Supplementary Information

Changes in reactivity as chemistry becomes confined to an interface. The case of free radical oxidation of $C_{30}H_{52}$ alkane by OH

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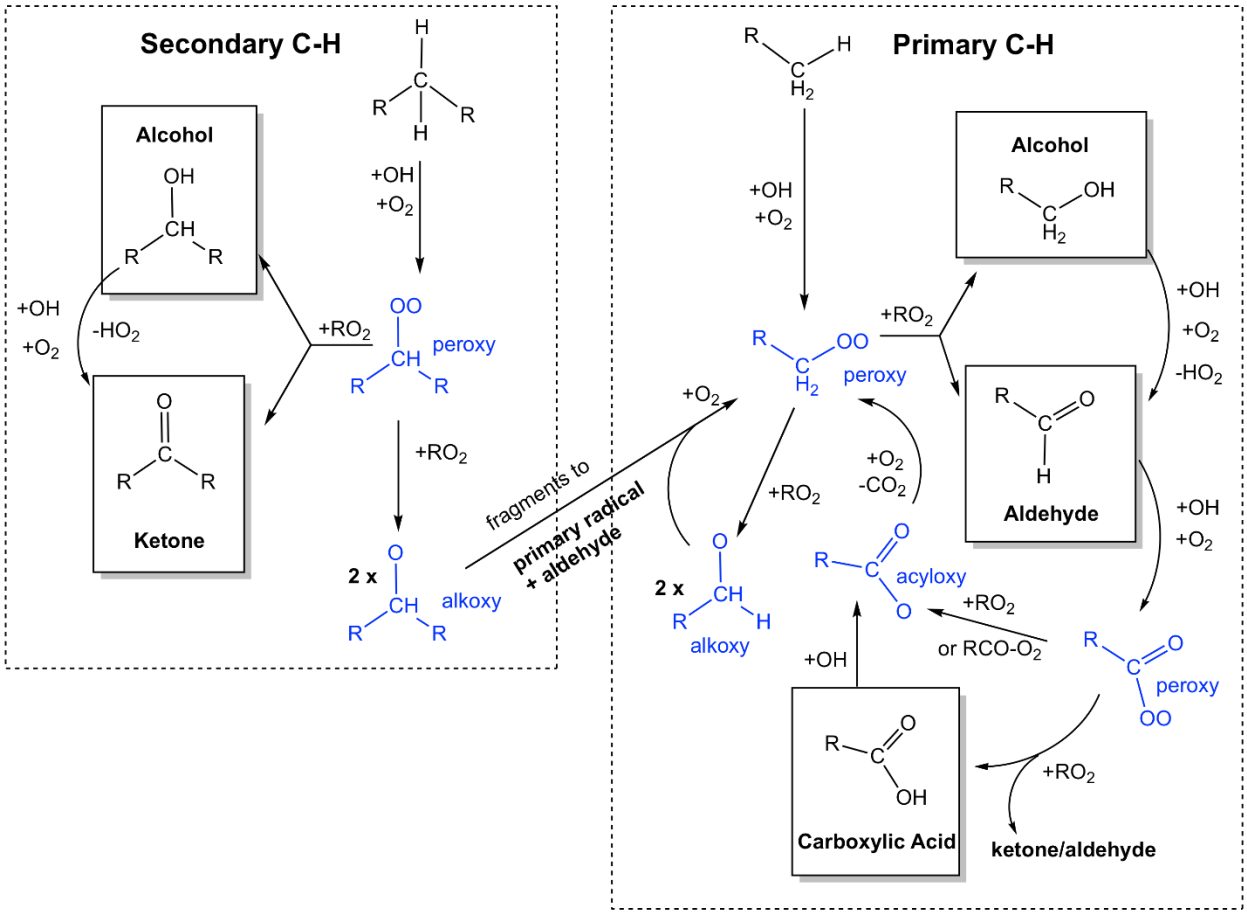
1. Reaction scheme

The full free radical reaction mechanism initiated by OH abstraction of H from $C_{30}H_{62}$ has been constructed and validated in previous studies.[1-2] Scheme S1 sketches out unimolecular and bimolecular routes to the main products: ketones, alcohols, aldehydes and carboxylic acids via several free radical intermediates.

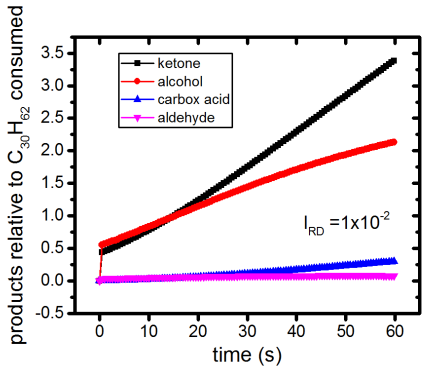


Scheme S1. General reaction scheme for OH abstraction initiated free radical oxidation of an alkane. Two main branches involving secondary and primary H abstraction free radical initiation steps are shown. These branches are applicable to straight-chain molecules; tertiary abstractions have similar reaction types. The branches are interconnected by alkoxy fragmentation. Several

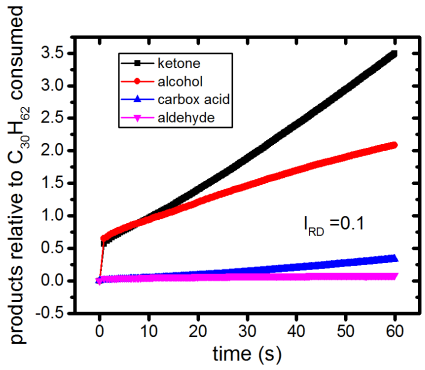
simplifications of the scheme should be noted. The notation "R" is generic and means alkanes or oxygenates of any chain length. Water formed from OH by H abstraction and O_2 from the RO_2 + RO_2 reactions are not shown for clarity. Also not shown are the details of acyl peroxy radical disproportionation products from reactions with peroxy radicals with alkyl peroxy or acyl peroxy radicals. The major product of reaction with alkyl peroxy is carboxylic acids and ketones/aldehydes, and the minor product is acyloxy radicals. The product of reaction with acyl peroxy radicals is two acyloxy radicals.

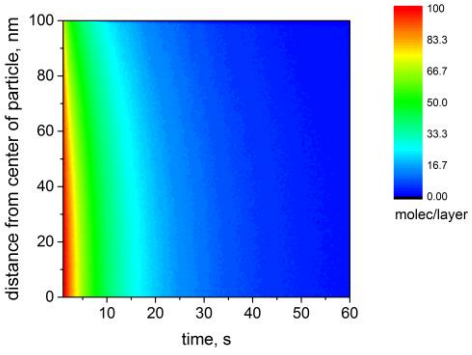
2. Particle compositions

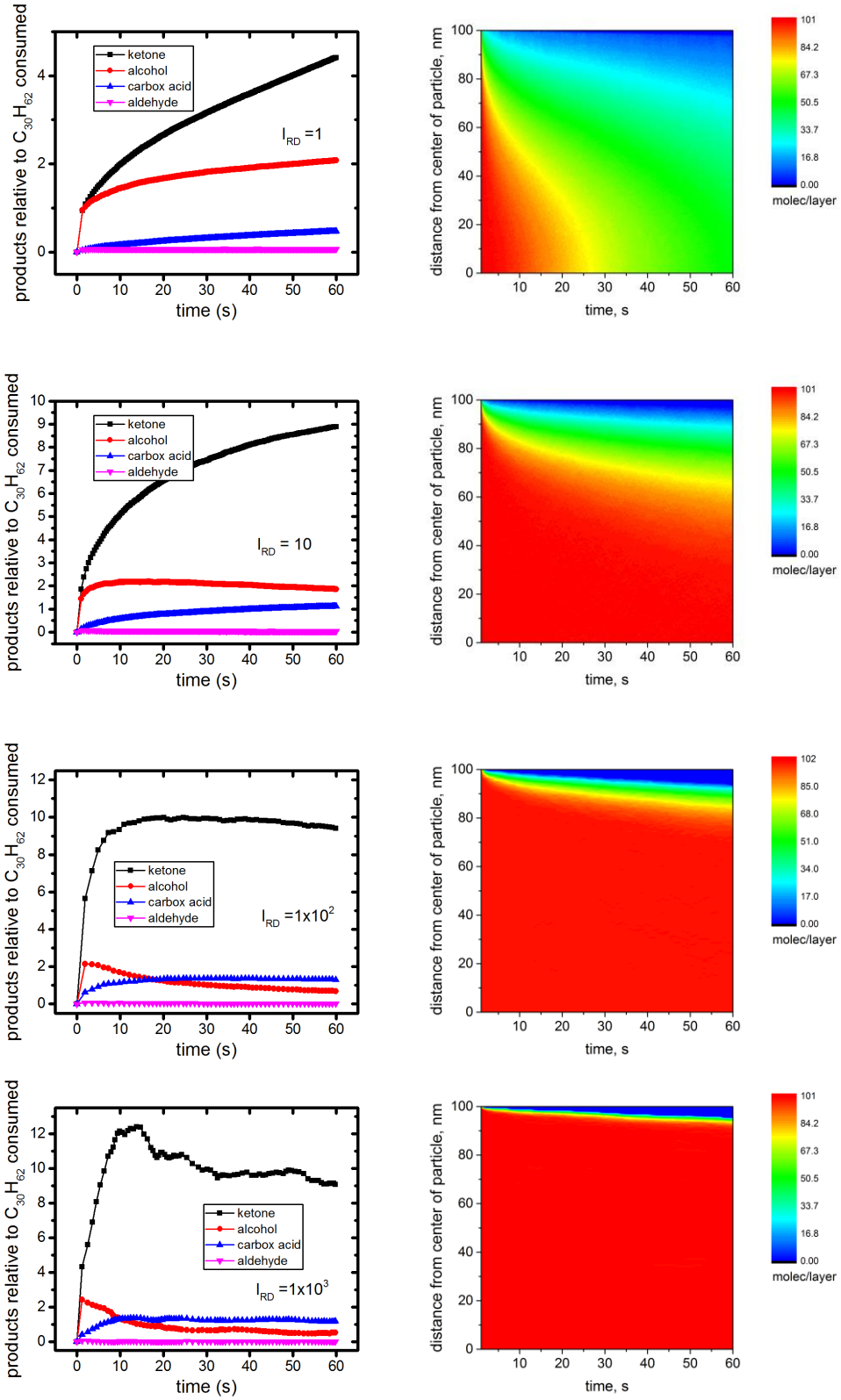
The amounts of functionalities per $C_{30}H_{62}$ reacted and the spatial distribution of unreacted $C_{30}H_{62}$, which shows extent of mixing during oxidation, are presented in Figure S1 as a function of I_{RD}. When I_{RD} = 1, the mixing and OH reaction rates are balanced.



This case was calculated using a single compartment, no spatial information is available.






products relative to $C_{30}H_{62}$ consumed
ketone
alcohol
carbox acid
aldehyde
I_{RD} =1
time (s)
distance from center of particle, nm
time, s
101
84.2
67.3
50.5
33.7
16.8
0.00
molec/layer
products relative to $C_{30}H_{62}$ consumed
ketone
alcohol
carbox acid
aldehyde
I_{RD} = 10
time (s)
distance from center of particle, nm
time, s
101
84.2
67.3
50.5
33.7
16.8
0.00
molec/layer
products relative to $C_{30}H_{62}$ consumed
ketone
alcohol
carbox acid
aldehyde
I_{RD} =1x10^2
time (s)
distance from center of particle, nm
time, s
102
85.0
68.0
51.0
34.0
17.0
0.00
molec/layer
products relative to $C_{30}H_{62}$ consumed
ketone
alcohol
carbox acid
aldehyde
I_{RD} =1x10^3
time (s)
distance from center of particle, nm
time, s
101
84.2
67.3
50.5
33.7
16.8
0.00
molec/layer

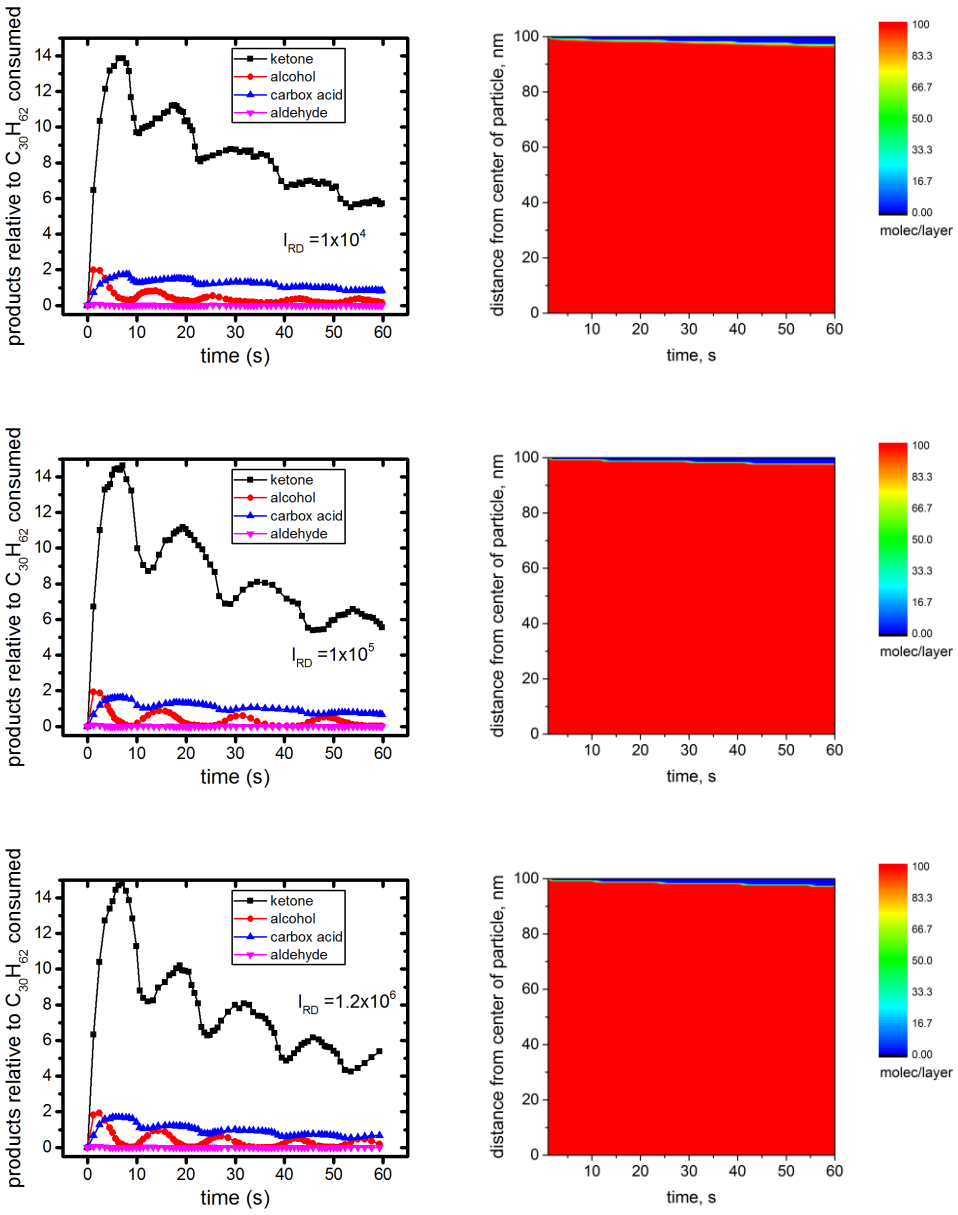


Figure S1. Functionalities formed per $C_{30}H_{62}$ consumed (left column) with corresponding spatial distributions of unreacted $C_{30}H_{62}$ (right column). The spatial distributions reveal the extent of mixing during the reaction, ranging from near-uniform to very little as I_{RD} increases from 10^{-2} to 10^{6}, corresponding to self-diffusion coefficients of 10^{-11} to approximately 10^{-18} cm^2/s. The oscillations in the data for $I_{RD} \geq 10^{3}$ are artifacts of the multilayer simulation. Each 0.5 nm thick layer is assumed to be a well-mixed compartment with no internal diffusion limits on the

availability of $C_{30}H_{62}$ for reaction. Each time a new layer is exposed, the $C_{30}H_{62}$ – OH reaction has the maximum rate. As $C_{30}H_{62}$ is consumed and products evaporate, the rate decreases until a new layer is exposed.

3. Reactivity metrics

Several key measures of reactivity are linked. As D is varied, I_{RD} varies as shown in Equation (5). If I_{RD} is set at a specific value, k_{rx} is calculated from Equation (5). The reacto-diffusion lengths L are calculated using Equation (2). k_{rx} is also plotted in Figure S2.

Table S1. Reactivity metrics calculated for each value of D used in the simulations.

D (cm^2 s^{-1})	I_{RD}	k_{rx} (cm^3/molec-s)	L (nm) [a]
Well-mixed	$\leq 10^{-2}$	2.01×10^{-12}	14.3
10^{-11}	1.02×10^{-1}	2.09×10^{-12}	4.6
10^{-12}	1.02	2.12×10^{-12}	1.5
10^{-13}	1.02×10^{1}	2.19×10^{-12}	0.5
10^{-14}	1.02×10^{2}	2.24×10^{-12}	0.15
10^{-15}	1.02×10^{3}	2.17×10^{-12}	4.7×10^{-2}
10^{-16}	1.02×10^{4}	2.10×10^{-12}	1.5×10^{-2}
10^{-17}	1.02×10^{5}	2.08×10^{-12}	4.6×10^{-3}
8.39×10^{-19}	1.22×10^{6}	2.10×10^{-12}	1.5×10^{-3}

[a] The simulation geometry has a maximum resolution of 0.5 nm, so L values less than this dimension are not directly simulated. Products characteristic of smaller L are inferred from the overall product distributions.

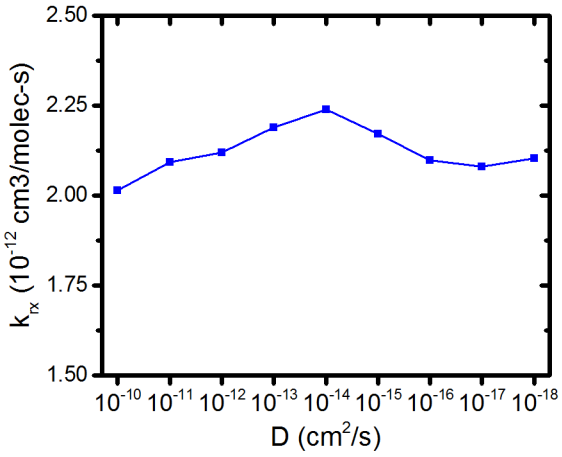


Figure S2. Apparent k_{rx} calculated from Equation (3) for each D in the simulation.

References

1. Wiegel, A. A.; Liu, M.; Hinsberg, W. D.; Wilson, K. R.; Houle, F. A., Diffusive Confinement of Free Radical Intermediates in the Oh Radical Oxidation of Semisolid Aerosol. *Physical Chemistry Chemical Physics* **2017**, *19*, 6814-6830.
2. Wiegel, A. A.; Wilson, K. R.; Hinsberg, W. D.; Houle, F. A., Stochastic Methods for Aerosol Chemistry: A Compact Molecular Description of Functionalization and Fragmentation in the Heterogeneous Oxidation of Squalane Aerosol by Oh Radicals. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4398-4411.