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Role of H-bonding in Modulating Reactivity with Criegee Intermediates

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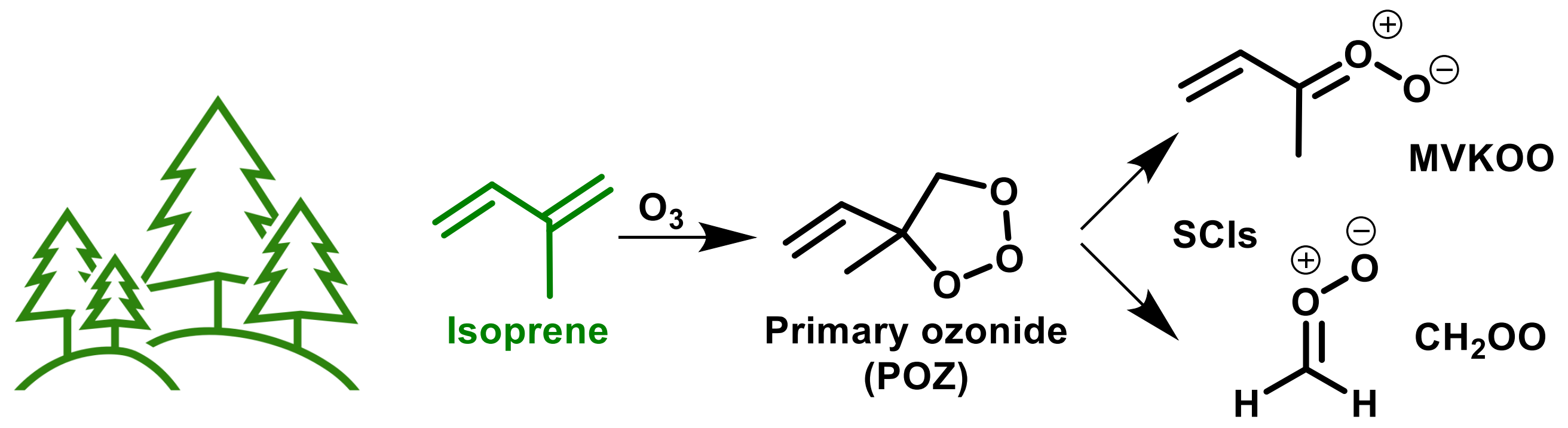
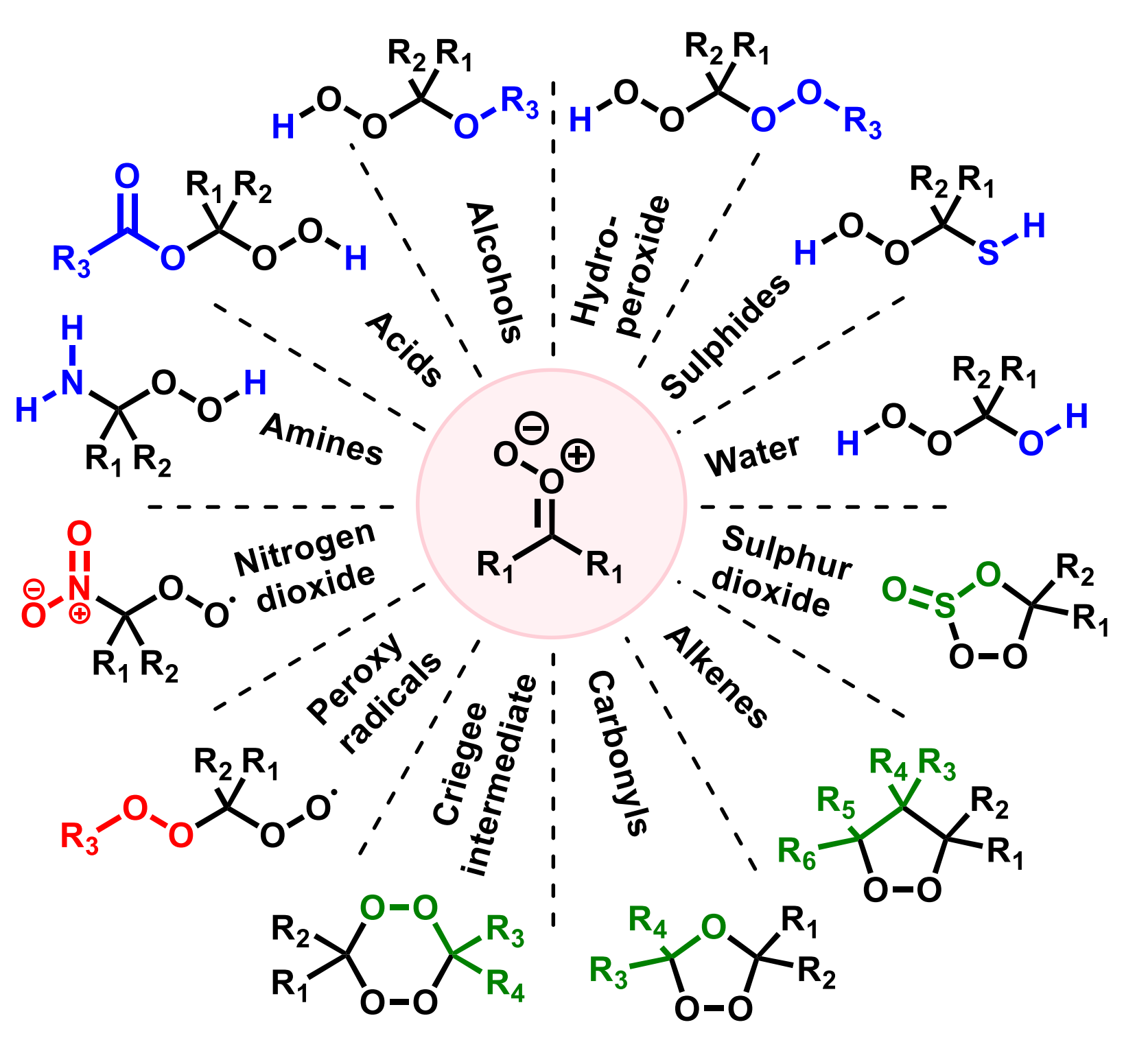
1. Background

Atmospheric relevance of Criegee intermediates

Formation: Stabilized Criegee intermediates (SCIs) are produced in the troposphere during ozonolysis of alkenes, primarily from natural emissions like isoprene.



Implicated: To transform the composition of Earth's troposphere and in the formation of secondary organic aerosol (SOA).



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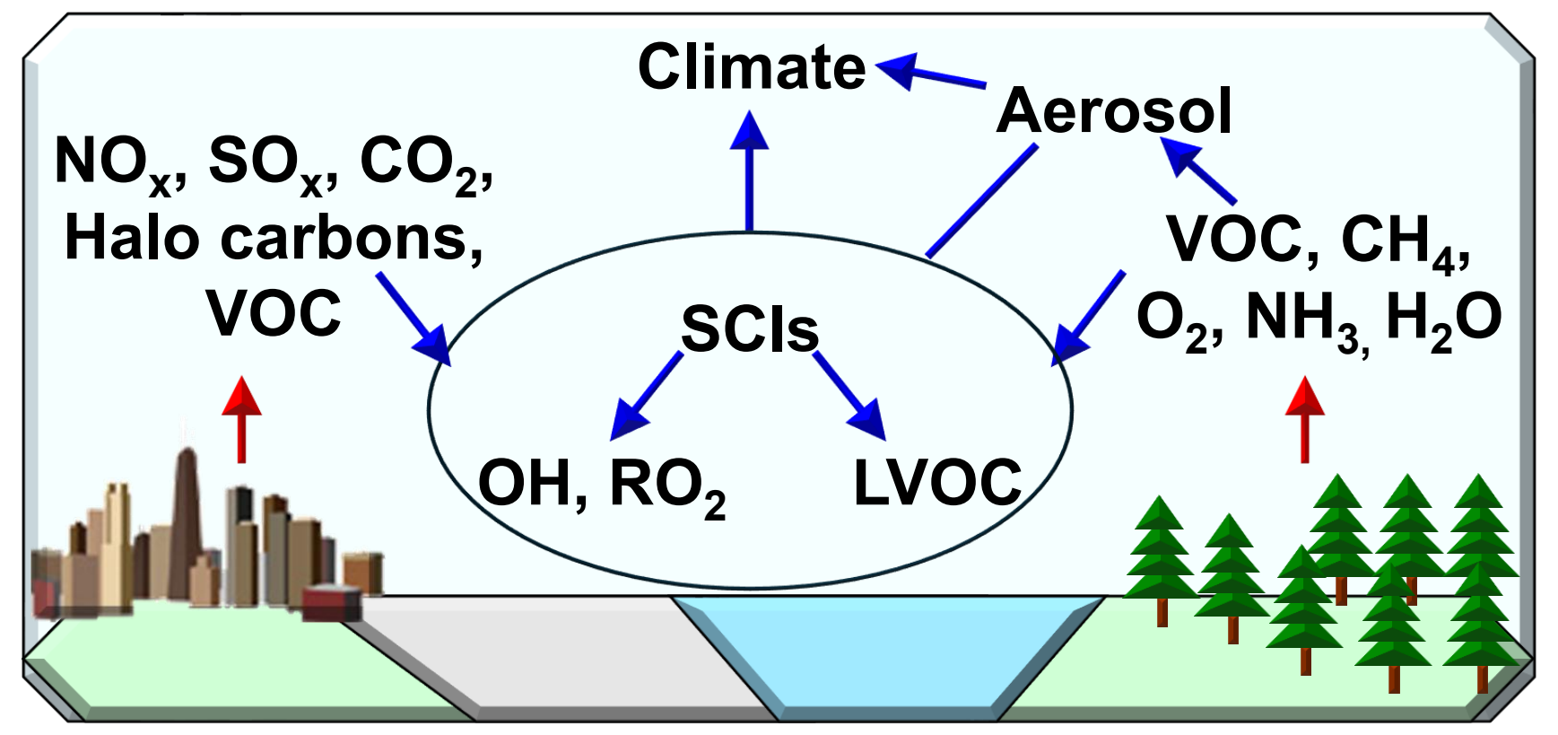
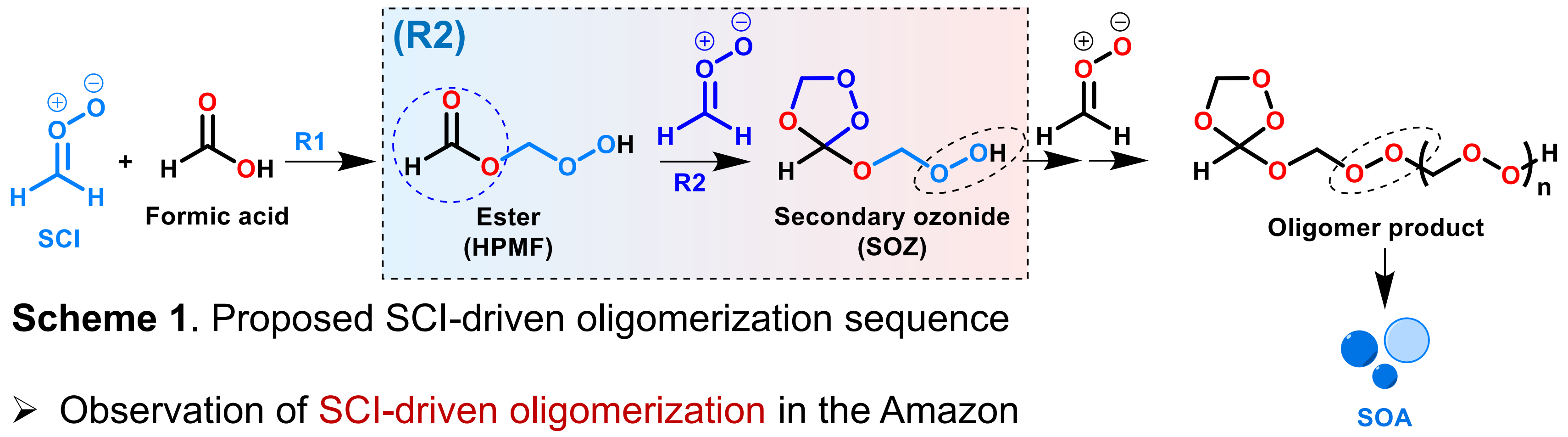


Research gaps

- SOA particle impact on climate and air quality remains poorly quantified
- Uncertainty in the SOA formation mechanism

2. Key objectives

Does SCI shape organic particle growth in the atmosphere?



Scheme 1. Proposed SCI-driven oligomerization sequence

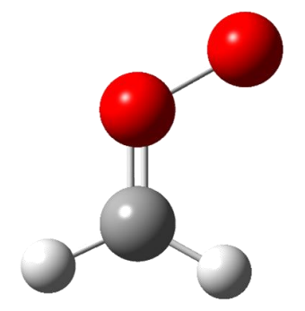
- ➢ Observation of SCI-driven oligomerization in the Amazon
  Nat. Geosci., **2024**, *17* (3): 219-226
- ➢ Atmospheric chemistry model underpredicted SOZ formation by ~2500×
- ➢ Do these reactions compete in a humid environment?

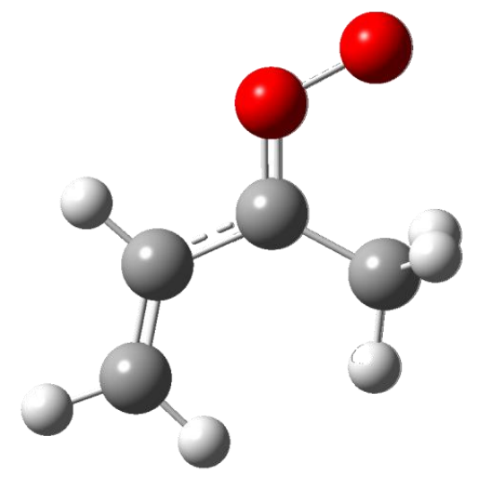
3. Methods

Our approach

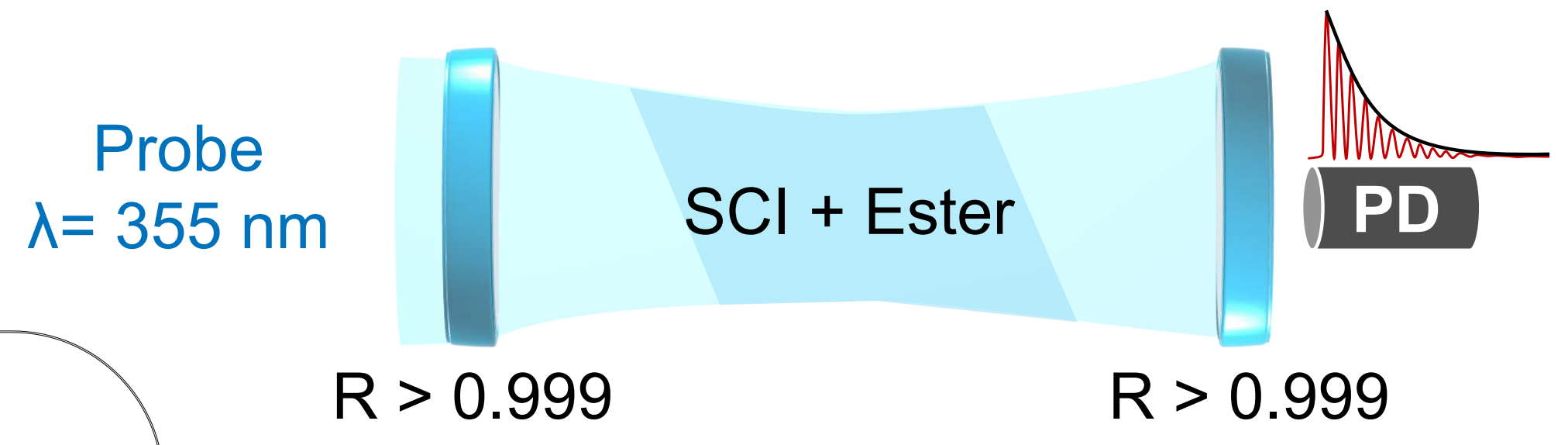
- ➢ Laboratory-generated SCIs for direct kinetic investigation of target reactions

CH_2I_2 + hv (355 nm) → CH_2I + I
CH_2I + O_2 → CH_2OO + I





$ICH_3C{=}CHCH_2I$ + hv (266 nm)
($\cdot C_4H_6I$) + I → ($\cdot C_4H_6I$) + O_2 ⇋ $IMVKOO^{\#}$
$IMVKOO^{\#}$ → MVKOO + I



Cavity ring-down spectroscopy (CRDS)

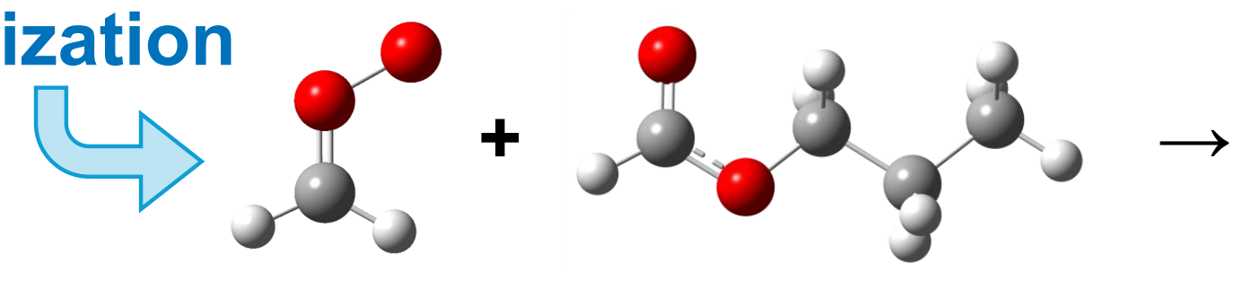
$$\tau = \frac{L}{c\,[(1-R)+\alpha d]}$$

- ➢ Isolate SCI–ester cycloaddition reaction: potentially important step in SCI-driven oligomerization (Scheme 1)

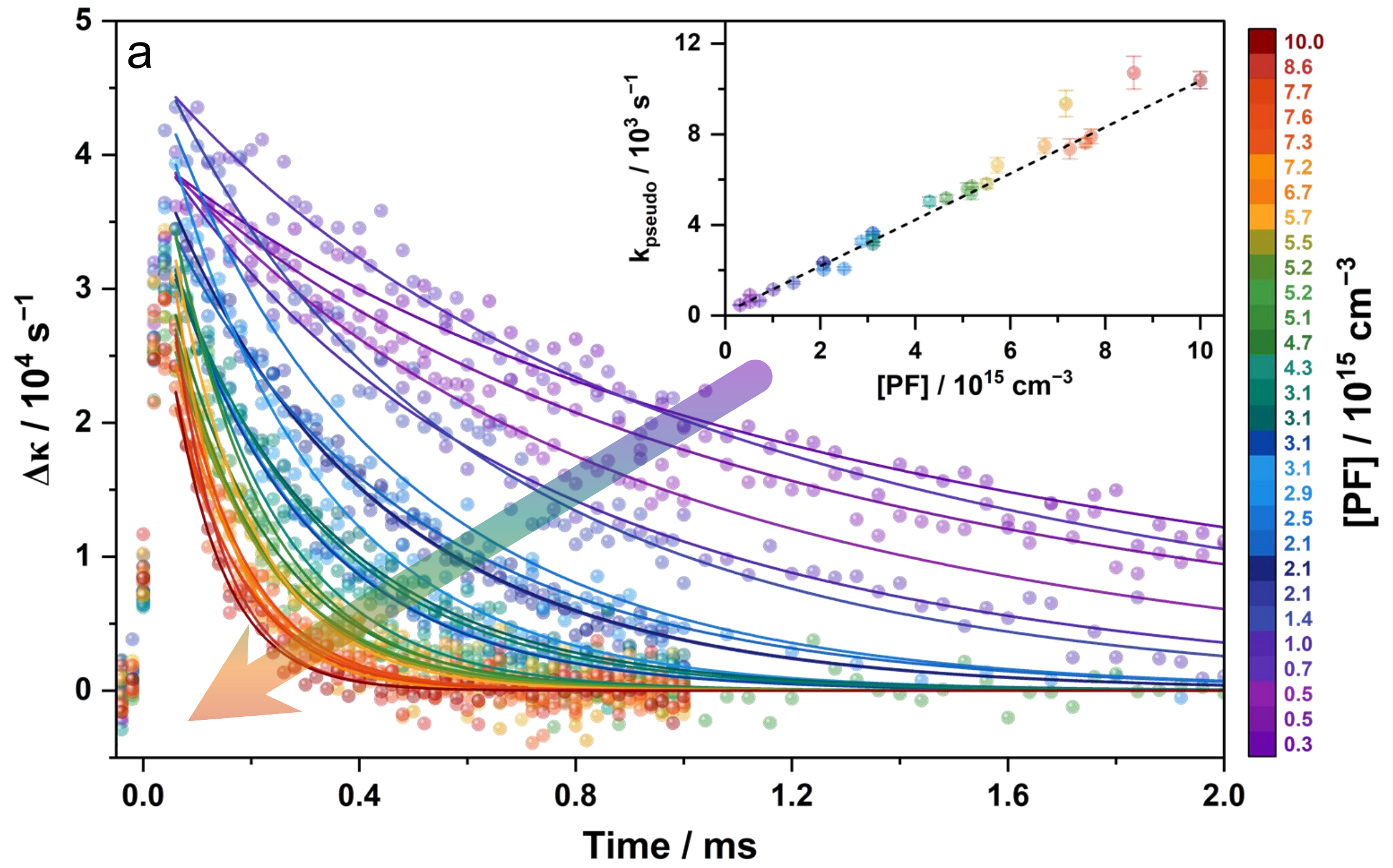
Direct kinetics of functionalized SCIs and VOCs are needed to improve model predictions

4. Results

Simplified mimetic system to probe Criegee-ester oligomerization



→ **SOZ** **(R2')**



CH_2OO temporal decay profiles recorded under excess propyl formate (PF), pseudo-first-order conditions. a) linear fit to the k_{pseudo} vs [PF] plot yielded bimolecular rate coefficient **(1.1 ± 0.2) × 10^{-12} cm^3 s^{-1}**

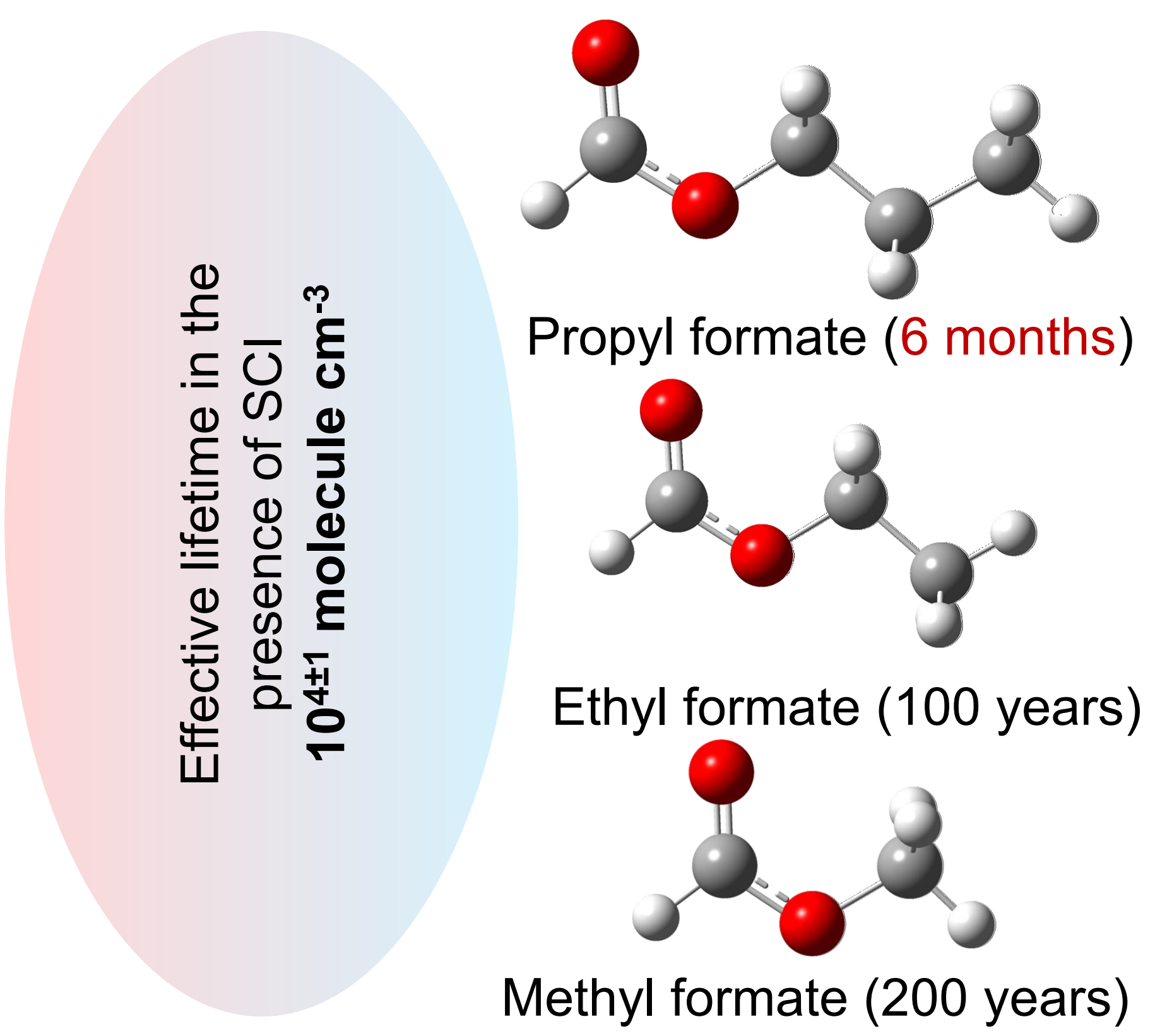
- ➢ Propyl formate exhibits a **~300-fold enhanced reactivity** relative to methyl formate
- ➢ Potential role of propyl chain (analogous to hydroperoxyl methyl chain in proposed R2 reaction)
- ➢ Non-linear increase in reaction rate with ester chain length from C1 to C3

- ➢ Increasing PF concentration accelerates SCI decay

SCI decay fitted to the kinetic model

$$\frac{d[CH_2OO]}{dt} = \underset{\substack{\uparrow\\ \text{self-reaction}}}{-2k_{SR}[CH_2OO]^2} - \underset{\substack{\uparrow\\ \text{bimolecular-reaction}}}{k_{pseudo}[CH_2OO]}$$

- ➢ **Complementary experiments with other esters reveal propyl formate is an outlier**



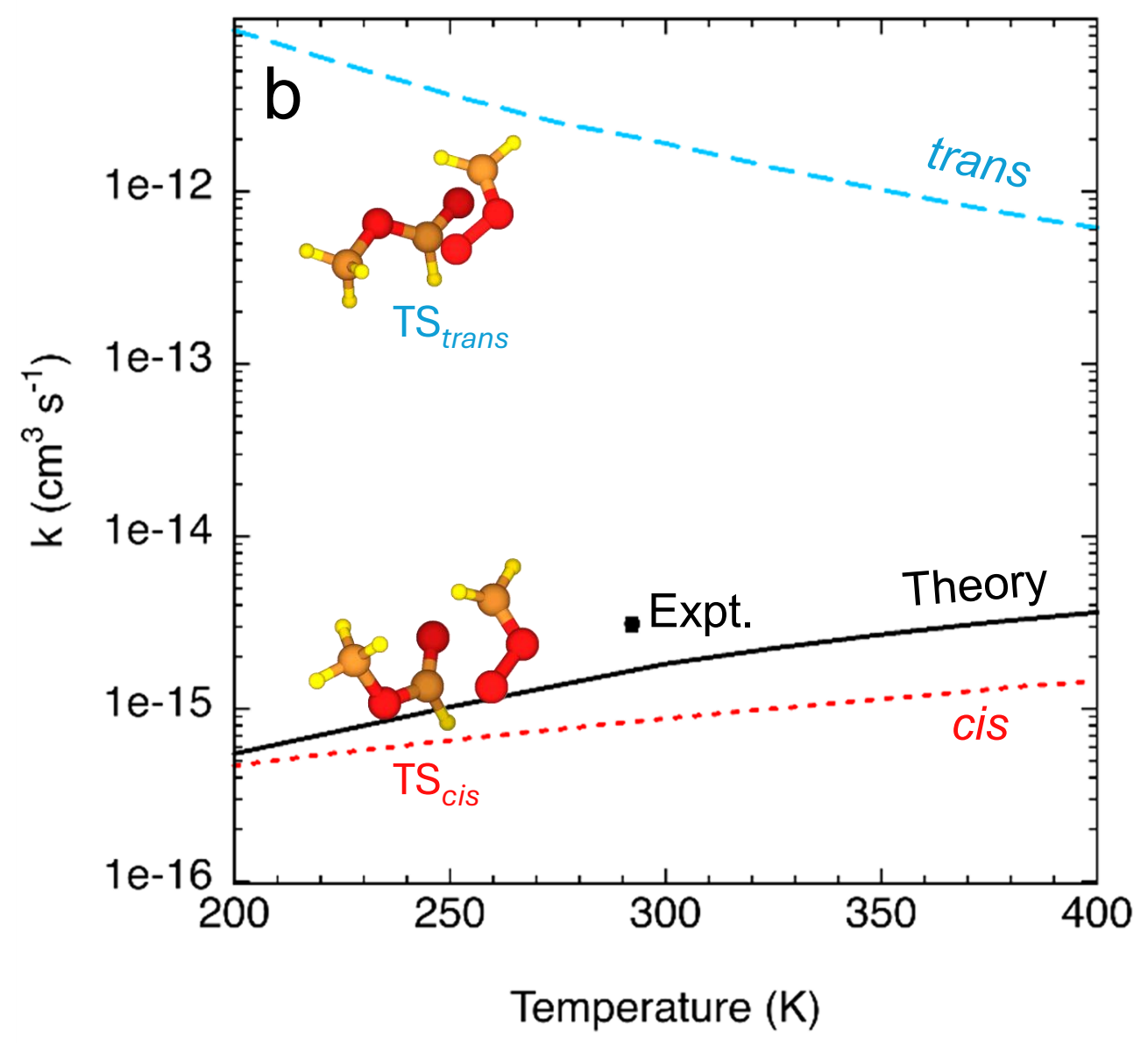
Propyl formate (6 months)

Ethyl formate (100 years)

Methyl formate (200 years)

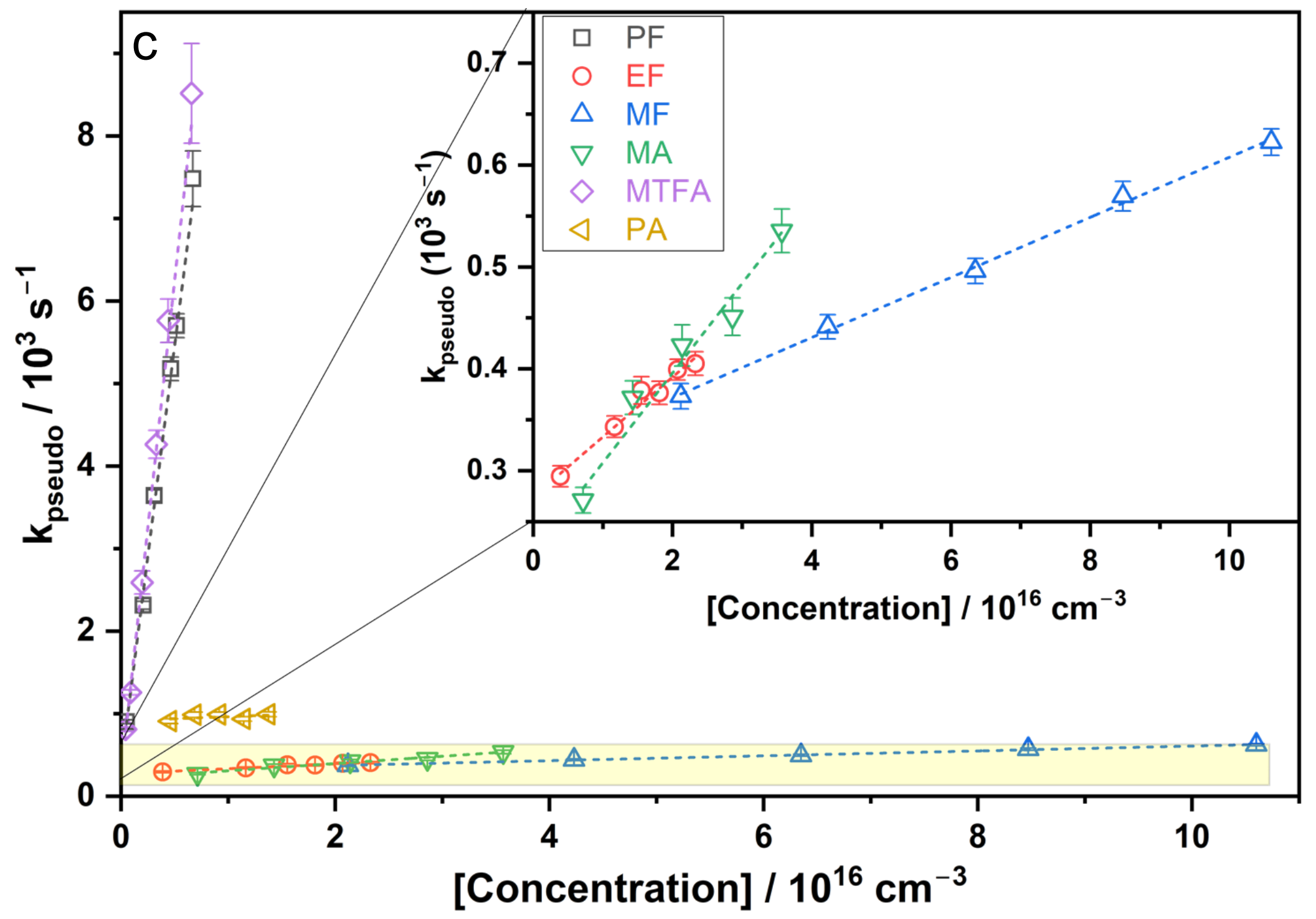
Theoretical kinetics

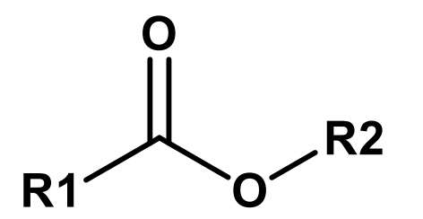
- ➢ High-level quantum calculations reproduce experimental kinetics for CH_2OO + methyl formate, supporting slow reaction of ester with SCI
- ➢ Mechanism: pre-reactive complex → submerged barrier → SOZ formation
- ➢ Distinct cis/trans conformer-dependent reactivity



- ➢ *trans* TS: CH_3 oriented away from reaction site (carbonyl), allowing favourable CH_2OO approach
- ➢ *cis* TS: CH_3 proximity enhances steric hindrance
- ➢ *cis* isomer dominates at room temperature, so overall reaction rate is closer to *cis* estimates.
- ➢ PF exhibits stabilized TS relative to MF, but identified TS insufficient to explain ~300× rate enhancement

- ➢ Evidence of H-bonding using CH_2OO reaction with substituted esters





Ester (R1, R2)

MF: (H, CH_3)
EF: (H, CH_2CH_3)
PF: (H, $CH_2CH_2CH_3$)
MTFA: (CF_3, CH_3)
PA: (CH_3, $CH_2CH_2CH_3$)
MA: (CH_3, CH_3)

- ➢ α-substitution significantly influences the reactivity trend, indicating steric hindrance limits hydrogen-bonding interactions.

5. Conclusions

✓ Criegee-ester reactions are intrinsically slow (10^{-15} cm^3 s^{-1}), owing to major cis population, a propyl tail enables hydrogen-bond–mediated rate enhancement in line with the proposed oligomerization pathway

Significance: This kinetic dataset will improve atmospheric predictions by enabling structure-informed kinetic models for complex, structure-dependent reactivity

Future direction: Validate that reactivity trends arise from functional group proximity, not molecule-specific effects, by extending to diverse systems

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