lead to aldehyde and carboxylic functionalities, as well as fragmentation to form
78 new alkyl radicals.^{5, 14} This chemistry is not represented explicitly in the simulations, rather, the
79 alkane is treated as a collection of functional groups and carbon backbones that track formation
80 of free radical intermediates (such as peroxy and acyloxy radicals), stable product functional
81 groups (such as ketones), and backbone fragments (such as C₂₄). This description allows the free
82 radical chemistry to be represented across the entire oxidation process, from a pure alkane to
83 complete conversion into CO₂, using a tractable number of reaction steps.

84 In this work, we focus on trends in reactivity that would be observed in a typical flow
85 tube experiment using the reaction scheme for triacontane, which is the same as for squalane but
86 does not have tertiary alkyl functionalities. Flow tubes are often used to provide data on aerosol
87 reactions that can be used for atmospheric chemistry models. Reaction-diffusion simulations
88 have been performed using a gas phase OH density of 5.04×10^{10} molec/cm³^{16, 17} and the reaction
89 time 60s, which are typical conditions for flow tube measurements. Liquid squalane has a self-
90 diffusion coefficient of 8.5×10^{-7} cm²/s,¹⁸ and is well-mixed. Test simulations revealed that this

behavior persists until a value of $1 \times 10^{-11} \text{ cm}^2/\text{s}$, therefore we restricted the $\text{C}_{30}\text{H}_{62}$ diffusion coefficients D to the range from $1 \times 10^{-11} - 8.39 \times 10^{-19} \text{ cm}^2/\text{s}$ (the self-diffusion coefficient of triacontane⁵). All product species in the simulation are assumed to diffuse with the same coefficient as the alkane. Viscosity changes may occur as a result of oxidation.^{5, 19} These effects are neglected in the present work in order to focus on broad trends. To provide a unified way to characterize reactivity across such a broad range of diffusion coefficients, we define a reaction-diffusion index (I_{RD}). I_{RD} is a dimensionless number calculated from timescales, and is similar to the Damköhler number, or the square of the Thiele modulus,²⁰

$$I_{RD} = k_{rx}[\text{gas}] \tau_{cd} \quad (2)$$

where k_{rx} is a phenomenological rate constant for consumption of starting material, as used in (1), and τ_{cd} is the characteristic complete mixing time for a particle of a specific diameter.⁶ The reaction-diffusion index can be written for the specific $\text{C}_{30}\text{H}_{62}$ viscosities (D), OH density ($[\text{OH}(\text{g})]$) and particle size:

$$I_{RD} = \frac{k_{rx}[\text{OH}(\text{g})]d_p^2}{4\pi^2 D} \quad (3)$$

If $I_{RD} \ll 1$, mixing is fast relative to arrival of OH at the aerosol surface and the supply of OH is rate limiting. If $I_{RD} \gg 1$, the rate of mixing to bring organic molecules to the aerosol surface is rate limiting. If $I_{RD} = 1$, then reaction rates and internal transport rates are balanced. This is the midpoint of the transition between kinetically limiting regimes.

Figure 1 shows the initial uptake coefficients, γ , calculated from simulated $\text{C}_{30}\text{H}_{62}$ disappearance curves as a function of D and I_{RD} : they undergo a significant decrease in the range $D = 10^{-12} - 10^{-14} \text{ cm}^2/\text{s}$. This sigmoidal dependence of γ on D is consistent with previous experimental observations in levoglucosan and citric acid as well as with predictions of Houle et

113al.⁴ The free radical reactions initiated by OH uptake generate oxygen-containing functionalities
 114(ketones, alcohols, aldehydes, carboxylic acids); their predicted fractions in the particle at 60s are
 115shown in Figure 2. When I_{RD} is small, *i.e.* the OH radical supply is rate limiting and the alkane is
 116liquid, ketones and alcohols are the primary products as found previously in simulations of
 117squalane oxidation.¹⁴ As D decreases, I_{RD} is large and mixing is rate limiting, and ketones become
 118the dominant functional group accompanied by a modest increase in carboxylic acids and
 119disappearance of aldehydes and alcohols. The full time-dependent product compositions and
 120maps

121

122**Figure 1.** Initial uptake coefficient calculated from $C_{30}H_{62}$ disappearance curves as a function of
 123diffusion coefficient and I_{RD} .

124.

125

126

127 **Figure 2.** Product functionality fractions in the aerosol as a function of diffusion coefficient and

128 I_{RD} .

129 of unreacted $C_{30}H_{62}$ within the particle are shown in Figure S1 in the Supplementary Information.

130 It is evident that the decrease in γ and change in product distributions is accompanied by a
 131 transition from chemistry under well-mixed conditions to chemistry under confinement to the
 132 near-surface region of the aerosol.

133 The extent of confinement for a particular D has been described in terms of a reacto-
 134 diffusion length, L . It is the thickness of a shell that is accessible for chemistry surrounding the
 135 particle core. L is given by

$$136 \quad L = \left(\frac{8D}{[gas]c\pi\sigma d_p^2} \right)^{1/2} \quad (4)$$

137 where $[gas]$ is the density of the gaseous reactant, and σ is the probability that a colliding gas
 138 molecule will stick to the aerosol surface long enough to react.⁴ In the limit of complete mixing
 139 on the timescale of the chemistry, $d_p = 2L$, and a more general form of (1) is

$$\gamma = \frac{2k_{rx}\rho_0 N_A}{3cM d_p^2} [d_p^3 - (d_p - 2L)^3] \quad (5)$$

Equations (4) and (5) predict that γ decreases as D and L decrease. Equation (4) also assumes that k_{rx} is constant under all conditions, i.e. the reactivity does not change. A value for k_{rx} applicable to a particular I_{RD} , $[\text{OH}(\text{g})]$ and D can be estimated from (5). For $I_{RD} = 1$, a 200 nm diameter particle under flow tube conditions and $D = 1 \times 10^{-12} \text{ cm}^2/\text{s}$, $k_{rx} = 2.12 \times 10^{12} \text{ molecules cm}^{-3} \text{ s}$. This is essentially the same as the phenomenological rate constant for the initial decay of $\text{C}_{30}\text{H}_{62}$ when the aerosol is well-mixed ($2.16 \times 10^{12} \text{ molecules cm}^{-3} \text{ s}$).¹⁵ When $D > 1 \times 10^{-12} \text{ cm}^2/\text{s}$ and $I_{RD} < 1$, the aerosol particle is reasonably well-mixed (Figure S1), and reaction is controlled by the arrival and reaction of OH at the aerosol surface. When $D < 1 \times 10^{-12} \text{ cm}^2/\text{s}$ and $I_{RD} > 1$, the reaction is controlled by the rate of internal mixing of the aerosol at a particular value of D , i.e. delivery of unreacted C-H bonds to the surface. As I_{RD} is varied from 10^{-2} to 10^6 , corresponding to the range of D used in the present calculations, k_{rx} varies about $\pm 6\%$ (see Table S1 and Figure S2 in the SI). This variation in rate coefficient is modest, and could be interpreted to mean that the chemical reaction does not change much over this very broad range in diffusivities. Such a conclusion is not consistent with the dramatic change in product distributions shown in Figures 2 and S1, however.

It is evident from equations (1), (3) and (5) that γ , L and I_{RD} are related. Substituting (3) into (4),

$$L = \left(\frac{2k_{rx}}{I_{RD} \pi^3 c \sigma} \right)^{1/2} \quad (6)$$

159 This relationship allows the reaction-diffusion length to be connected to the balance between
160 reaction and diffusion to be assessed over the entire range of conditions linking the limiting
161 cases.

162 What does this tell us about trends in product formation? Figures 2 and S1 show that
163 disproportionation chemistry to form ketones and alcohols is favored when the reactions are
164 limited by OH – particle collisions ($I_{RD} < 0.1$). As the reactions become mixing limited ($I_{RD} > 10$)
165 and diffusively confined to the interface, ketones are the major component of the particle
166 because alcohols and aldehydes are consumed by abstraction by OH and by reaction with
167 additional peroxy radicals that are formed by fragmentation during the free radical chain reaction
168 (see Scheme S1). Further insights are possible using marker species in the simulations, which is
169 straightforward using the stochastic simulation methodology, to determine the nature of
170 reactivity as I_{RD} varies. Abstraction markers track the number of OH abstraction events, which
171 occur predominately at the surface of the aerosol and initiate the free radical chain reaction.^{4, 21}
172 Disproportionation markers track the number of bimolecular reaction events involving peroxy
173 radicals of all types. Fragmentation is the major chain propagation process. C_{30} fragmentation
174 markers track dissociation of the initial $C_{30}H_{62}$ alkane backbone at random locations via alkoxy
175 radical formation and decomposition, which leads to formation of volatile fragments and mass
176 loss from the particle. Acyloxy radical fragmentation markers track CO_2 loss from the end of the
177 oxidized alkane, an “unzipping” process that becomes important when the aerosol has become
178 heavily oxidized.⁵

179

180

181 **Figure 3.** Frequency of disproportionation and fragmentation and acyloxy radical fragmentation
 182 reactions, and fraction of each functionality formed during the oxidation reaction, as a function of
 183 the reacto-diffusion length L . The reaction frequencies are calculated by normalizing the number
 184 of events of each type to the number of abstraction events. The range for L corresponds to $10^{-1} \leq$
 185 $I_{RD} \leq 10^2$, and $10^{-14} \text{ cm}^2/\text{s} \leq D \leq 10^{-11} \text{ cm}^2/\text{s}$. Disproportionation and fragmentation occur
 186 essentially uniformly over this range, denoted as L_1 . Acyloxy fragmentation has a much smaller
 187 characteristic reacto-diffusion length, L_2 , and leads to a significant change in functionalities
 188 formed.

189

190 By normalizing disproportionation, C_{30} fragmentation and acyloxy fragmentation to OH
 191 abstraction events for each value of D and using Equation (6), we can establish a measure of the
 192 relative importance of each of these parts of the free radical chain reaction as a function of the

193reacto-diffusion length L as shown in Figure 3. Disproportionation and C_{30} fragmentation both
194involve reactions that are second order in peroxy radical concentration, and have a characteristic
195 L_1 that extends up to the center of the particle when viscosity is low.^{5, 14} Acyloxy fragmentation,
196on the other hand, is very different. The unimolecular “unzipping” reaction is only kinetically
197significant at a much smaller L_2 ($< 1\text{nm}$), and the oxidation process is confined to the outer
198surface of the aerosol. This indicates that as the reaction-diffusion length for a system changes,
199not only does the average composition of the particle change, the dominant part of the reaction
200mechanism also changes. This result shows that it cannot be assumed that measurements of γ
201trends and k_{rx} for a particular system are easily connected to the chemical reactions of a particular
202aerosol across a range of conditions.

203 Finally, the simulations show that measurements of composition at the exit of the flow
204tube are meaningful as snapshots, but cannot be assumed to reveal the dominant chemistry. As
205seen in Figure S1, at the earliest times for all D and I_{RD} , ketone and alcohol functionalities are
206produced at the same rate, but then diverge. This indicates that while C-H bonds are abundant,
207the Russell mechanism for disproportionation is operative. As C-H bonds become constrained,
208ketones become the dominant product functionality at all times. This represents a transition from
209disproportionation chemistry to functionalization + fragmentation chemistry. The extent of this
210transition is clearly time-dependent as well as D -dependent, indicating that there is no clear
211steady-state regime for the reaction under flow tube conditions.

212

213CONCLUSIONS

214

215 Detailed simulations such as those presented here are essential to connect observations to
216 fundamental reactivity. We show evidence that internal mixing times in organic aerosols have a
217 substantial effect on the product distributions, going well beyond simple considerations of rates
218 under limiting regimes. We have used I_{RD} to connect quantitatively trends in reactivity with
219 diffusion coefficient D to reacto-diffusion lengths L using a single chemical mechanism. The
220 results show that specific elementary reaction pathways (within a network of possible elementary
221 steps) have characteristic L and can become dominant under certain transport conditions, leading
222 to substantial and nonlinear changes in overall aerosol chemistry with changes in diffusion. This
223 means that measurements of uptake coefficients and extraction of effective rate constants for
224 various classes of chemicals are challenging to use directly to predict the oxidative evolution of
225 average aerosol properties such as size, average carbon oxidation state, optical and cloud
226 nucleation properties in very different environments such as the atmosphere. Construction of
227 detailed models such as that reported here provides an effective tool for identifying dominant
228 factors controlling reactivity and creating realistic models for aerosol reactions in the
229 troposphere.

230

231 METHODS

232

233 All simulations were performed using Kinetiscope, a stochastic chemical kinetics
234 simulation software package.²² The initial aerosol diameter is chosen to be 200 nm, and is
235 represented in the simulation by a stack of 200 $13.17\text{ nm} \times 13.17\text{ nm} \times 0.5\text{ nm}$ compartments
236 along the radius spanning the center to the outer surface of the particle. The compartment

237volumes are allowed to vary according to product densities and the extent of gas product
238volatilization in order to maintain accurate concentrations.

239

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249the course of this work.

250

251**SUPPORTING INFORMATION.** Reaction scheme for free radical reactions in alkanes
252initiated by OH reactions. Particle compositions as a function of time. Table of reactivity metrics
253for each simulation. Plot of apparent rate constants. This material is available free of charge via
254the Internet at <http://pubs.acs.org>.

255

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