Toward automated inclusion of representative autoxidation chemistry in explicit models

VILMA

Lauri Franzon

Richard Valorso, Marie Camredon, Bernard Aumont, Julia Lee-Taylor, John Orlando, Anni Savolainen, Siddharth Iyer, Matti Rissanen & Theo Kurtén

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Laboratoire Inter-universitaire des Systèmes Atmosphériques

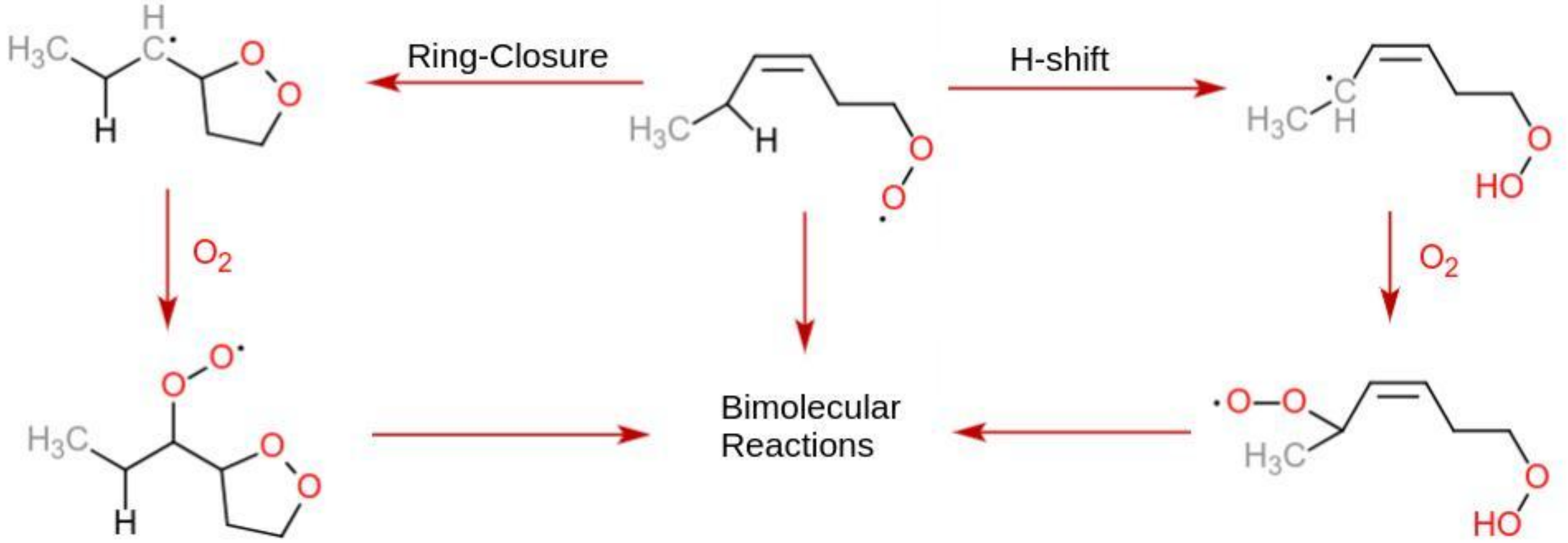
University of Helsinki

NCAR
ACOM

Tampere University

European Geophysical Union General Assembly 29.4.2025

Autoxidation: What and why?



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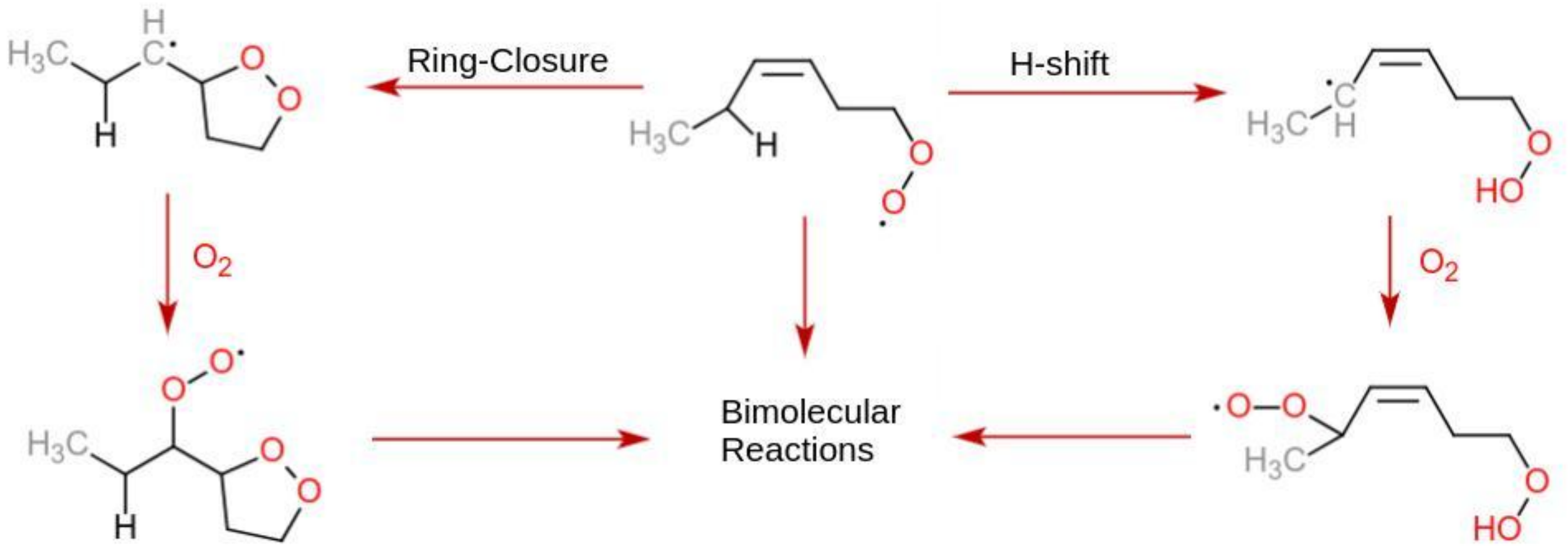
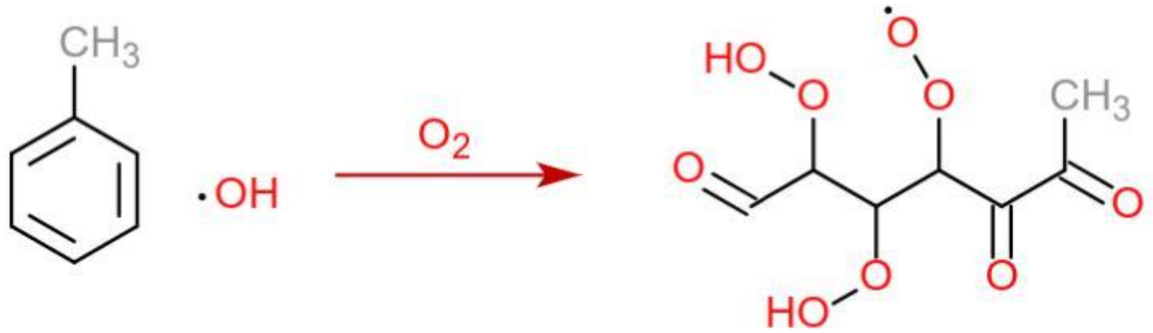
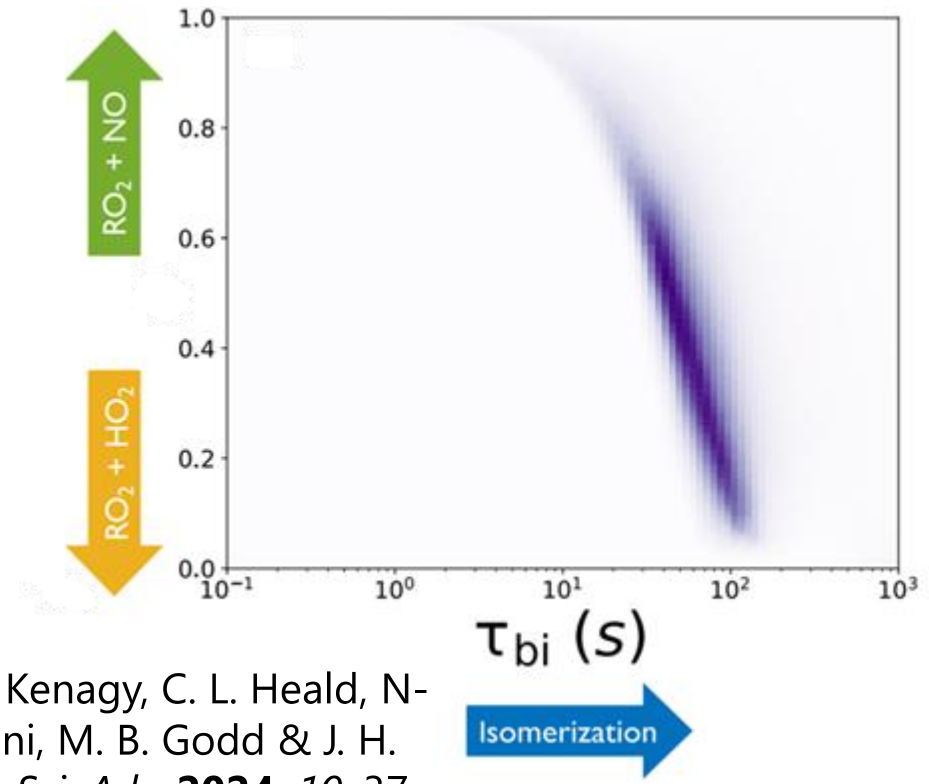




k_r = Fast

S. Iyer *et al., Nat. Comm.* **2023**, *14*, 4984

Autoxidation: Why is it hard to model?



H. S. Kenagy, C. L. Heald, N-Tahsini, M. B. Godd & J. H. Kroll, *Sci. Adv.* **2024**, *10*, 37

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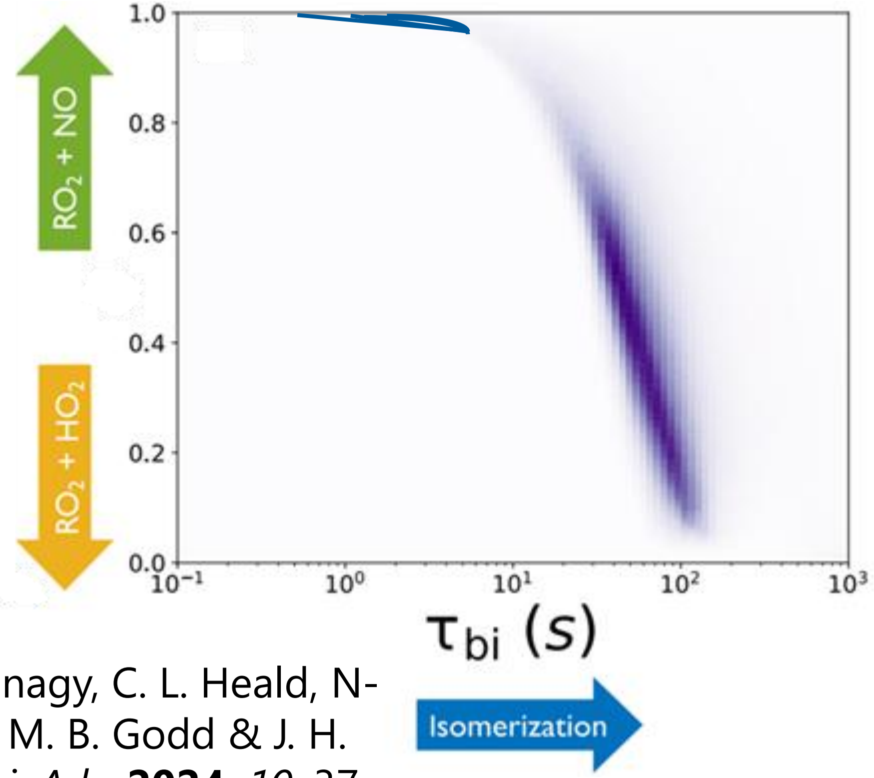

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RO_2 bimolecular lifetimes range from 10^2 s to 10^{-2} s.

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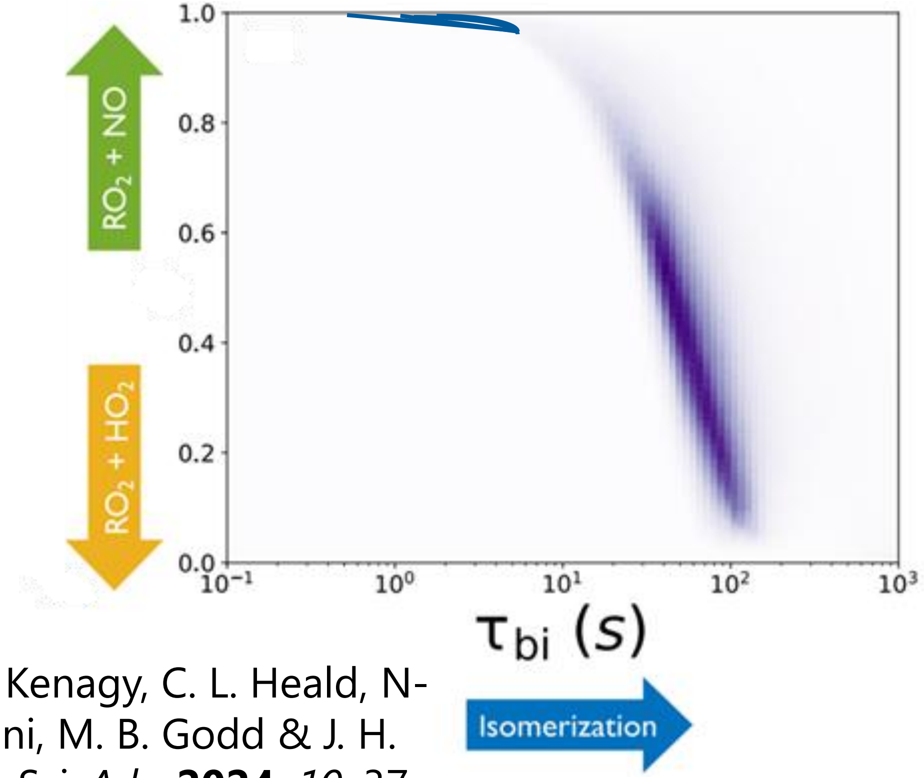

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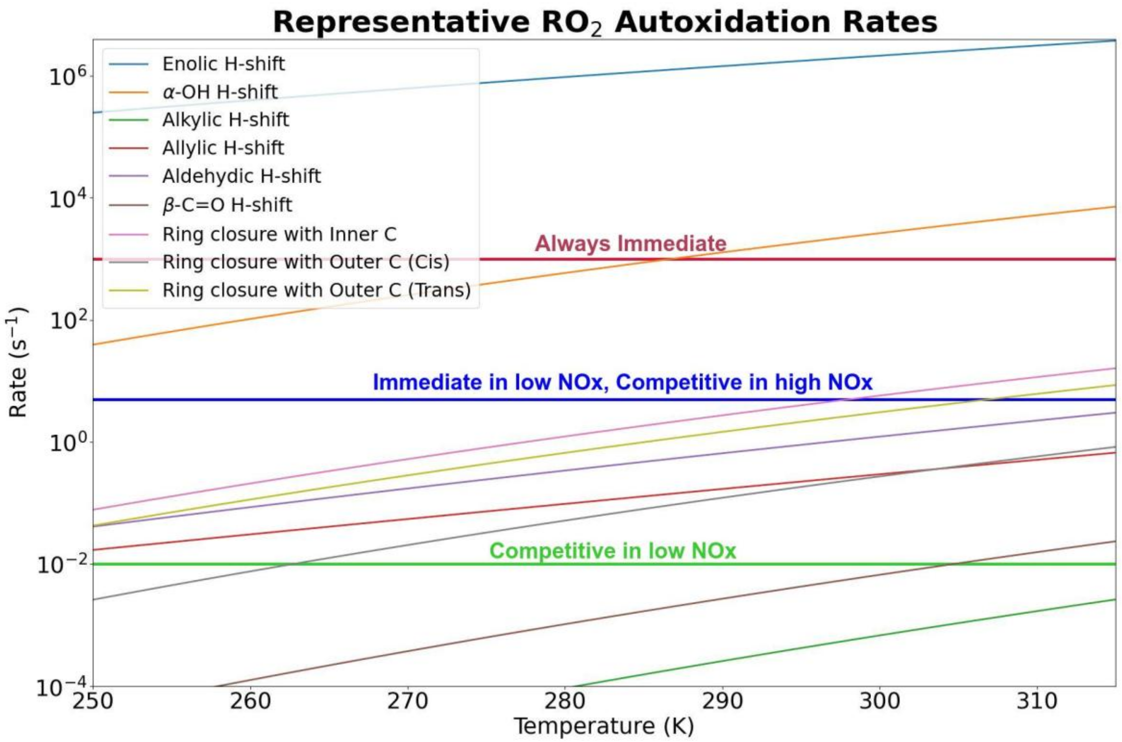

Autoxidation rates vary even more…

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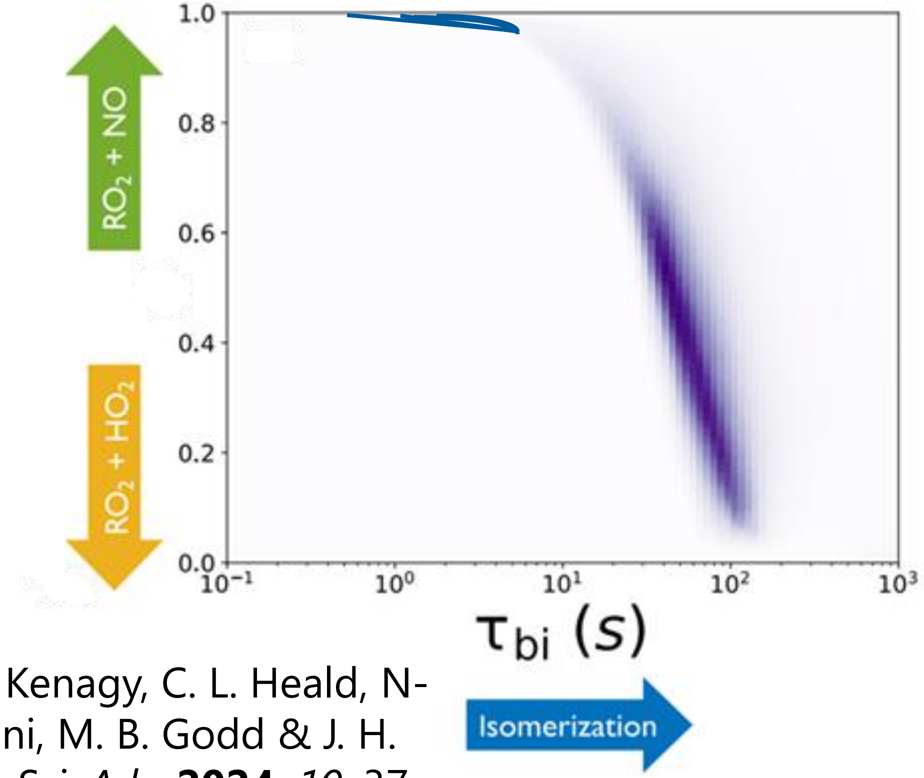

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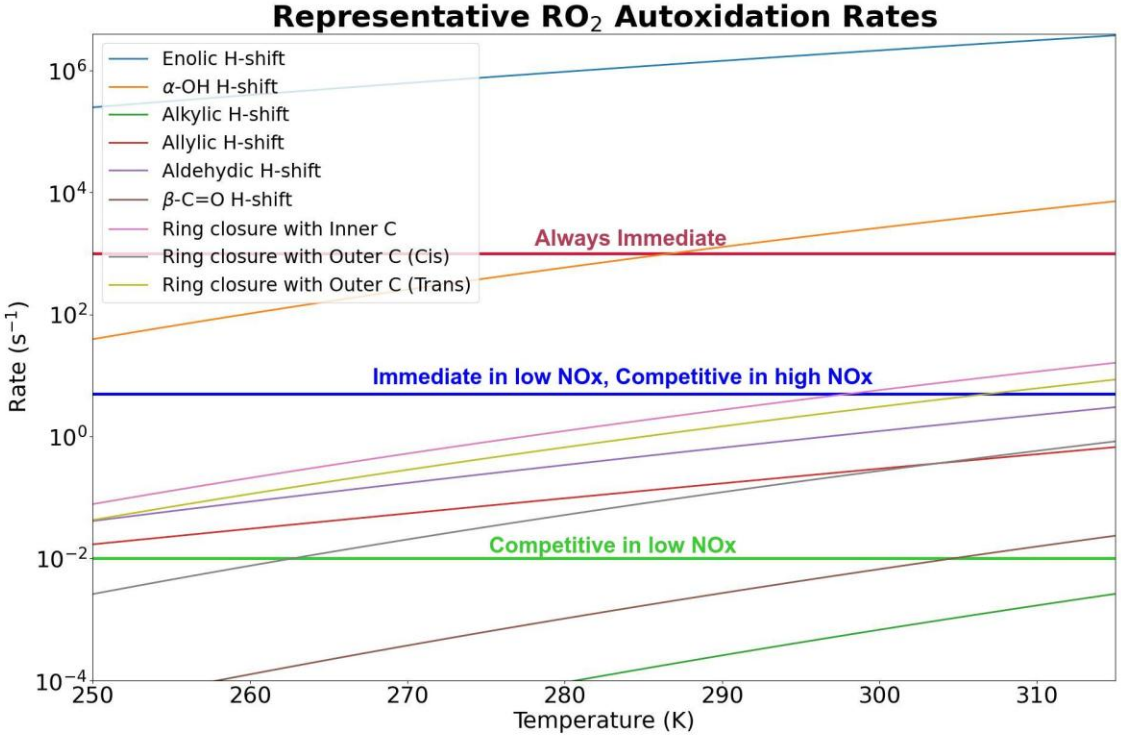
RO$_2$ bimolecular lifetimes range from 10^2 s to 10^{-2} s.

10^{10} cm^{-3} NO, T = 300 K



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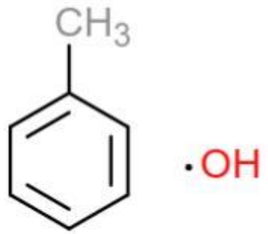
Use cases:



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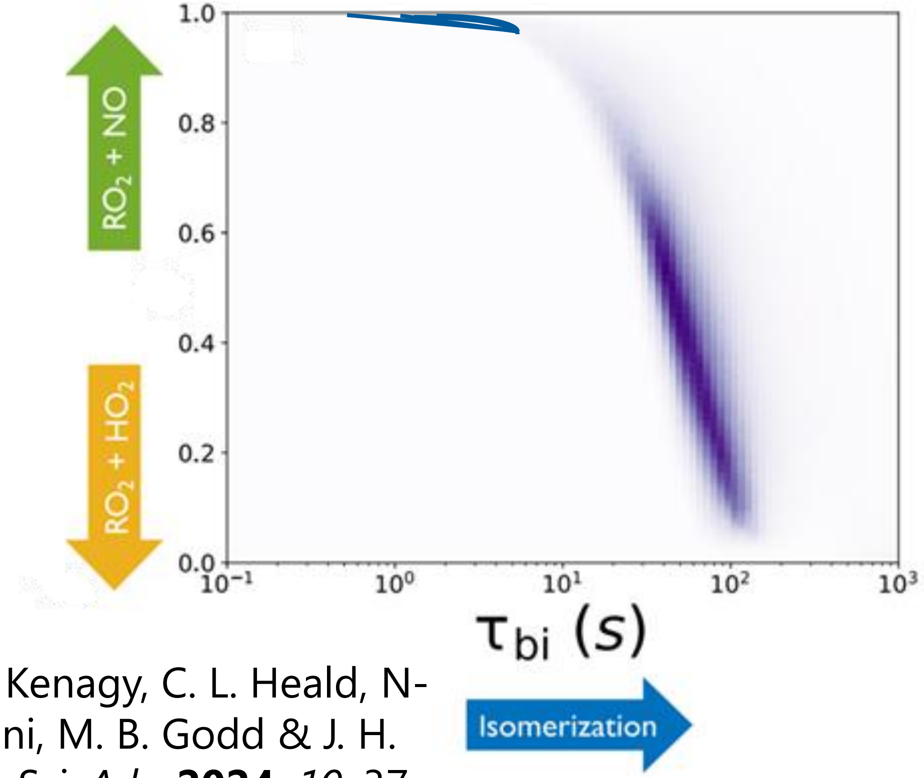

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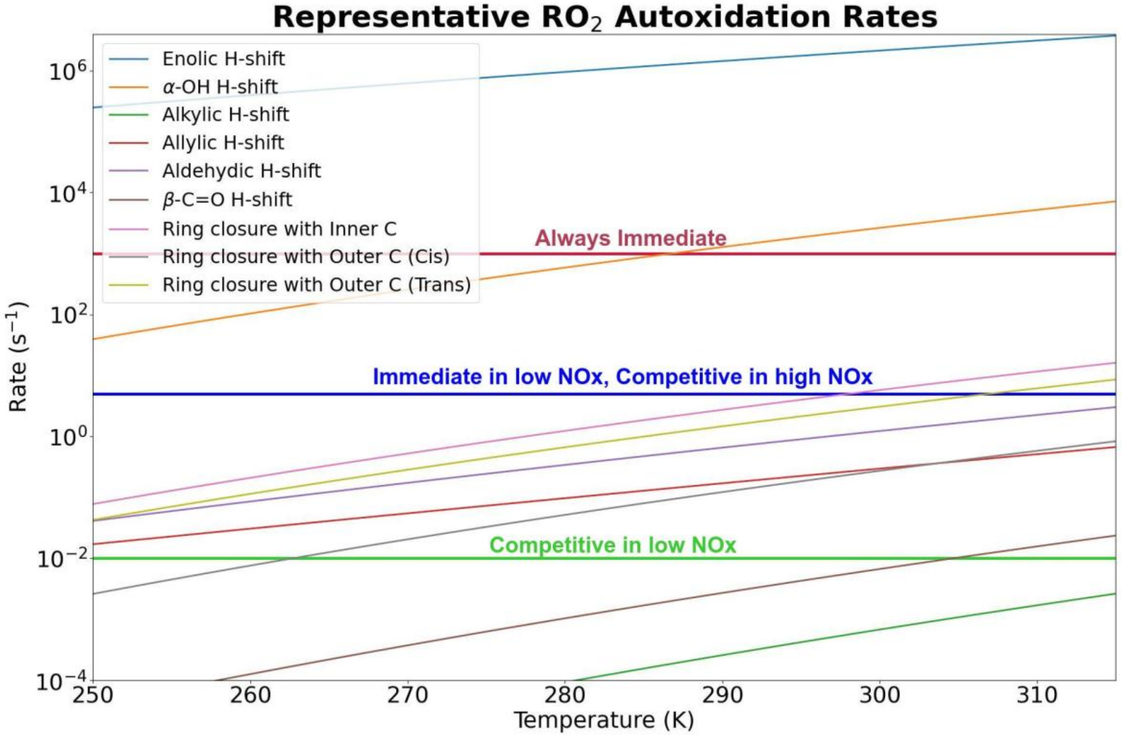
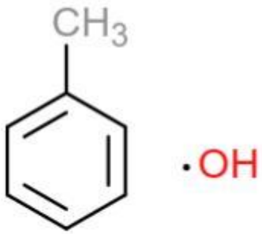


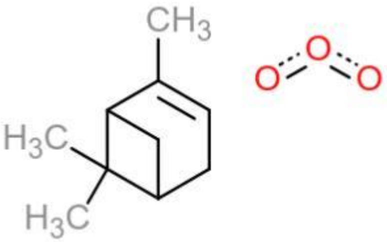
Autoxidation rates vary even more…

10^{10} cm^{-3} NO, T = 300 K

10^9 cm^{-3} NO, T = 280 K

Use cases:





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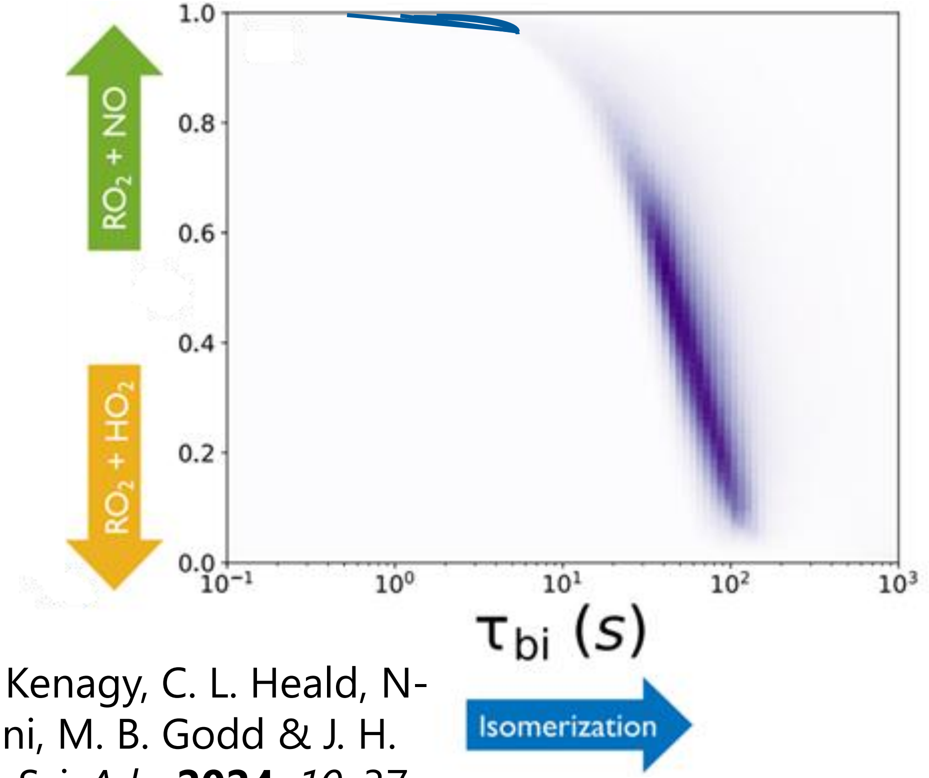

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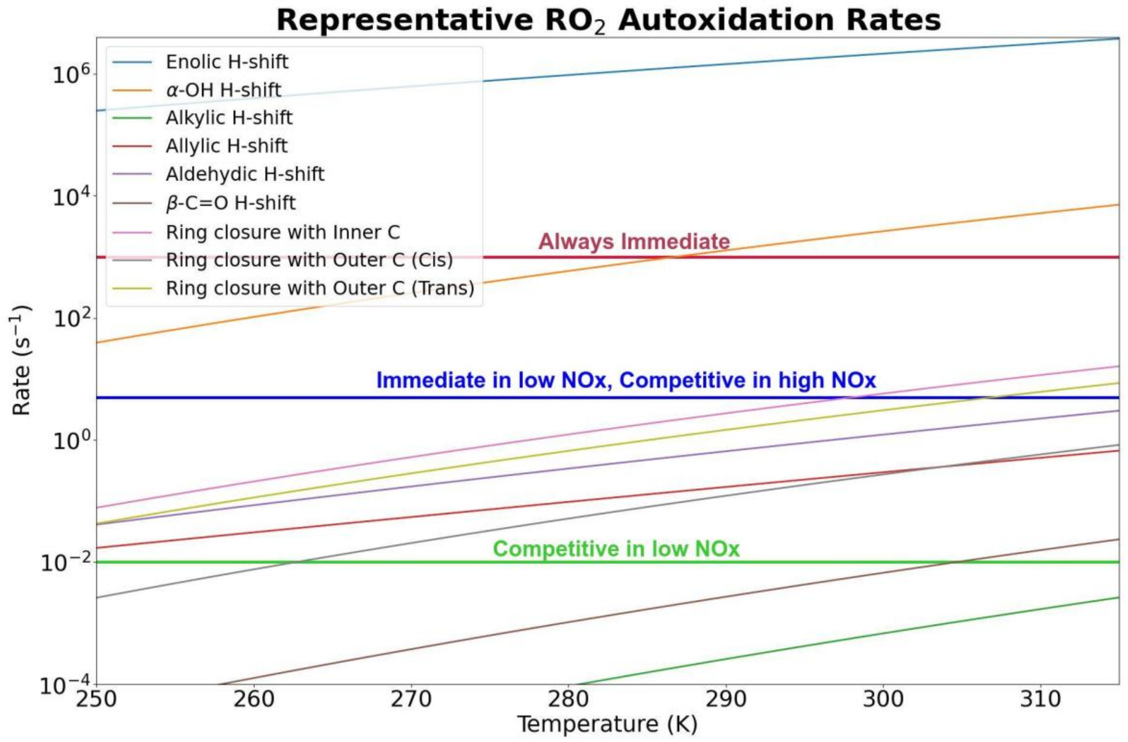

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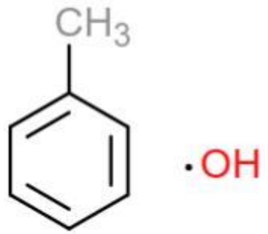
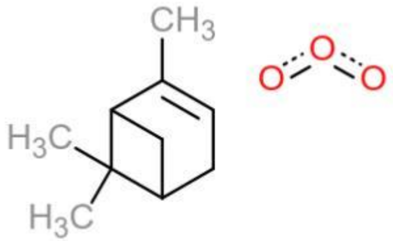
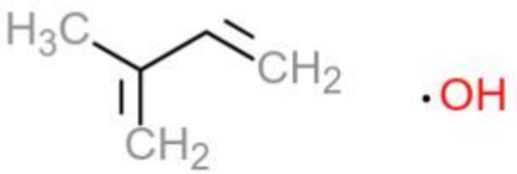


10^{9} cm^{-3} NO, T = 280 K



10^{8} cm^{-3} NO, T = 250 K



GECKO-A

Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere

GECKO-A

Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere

B. Aumont, S. Szopa & S. Madronich
Atmos. Chem. Phys., **2005**, *5*, 9, 2497–2517

GECKO-A

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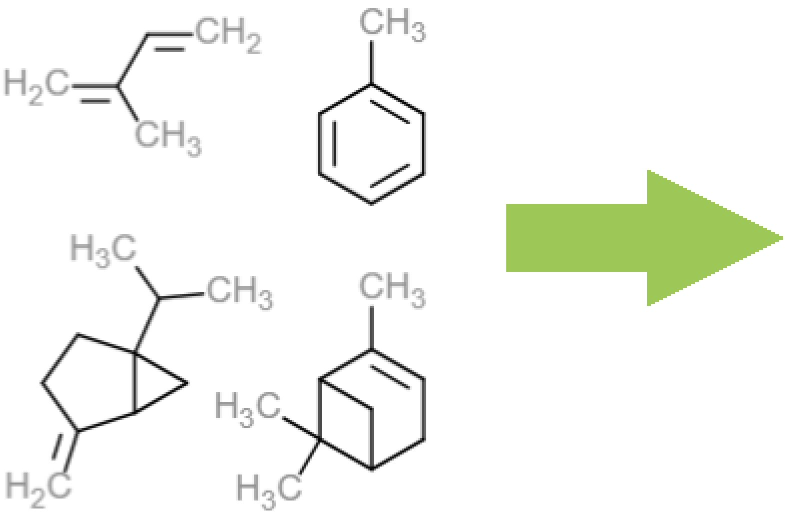

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Volatile Organic Compounds

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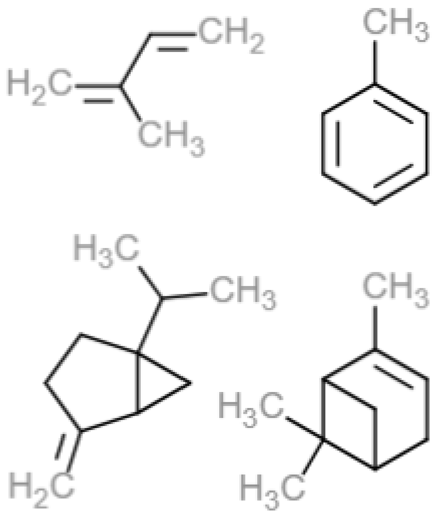

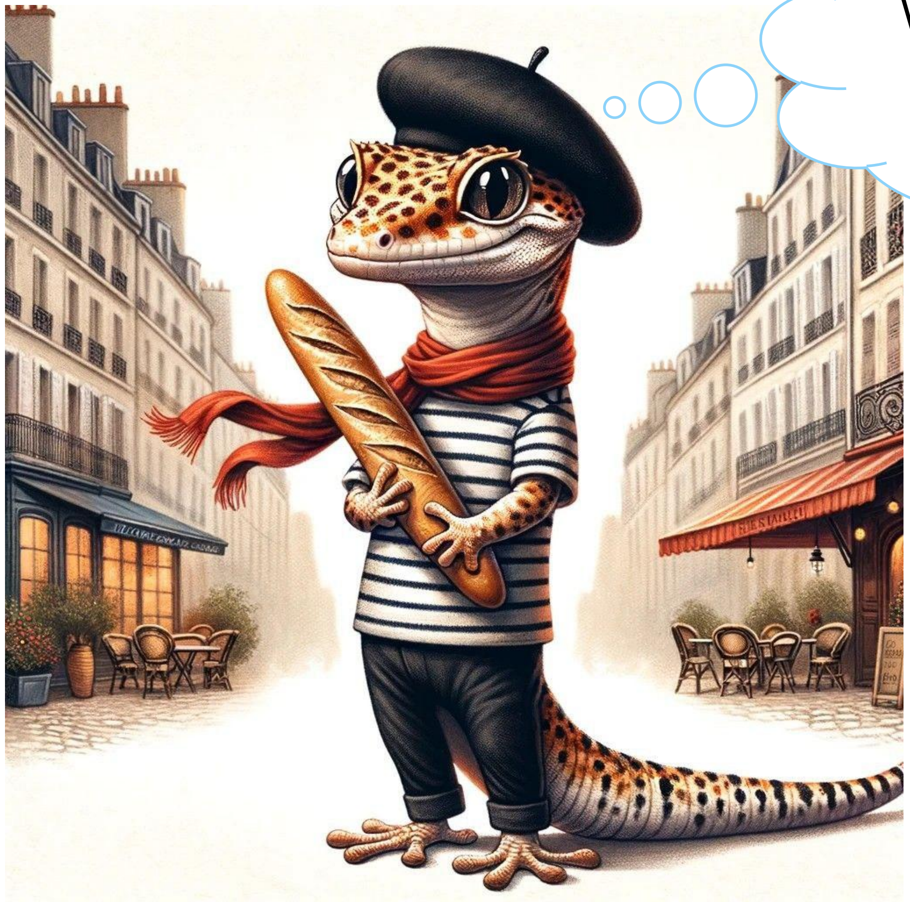

What would OH do?
What would NO_3 do?
What would O_3 do?
What would *hv* do?

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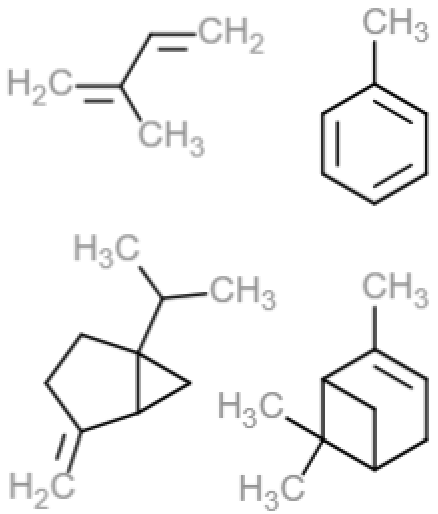

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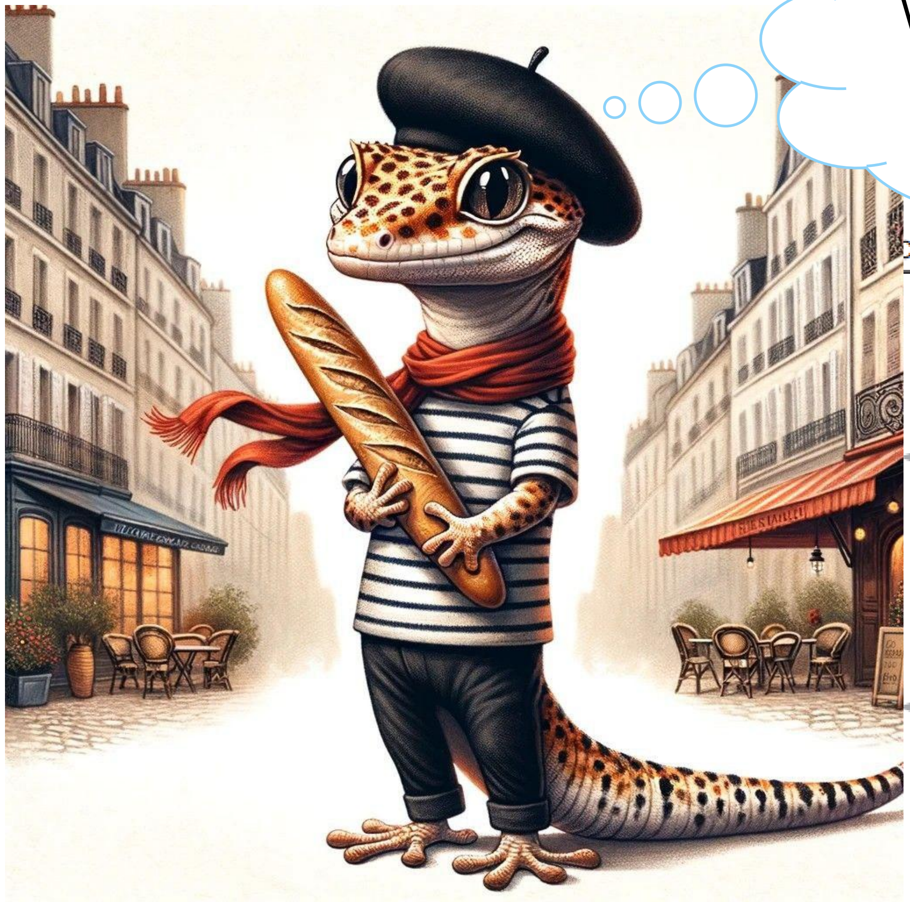

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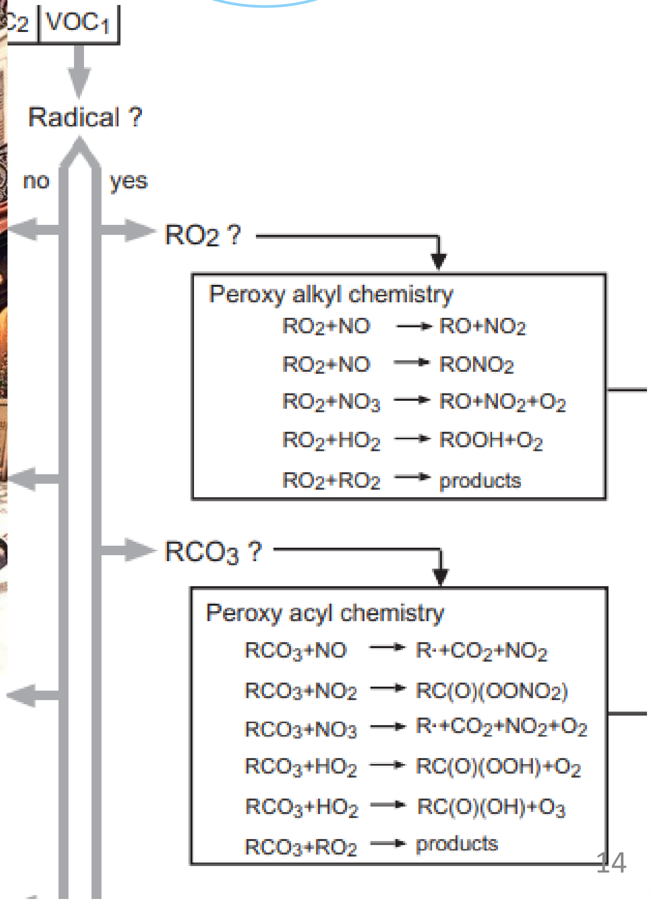

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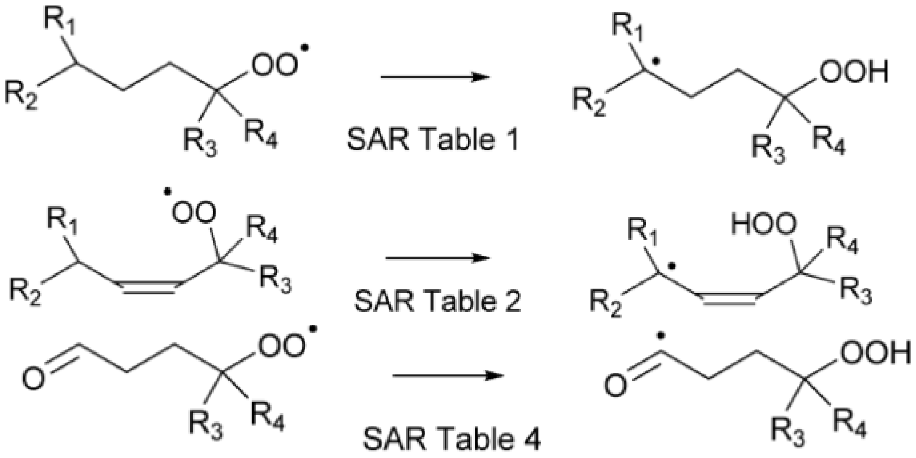
Which reactions?

Which reactions?

L. Vereecken & B. Nozière,
Atmos. Chem. Phys. **2020**, *20*, 7429–7458



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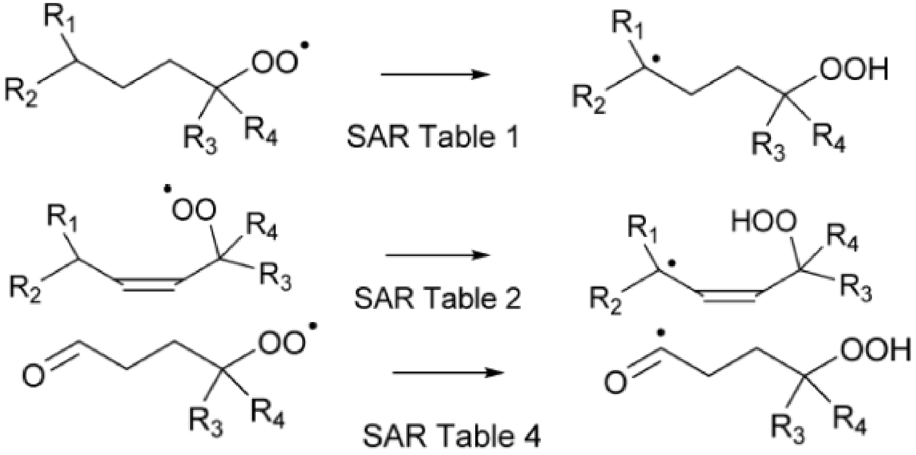

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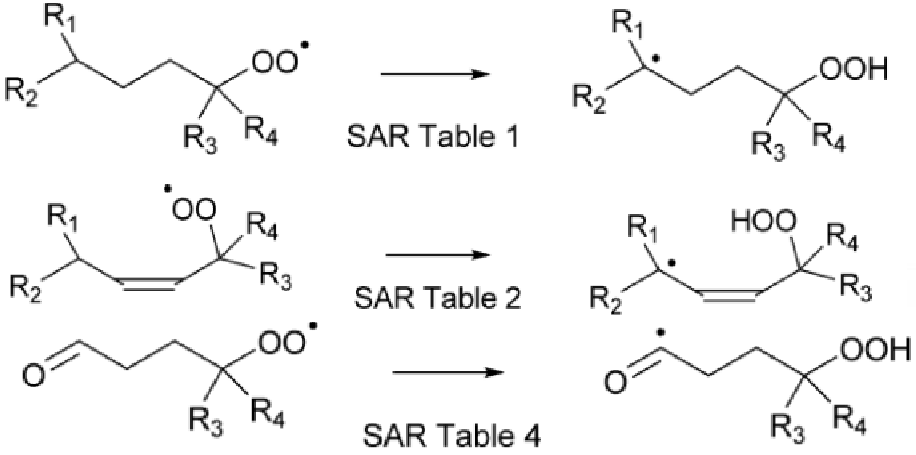

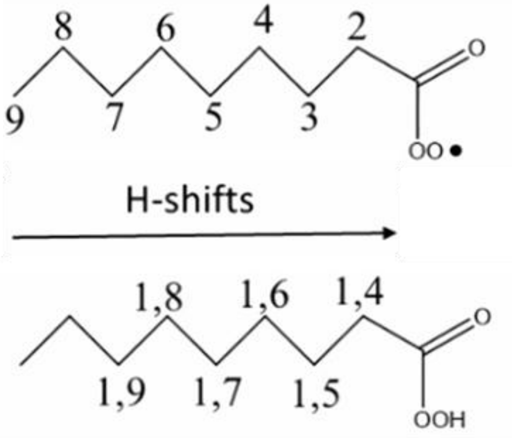

P. Seal, S. Barua, S. Iyer,
A. Kumar & M. Rissanen,
Phys. Chem. Chem. Phys.,
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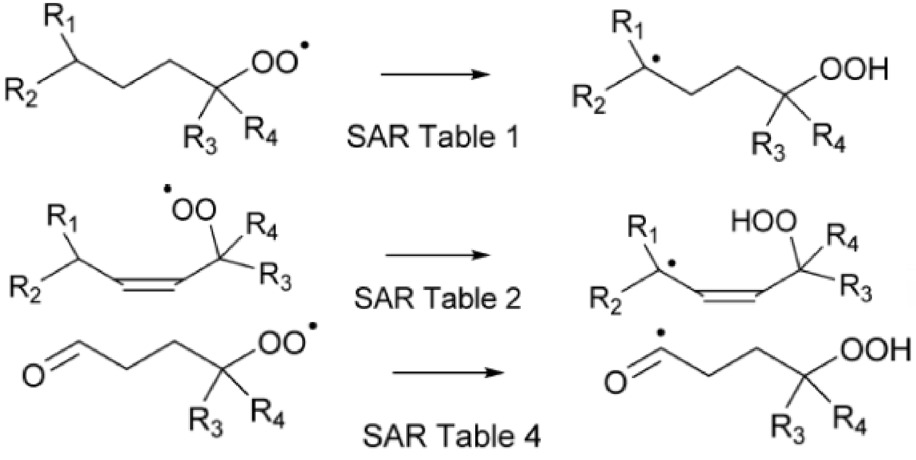

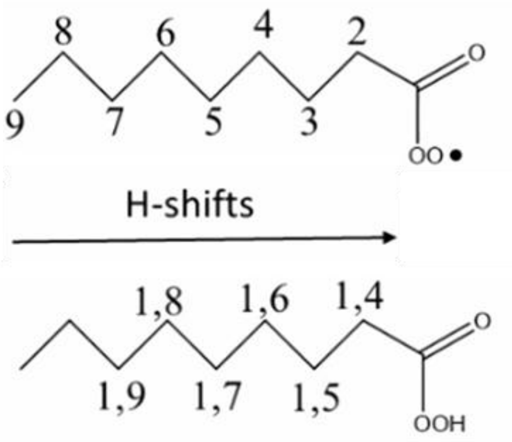

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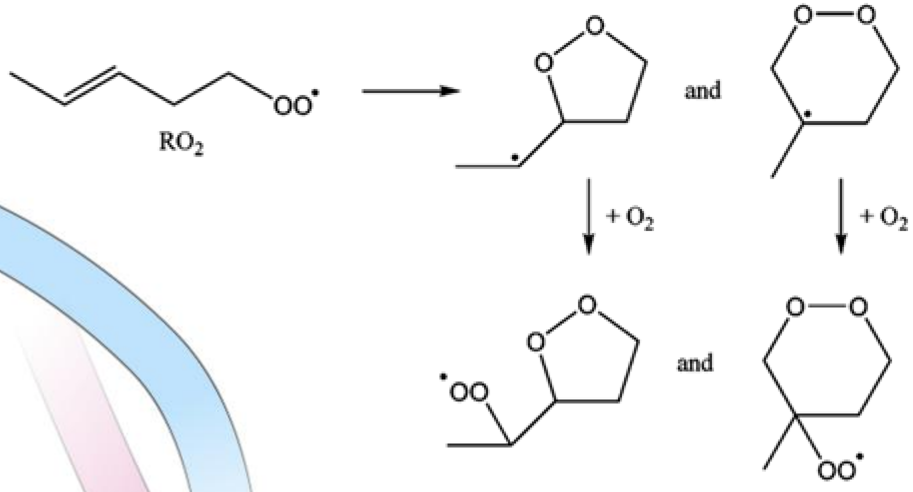

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& H. M. T. Nguyen, *Phys. Chem. Chem. Phys.*
2021, *23*, 16564

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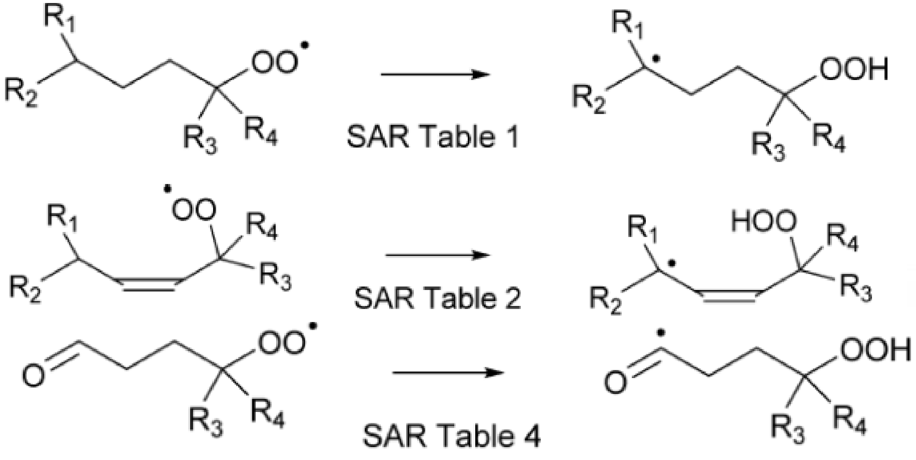

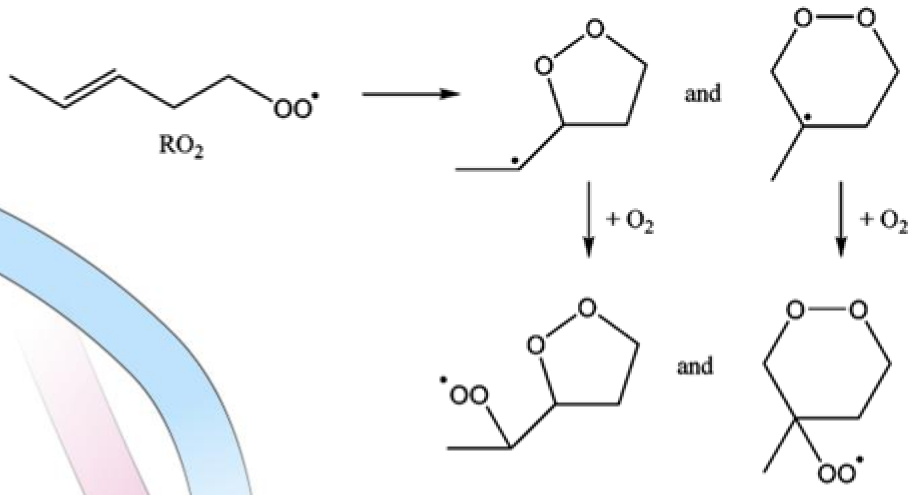

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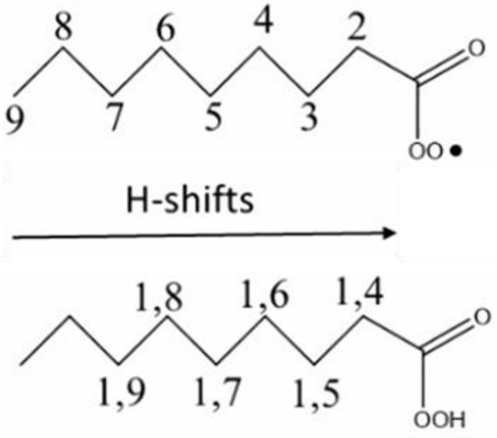

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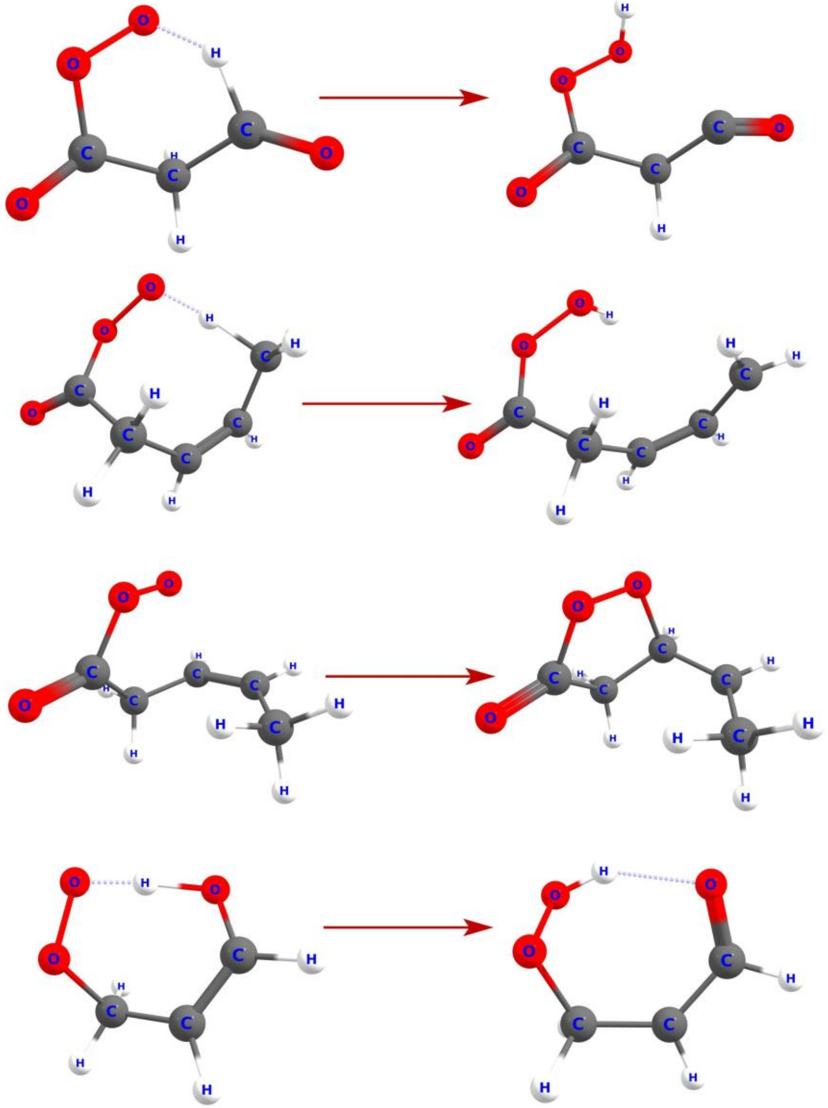
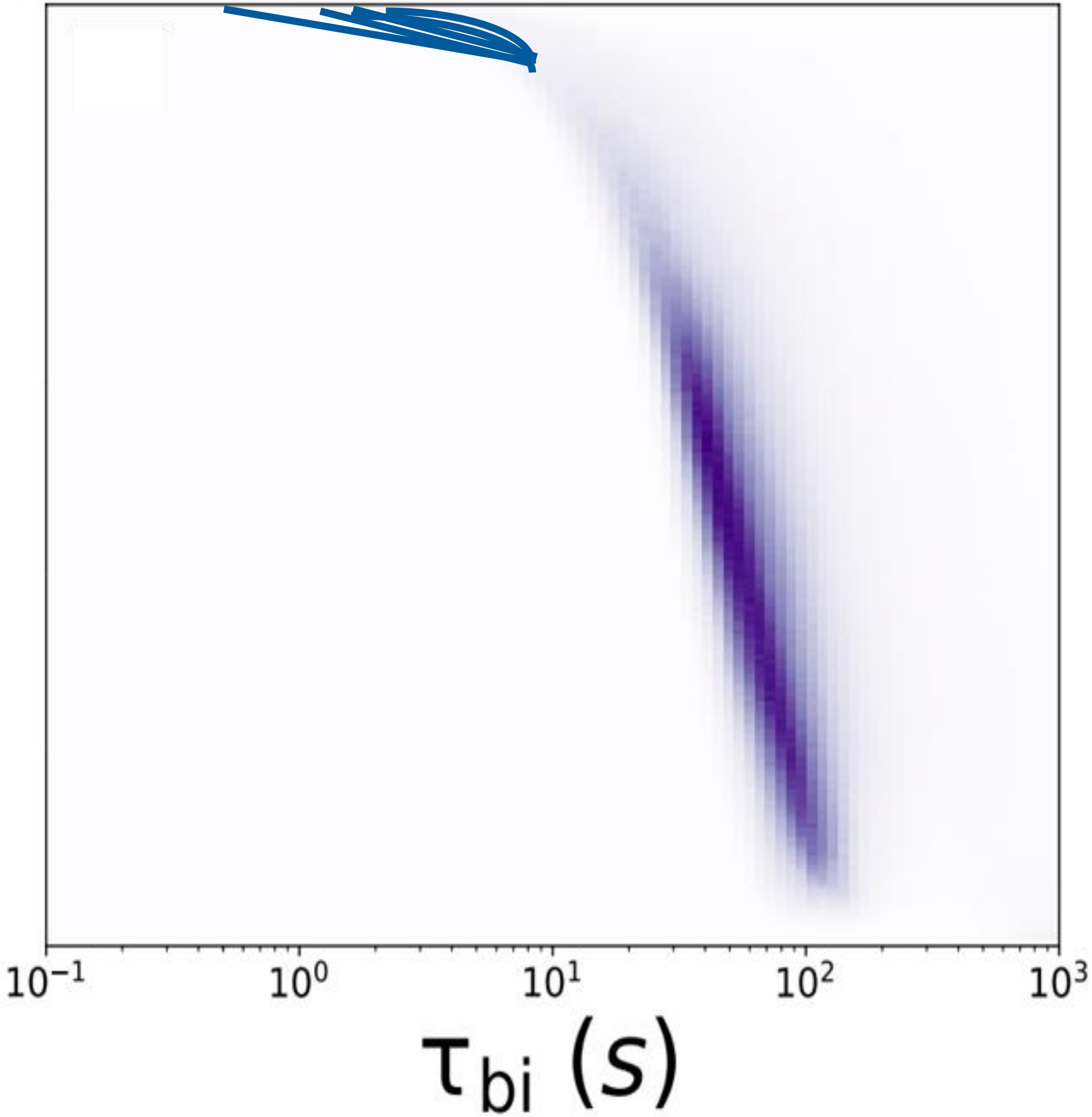


L. Franzon, A. Savolainen, S. Iyer, M. Rissanen & T. Kurtén
In Review (Ask me later about the methods, theorists)

New data on $RC(O)O_2$ autoxidation



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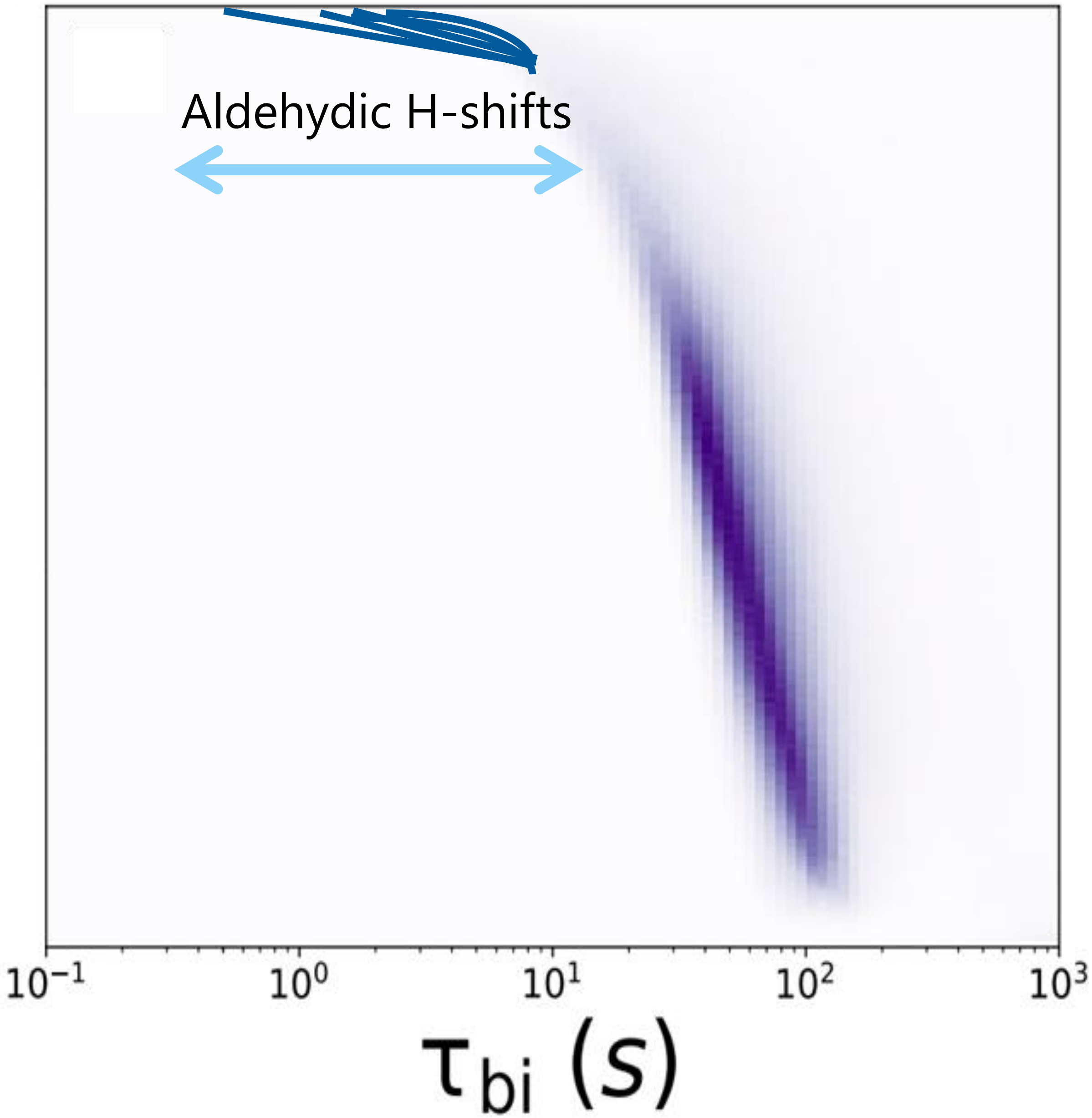

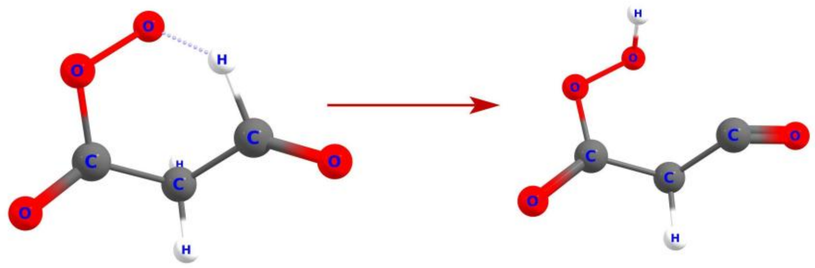

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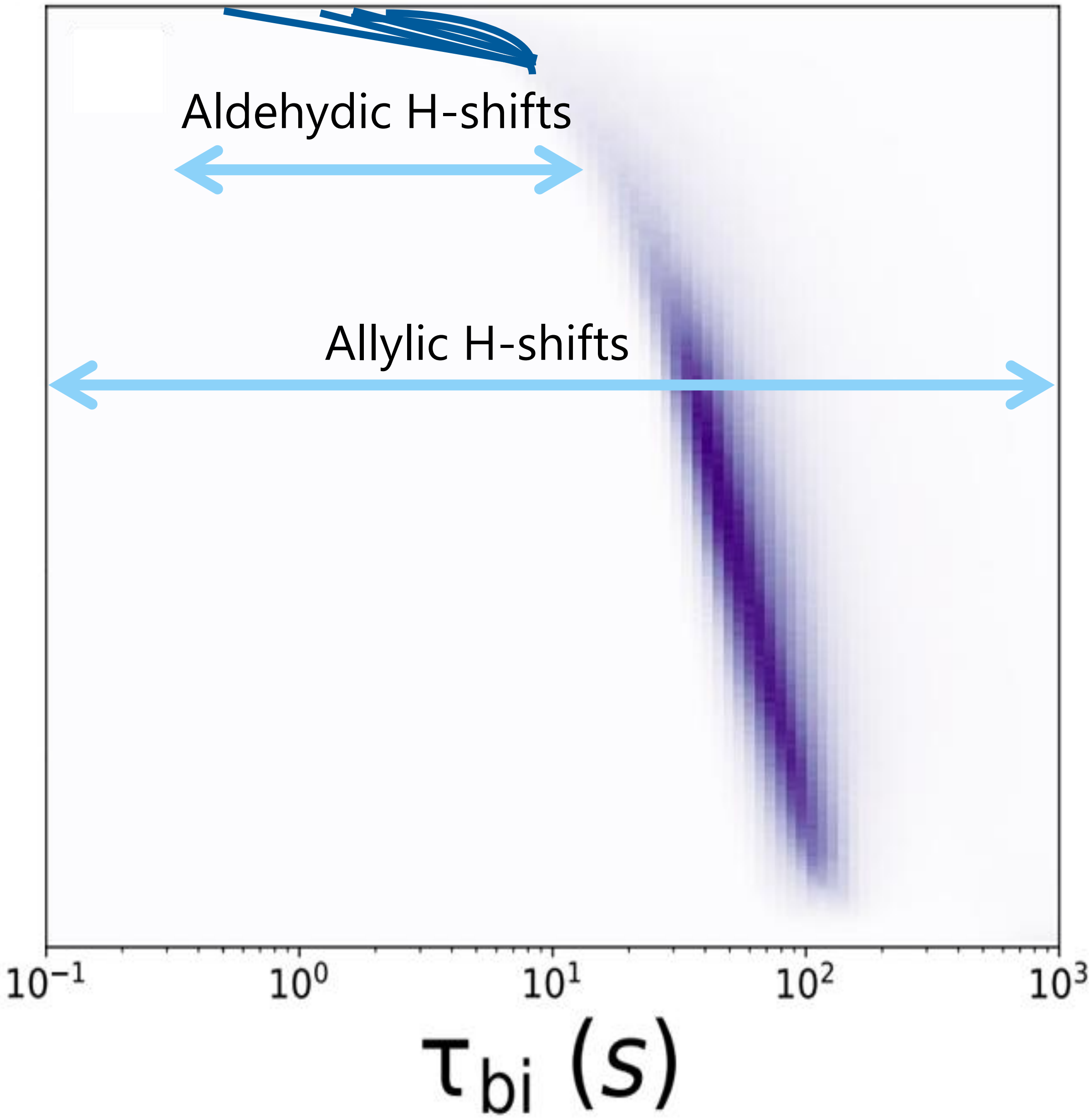

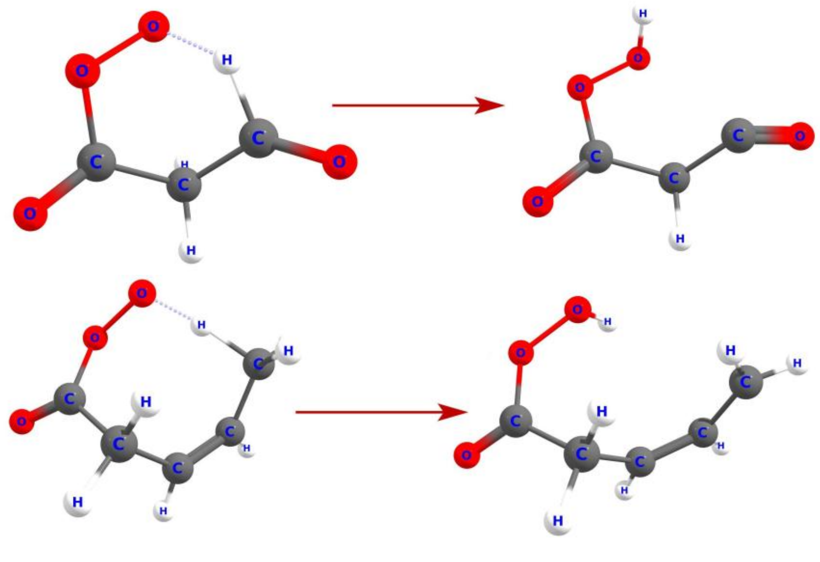

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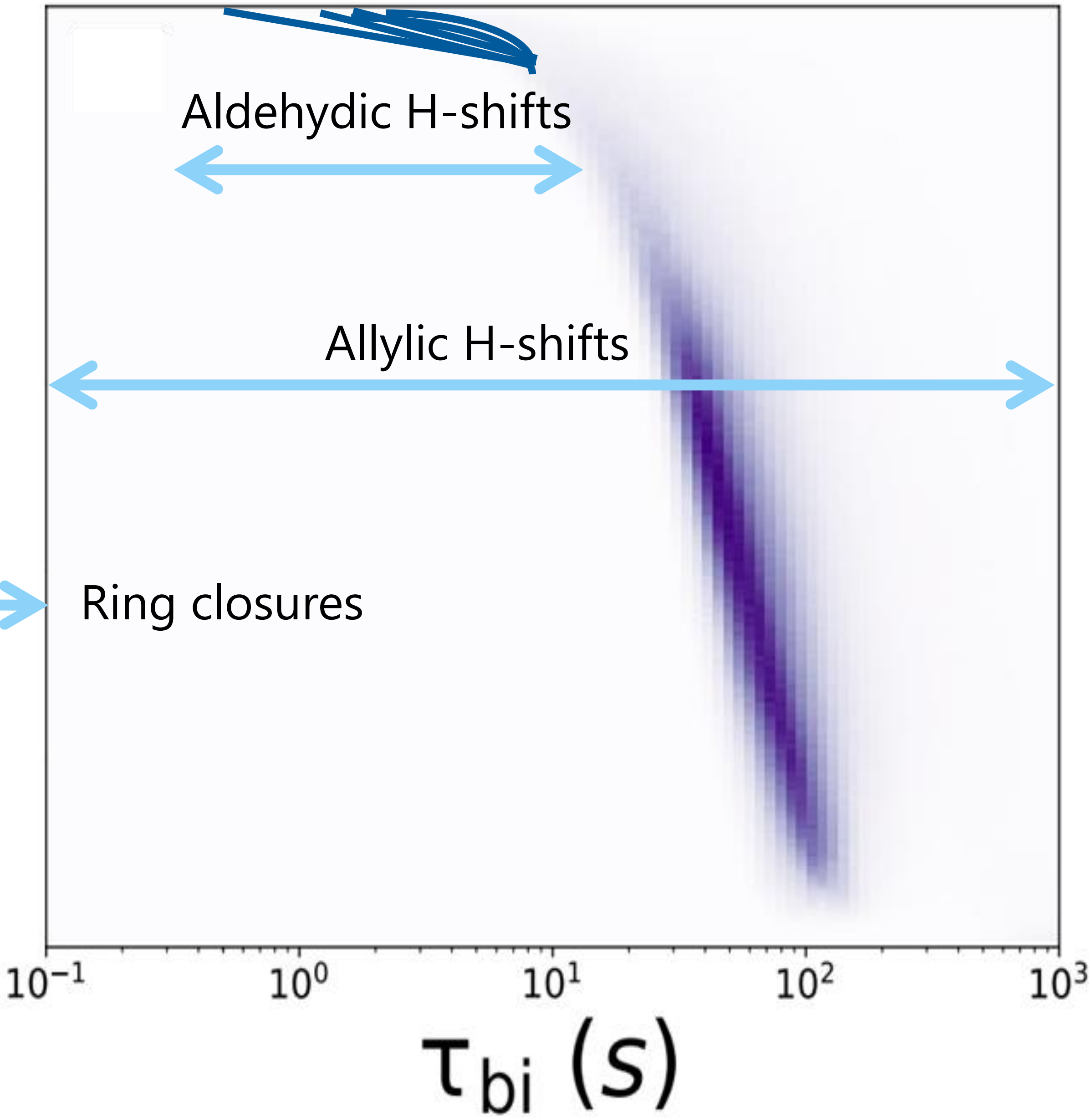
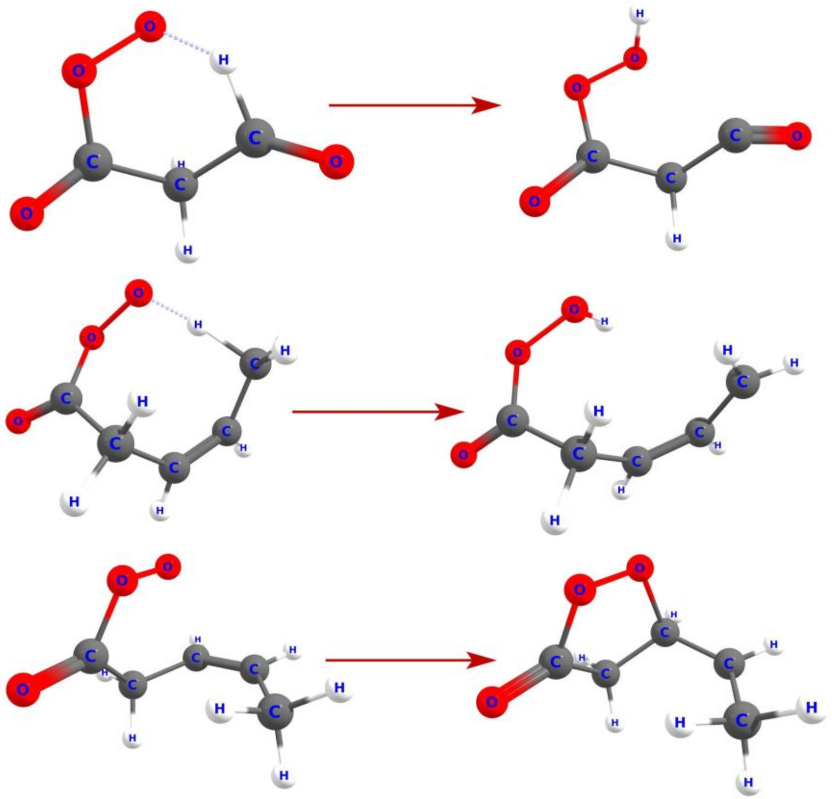


Fastest rate:
$3 \cdot 10^6 s^{-1}$



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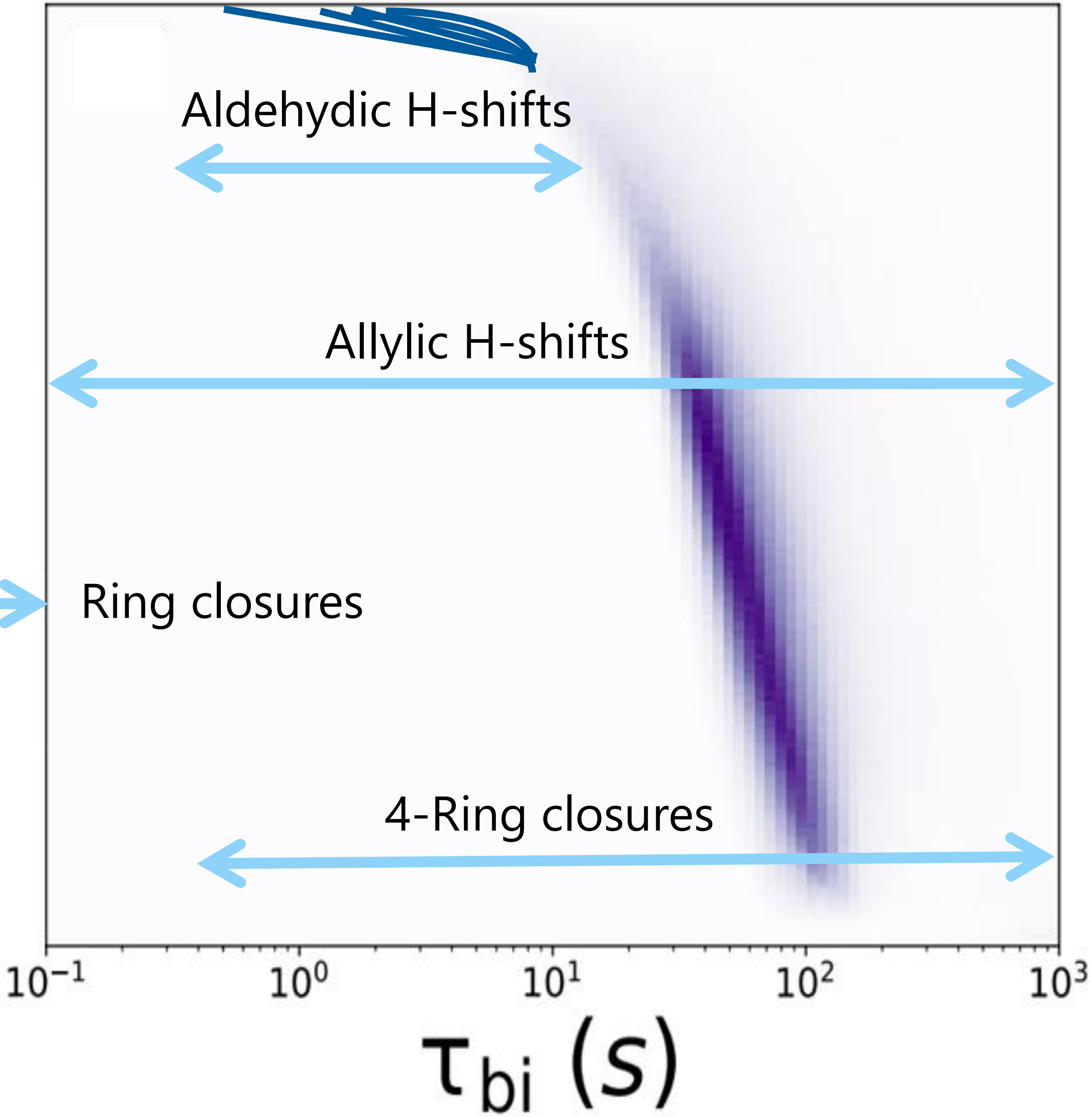

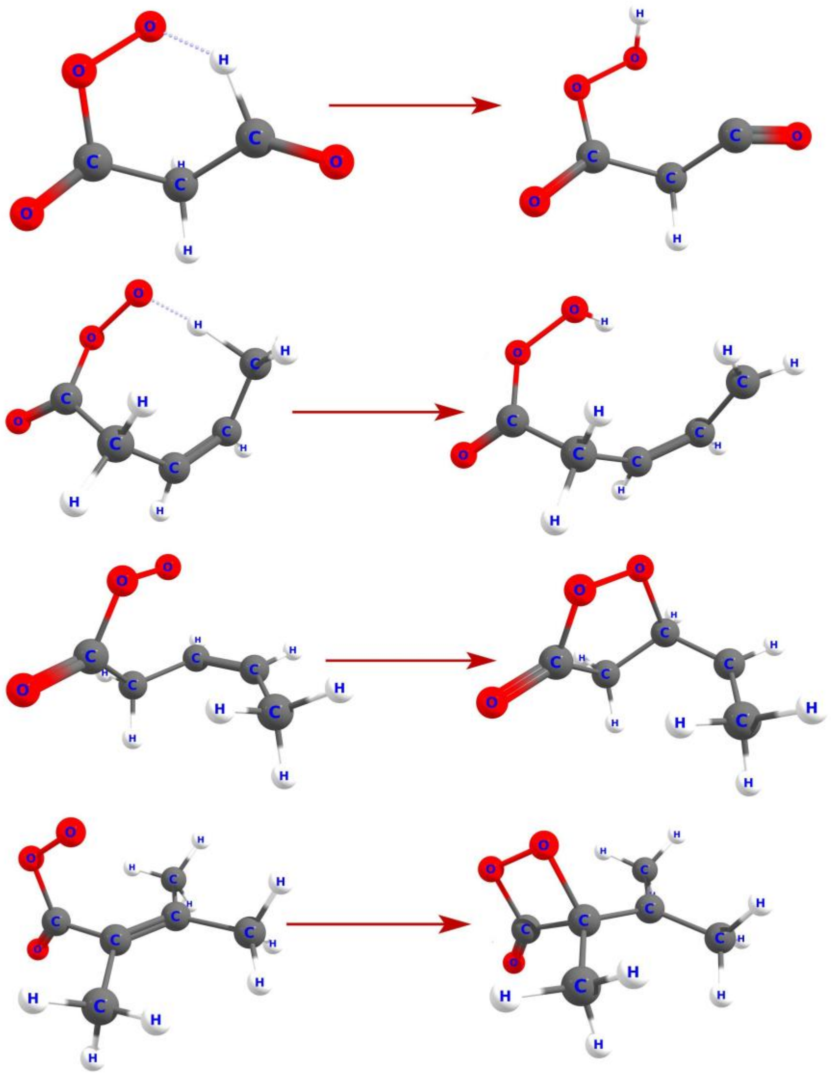

Credit of discovery to Anni Savolainen

Autoxidation in mechanism generation

Autoxidation in mechanism generation

$$RO_2 \rightarrow \begin{cases} \text{H shift SAR} \\ \text{Ring closure SAR} \end{cases} \rightarrow$$

$$k_{tot}(T) = \sum_{h}^{n_h} k_h(T) + \sum_{r}^{n_r} k_r(T)$$

(H-scrambling not included in sum)

Autoxidation in mechanism generation

k_{high}

k_{low}

$$RO_2 \rightarrow \begin{cases} \text{H shift SAR} \\ \text{Ring closure SAR} \end{cases} \rightarrow$$

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(H-scrambling not included in sum)

$k_{tot}(T) > k_{\text{high}}$ Only unimolecular reactions

$RO_2 \rightarrow R(O_2)O_2$ or $R{=}O + OH$

k_{high}

$k_{\text{low}} < k_{tot}(T) < k_{\text{high}}$
Both uni- and bimolecular reactions

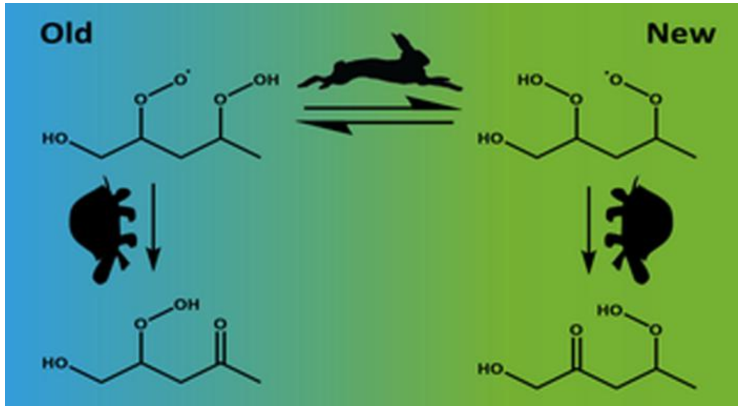
$RO_2 \rightarrow$
$RO_2 + NO \rightarrow$
$RO_2 + NO_2 \rightarrow$
$RO_2 + NO_3 \rightarrow$
$RO_2 + HO_2 \rightarrow$
$RO_2 + RO_2 \rightarrow$

k_{low}

$k_{tot}(T) < k_{\text{low}}$
Only bimolecular reactions

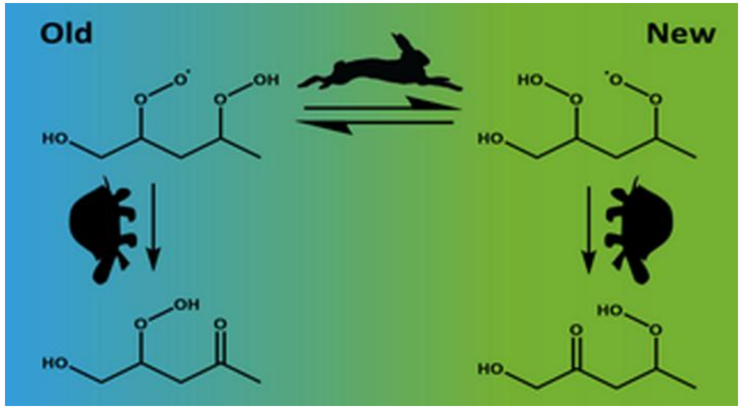
$RO_2 + NO \rightarrow$
$RO_2 + NO_2 \rightarrow$
$RO_2 + NO_3 \rightarrow$
$RO_2 + HO_2 \rightarrow$
$RO_2 + RO_2 \rightarrow$

H-scrambling in mechanism generation



S. Jørgensen, H. Knap, R. Otkjær, A. Jensen, M. Kjeldsen, P. Wennberg & H. Kjaergaard,
J. Phys. Chem. A, **2016,** *120,* 266-275

H-scrambling in mechanism generation



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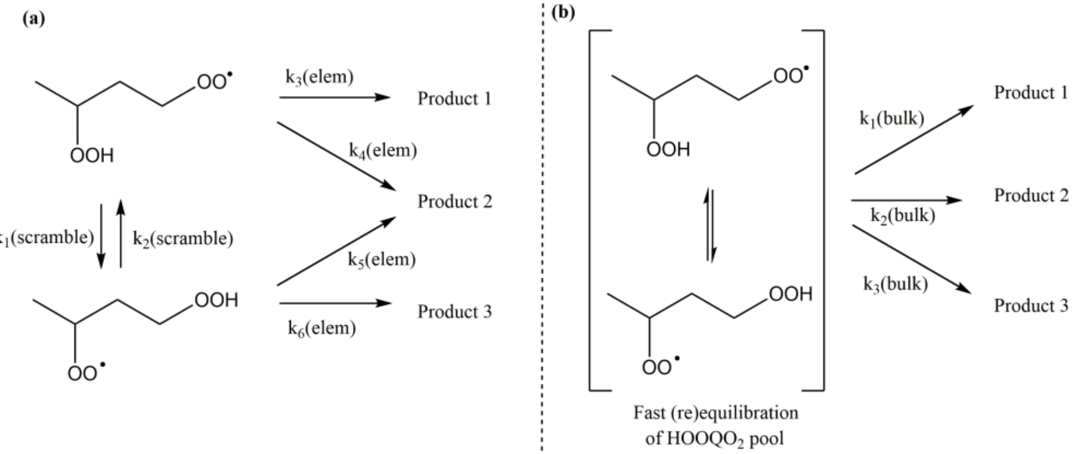
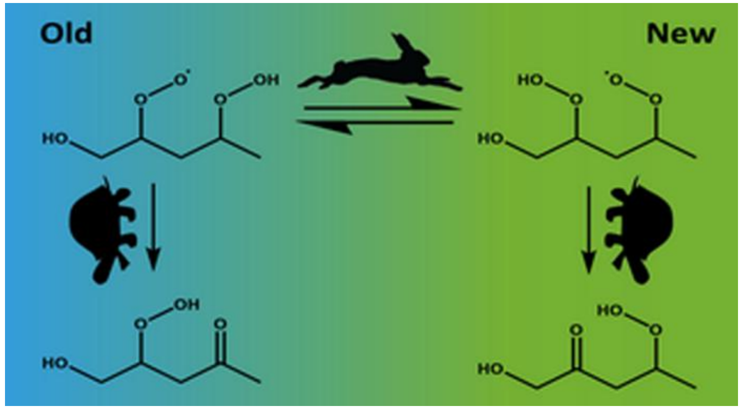
L. Vereecken & B. Nozière, *Atmos. Chem. Phys.* **2020**, *20*, 7429–7458



H-scrambling in mechanism generation



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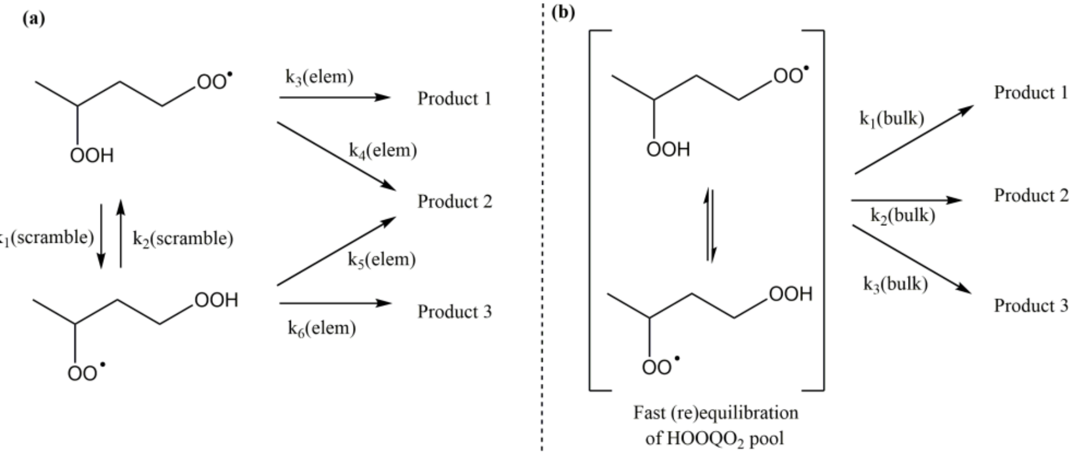
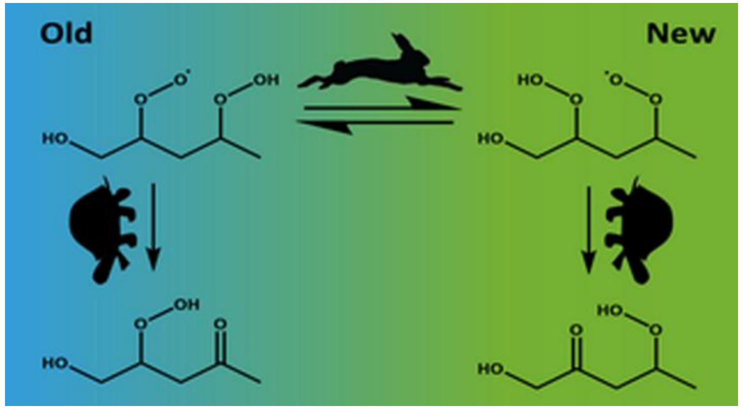


$R(OOH)O_2$ → Find all n_{OOH} + 1 scrambling isomers

$$\text{All } R(OOH)O_2 \rightarrow \begin{cases} \text{H shift SAR} \\ \text{Ring closure SAR} \end{cases} \rightarrow$$

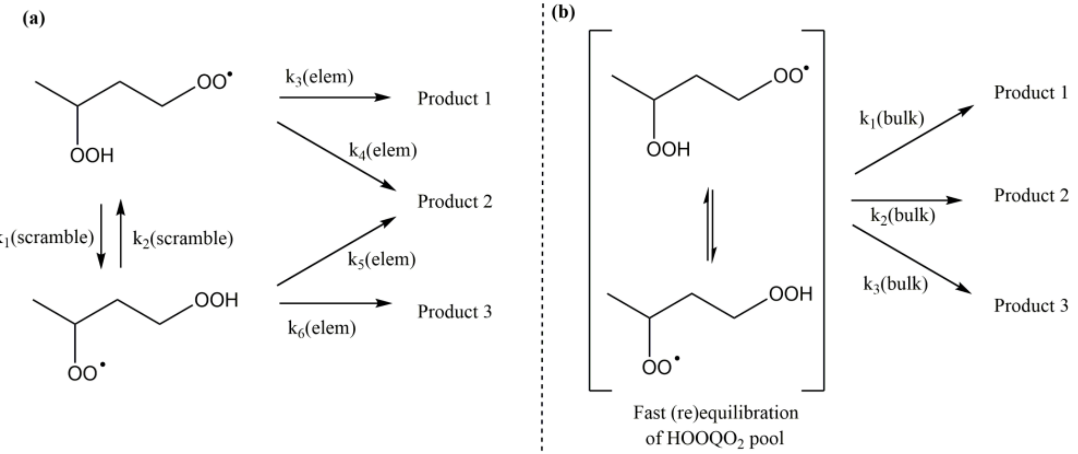
$$k_{tot}(T) = \left\langle \sum_{h}^{n_h} k_h(T) + \sum_{r}^{n_r} k_r(T) \right\rangle$$

H-scrambling in mechanism generation



S. Jørgensen, H. Knap, R. Otkjær, A. Jensen, M. Kjeldsen, P. Wennberg & H. Kjaergaard, *J. Phys. Chem. A*, **2016,** *120*, 266-275

L. Vereecken & B. Nozière, *Atmos. Chem. Phys.* **2020**, *20*, 7429–7458



$R(OOH)O_2$ → Find all n_{OOH} + 1 scrambling isomers

$$\text{All R(OOH)O}_2 \rightarrow \begin{cases} \text{H shift SAR} \\ \text{Ring closure SAR} \end{cases} \rightarrow$$

$$k_{tot}(T) = \left\langle \sum_{h}^{n_h} k_h(T) + \sum_{r}^{n_r} k_r(T) \right\rangle$$

Exception 1: $R(OOH)C(O)O_2$ -> $R(O_2)C(O)OOH$ is immediate and irreversible.

H. Knap & S. Jørgensen, *J. Phys. Chem. A*, **2017**, *121*, 1470–1479

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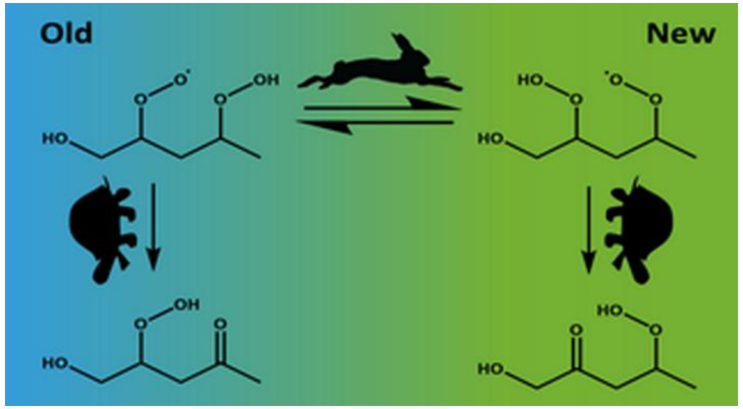

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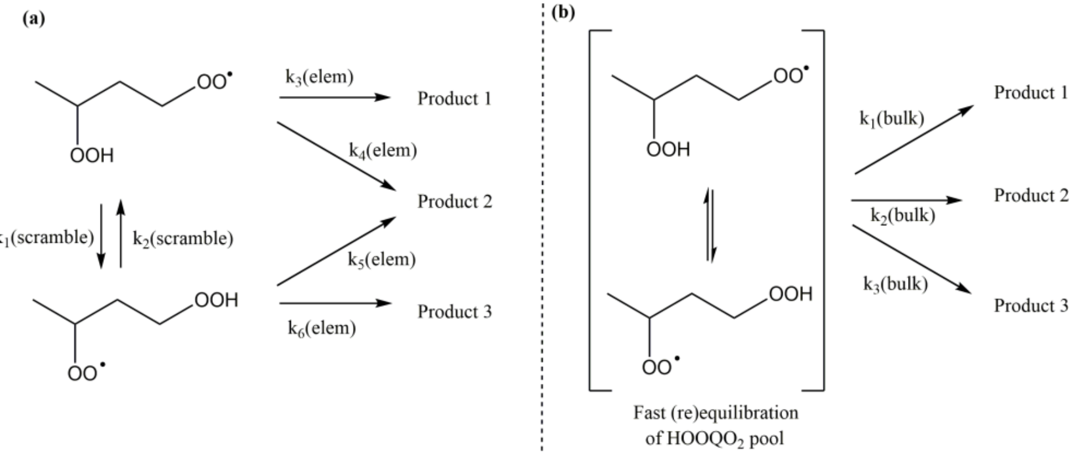

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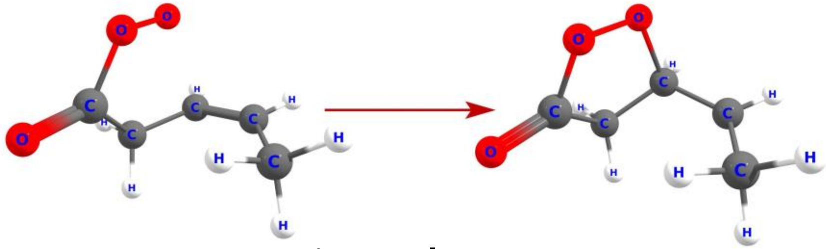

Exception 2: $RC(O)O_2$ ring closures outcompete H-scrambling.

L. Franzon, A. Savolainen, S. Iyer, M. Rissanen & T. Kurtén *In Review*

Final thoughts

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Thank you for listening! Questions?

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