



# Reactive Dimerization of Small Aromatics Drives Soot Nucleation

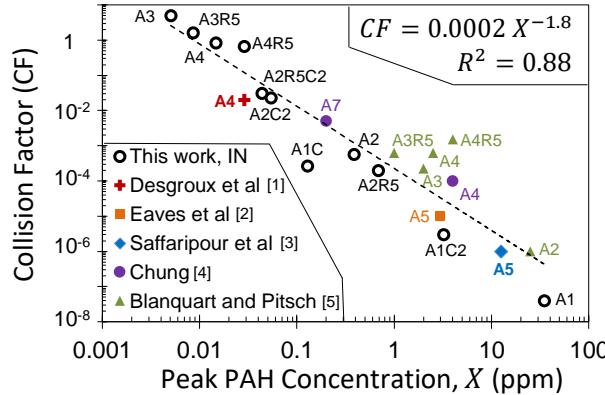
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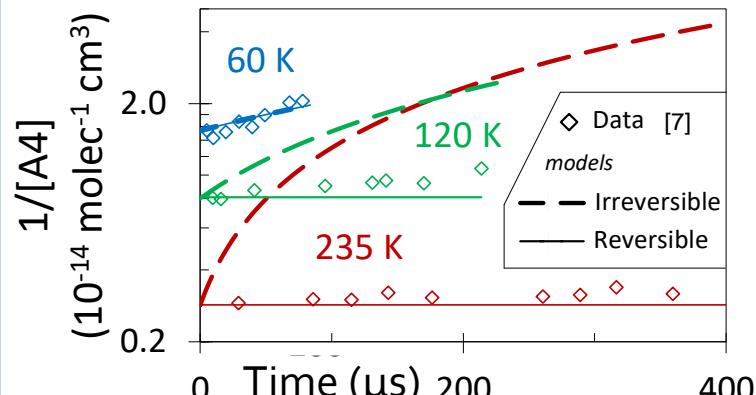
## Motivation

Nucleation of incipient soot and carbon black affects particle size distribution, morphology and composition. However, nucleation is poorly understood. Clusters of large Polycyclic Aromatic Hydrocarbons (PAH) with physical or chemical forces are often considered as soot nuclei. Here a kinetic model is developed to investigate soot nucleation mechanisms, dominant species and oligomers in a so called "nucleation" premixed flame.

### For Classic Nucleation, any PAH can be used!



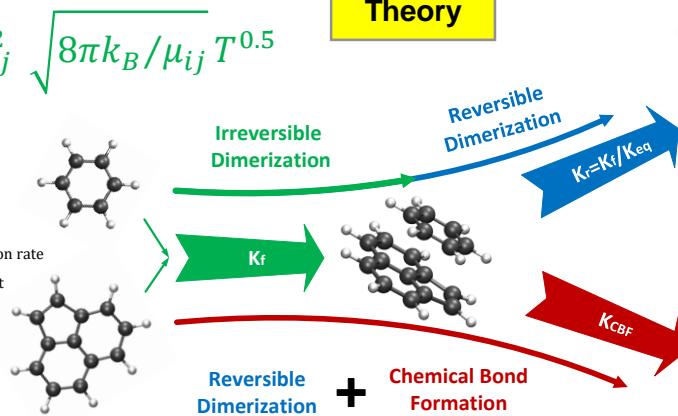
### Physical Nucleation is Reversible and Weak



Collision factors used for modeling soot nucleation with irreversible nucleation model (IN) vs. peak PAH concentration in different flames.

### Theory

$k_f \approx CF d_{ij}^2 \sqrt{8\pi k_B / \mu_{ij}} T^{0.5}$   
 CF = collision factor  
 $d_{ij}$  = collision diameter  
 $E_a$  = Activation energy  
 $k_B$  = Boltzman constant  
 $k_{eq}$  = equilibrium constant  
 $k_{f,r}$  = forward, reverse dimerization rate  
 $MW_{ij}$  = Reduced molecular weight  
 $R_u$  = Gas constant  
 T = Temperature  
 $\mu_{ij}$  = Reduced mass  
 $\varepsilon$  = Intermolecular forces



$$k_r = \frac{k_f}{k_{eq}}$$

$$k_{eq} = 10^{\frac{a}{R_u T} + b}$$

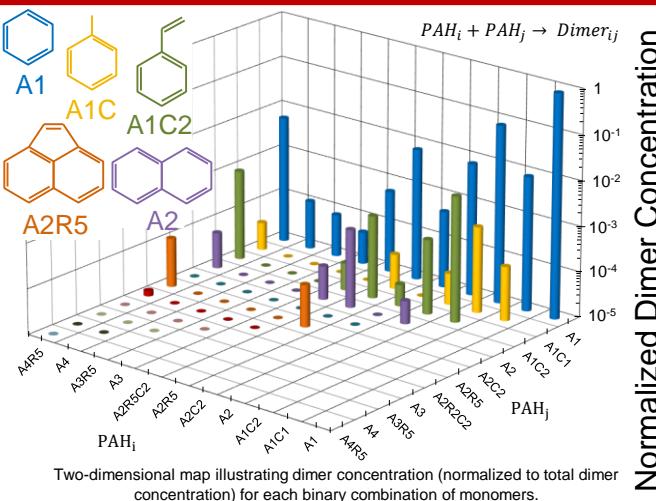
$$\varepsilon = c MW_{ij} - d$$

$$k_{CBF} \approx T^{0.5} e^{(-E_a / R_u T)}$$

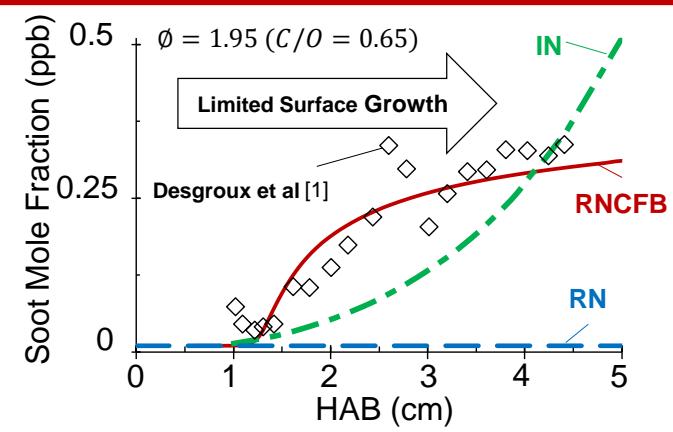
$$E_a \approx 25 \text{ kcal/mol}$$

Full Story in: Kholghy, M.R., Kelesidis, G.A., & Pratsinis, S.E. (2018). *Phys Chem Chem Phys*, 20, 10926.

### Small Aromatics Contribute the Most



### Chemical Bonding is Required for Nucleation



Evolution of soot concentration measured by LII and predicted by Reversible Nucleation and PAH Chemical Bond Formation (RNCBF), Irreversible Nucleation (IN) and Reversible Nucleation (RN) models.

### References

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### Conclusions

1. Physical nucleation must be modeled reversible and cannot explain soot nucleation at high temperatures.
2. An irreversible nucleation model using a collision factor cannot capture the temperature dependency of nucleation.
3. Only by accounting for a nucleation process that involves chemical bond formation, soot nucleation kinetics can be modeled.
4. Soot nucleation at high temperature has a thermodynamic barrier of 21 kcal/mol.