The Importance of Peroxy Radical Hydrogen Shift Reactions in Atmospheric Isoprene Oxidation

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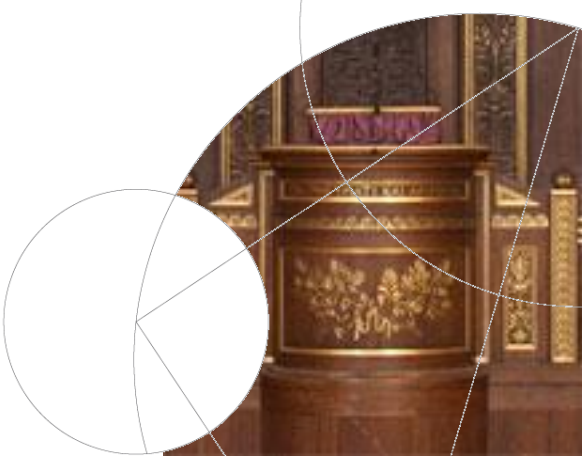
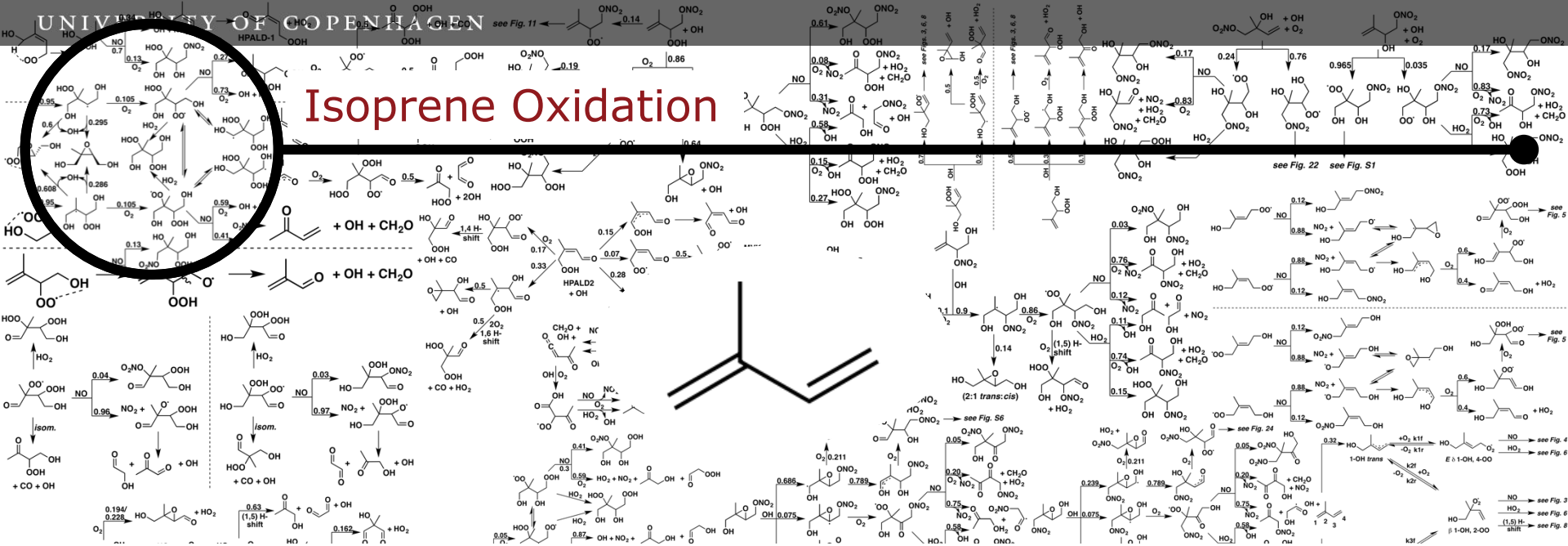
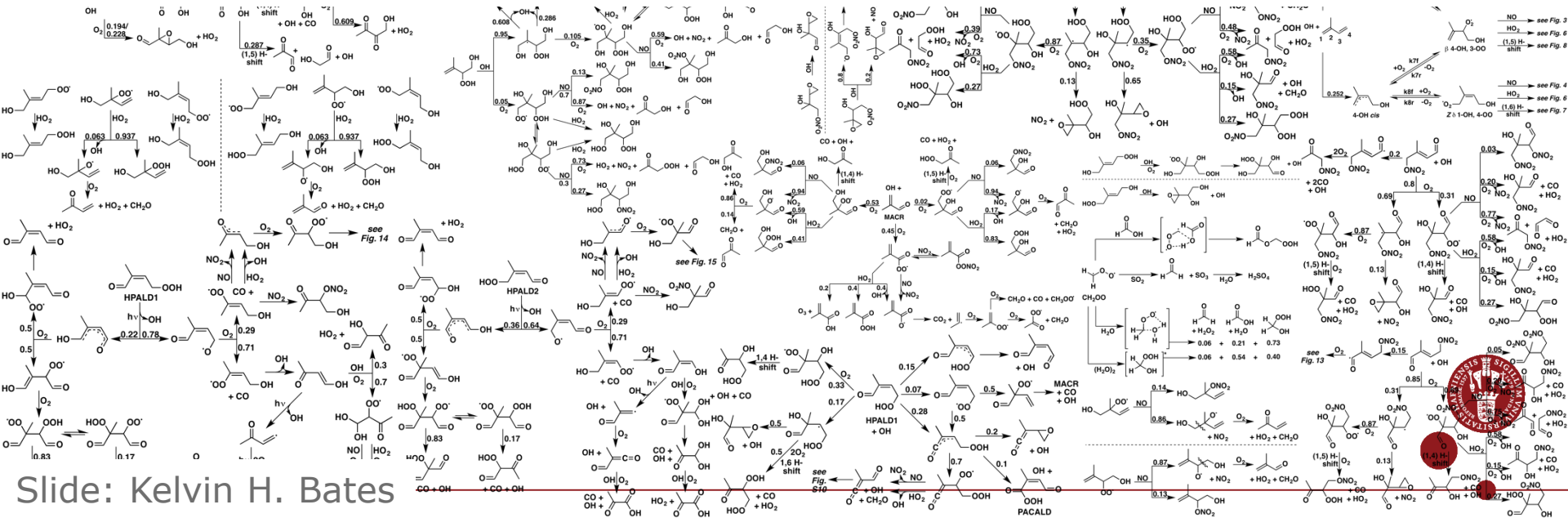


Isoprene Oxidation



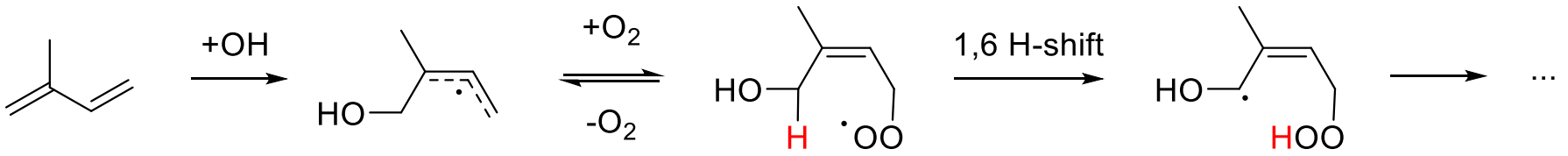
"Gas-Phase Reactions of Isoprene and Its Major Oxidation Products" *Chem. Rev.*, **2018**, *118* (7), pp 3337–3390



Slide: Kelvin H. Bates

1,6 H-shift in Isoprene

Simplified scheme for 1-OH:



H-shift rate constants (297 K, s^{-1})

	Experiment[1]	Theory[2]
1-OH system	0.36	0.49
4-OH system	3.7	5.4

[1] *Teng et al. J. Am. Chem. Soc.*, **2017**, *139*, 5367–5377
[2] Peeters *et al.*, J. Phys. Chem. A, **2014**, *118*, 8625-8643

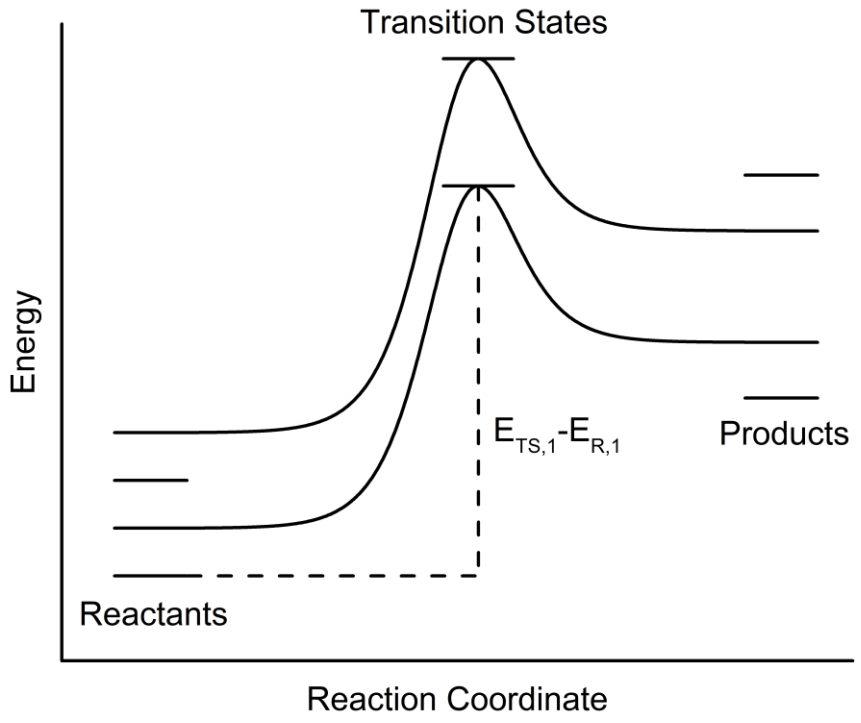
Multi-Conformer Transition State Theory

Conventional TST, unimolecular reaction:

$$k = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} e^{\frac{-(E_{TS}-E_R)}{k_B T}}$$

MC-TST, unimolecular reaction:

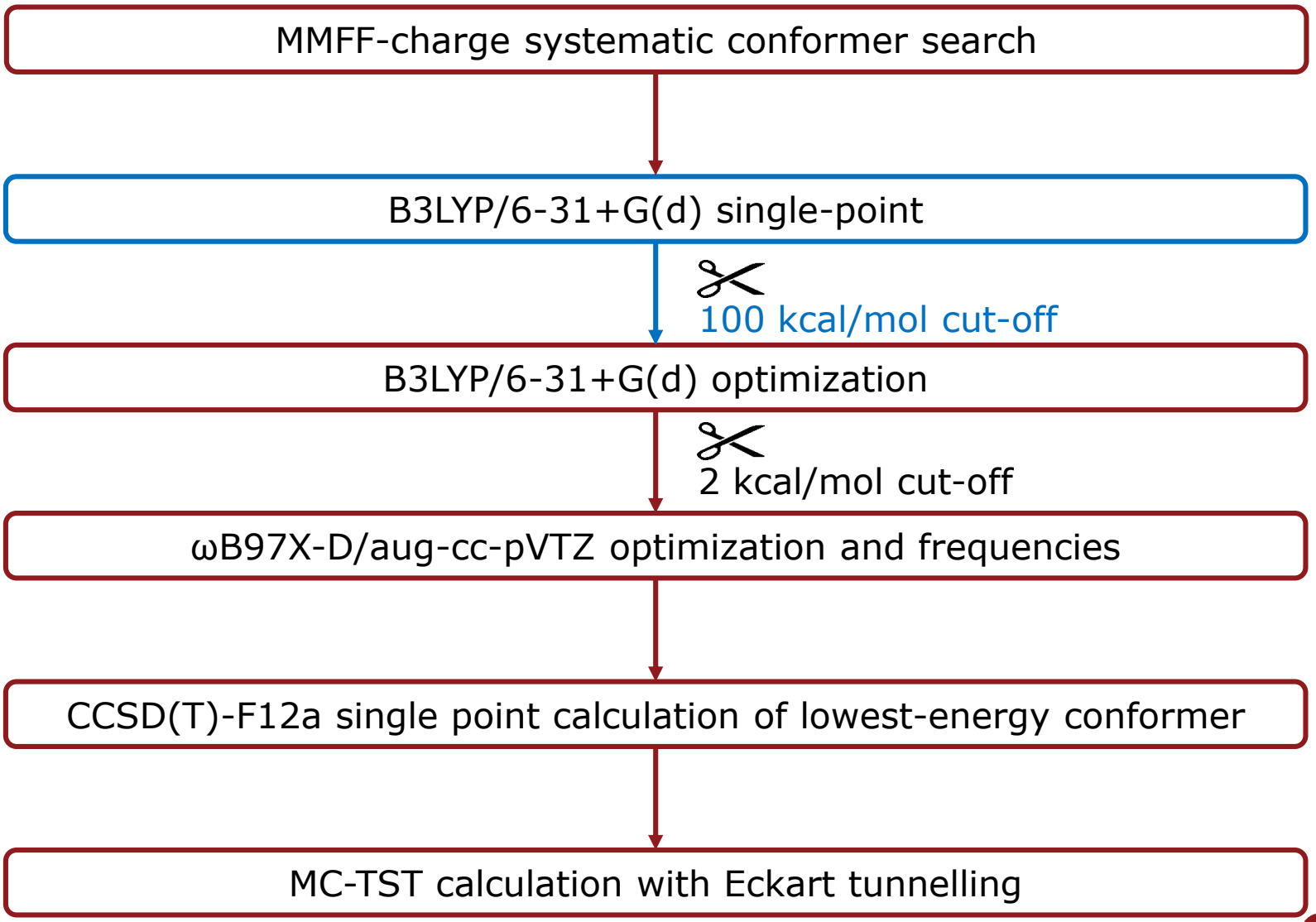
$$k = \kappa \frac{k_B T}{h} \frac{\sum_i^{TS} e^{-\frac{\Delta E_i}{k_B T}} Q_{TS,i}}{\sum_j^{R} e^{-\frac{\Delta E_j}{k_B T}} Q_{R,j}} e^{\frac{-(E_{TS,1}-E_{R,1})}{k_B T}}$$



$E_{TS,1} - E_{R,1}$ = Energy difference between lowest-energy conformer of reactant and transition state

Vereecken *et al.*, J. Chem. Phys., **2003**, *119*, 5159-5170
Møller *et al.*, J. Phys. Chem. A, **2016**, *120*, 10072-10087

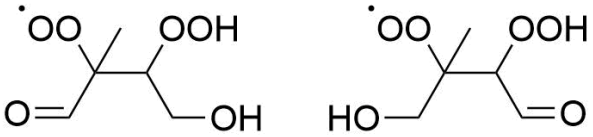
Theoretical Approach



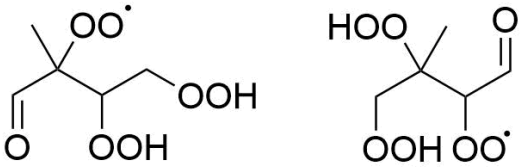
Møller *et al.*, J. Phys. Chem. A, **2016**, *120*, 10072-10087

Peroxy Radicals Studied

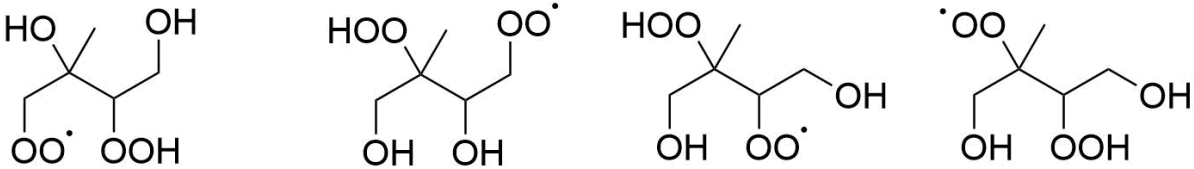
δ-ISOPOO + NO



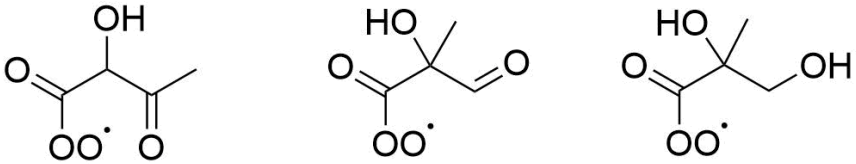
Following 1,6 H-shift in Z-ISOPOO



β-ISOPOOH + OH

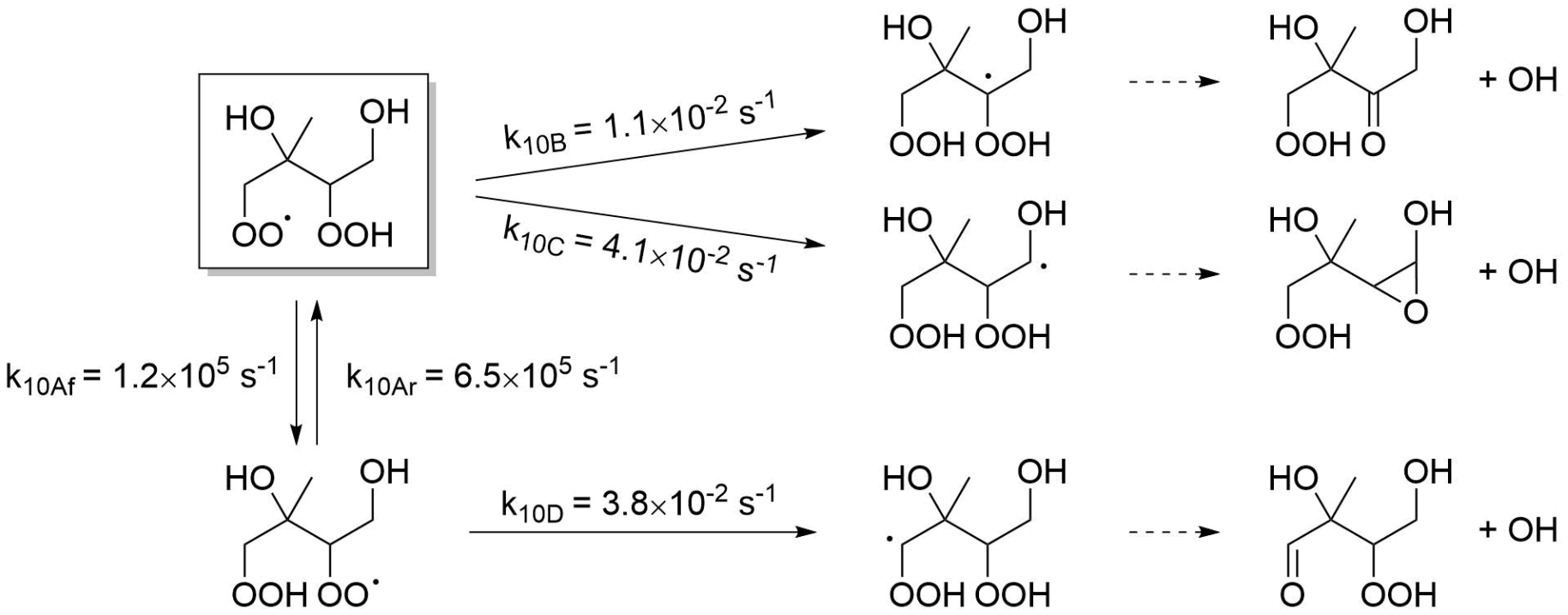


IEPOX + 2 OH



Peeters *et al.*, J. Phys. Chem. A, **2012**, *116*, 6134-6141
Peeters *et al.*, J. Phys. Chem. A, **2014**, *118*, 8625-8643
St. Clair *et al.*, J. Phys. Chem. A, **2016**, *120*, 1441-1451
Bates *et al.*, J. Phys. Chem. A, **2016**, *120*, 106-117
Jørgensen *et al.*, J. Phys. Chem. A, **2016**, *120*, 266–275

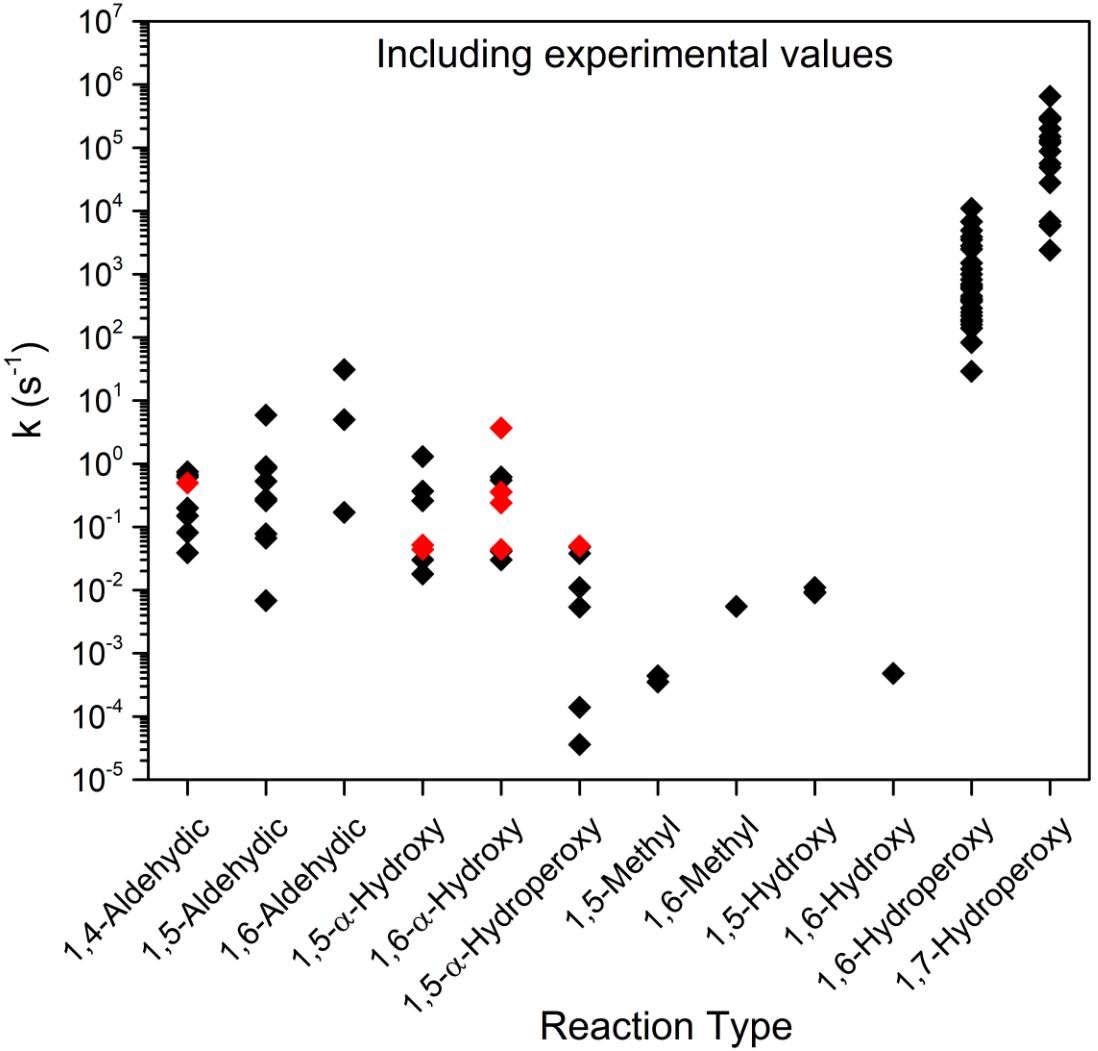
Example Reaction Scheme

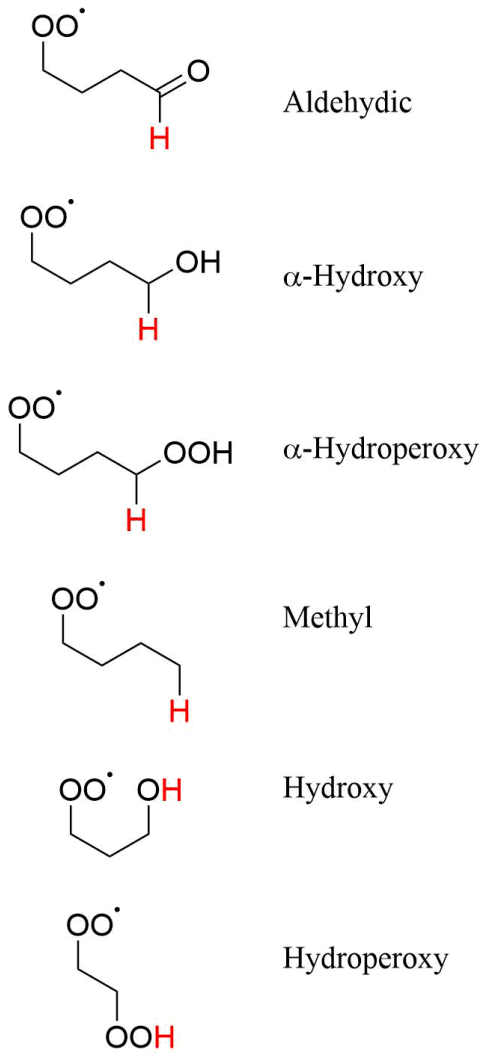


β-ISOPOOH + OH

D'Ambro *et al.*, Environ. Sci. & Technol, **2017**, *51*, 4978-4987
Jørgensen *et al.*, J. Phys. Chem. A, **2016**, *120*, 266–275

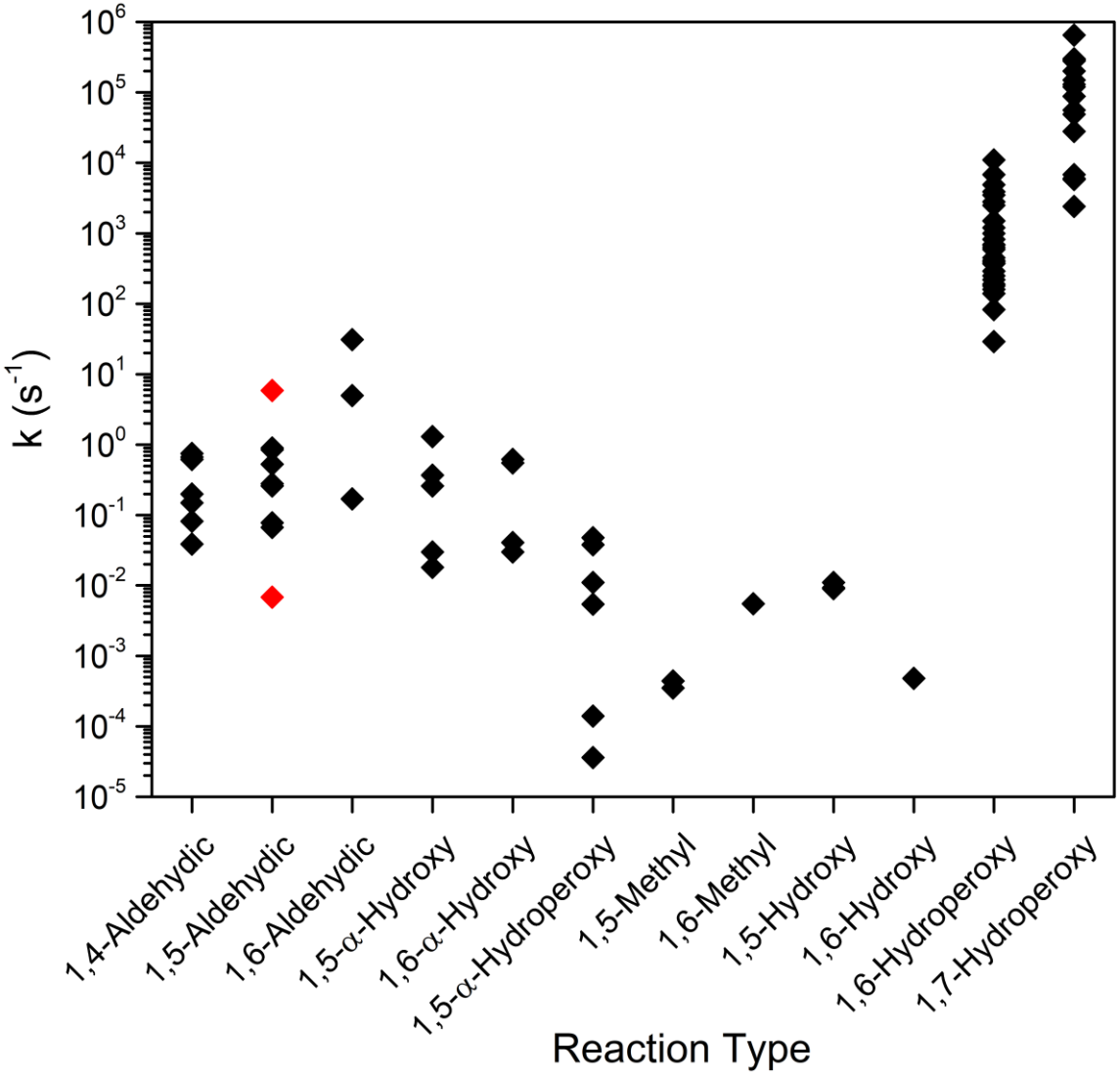
Rate Constants





Crounse *et al., J. Phys. Chem. A*, **2012**, *116*, 5756–5762
Teng *et al., J. Am. Chem. Soc.*, **2017**, *139* (15), pp 5367–5377
Praske *et al., Proc. Natl. Acad. Sci.*, **2018**, *115*, 64-69
Praske *et al., J. Phys. Chem. A,* under review

Stereoisomerism: Effect

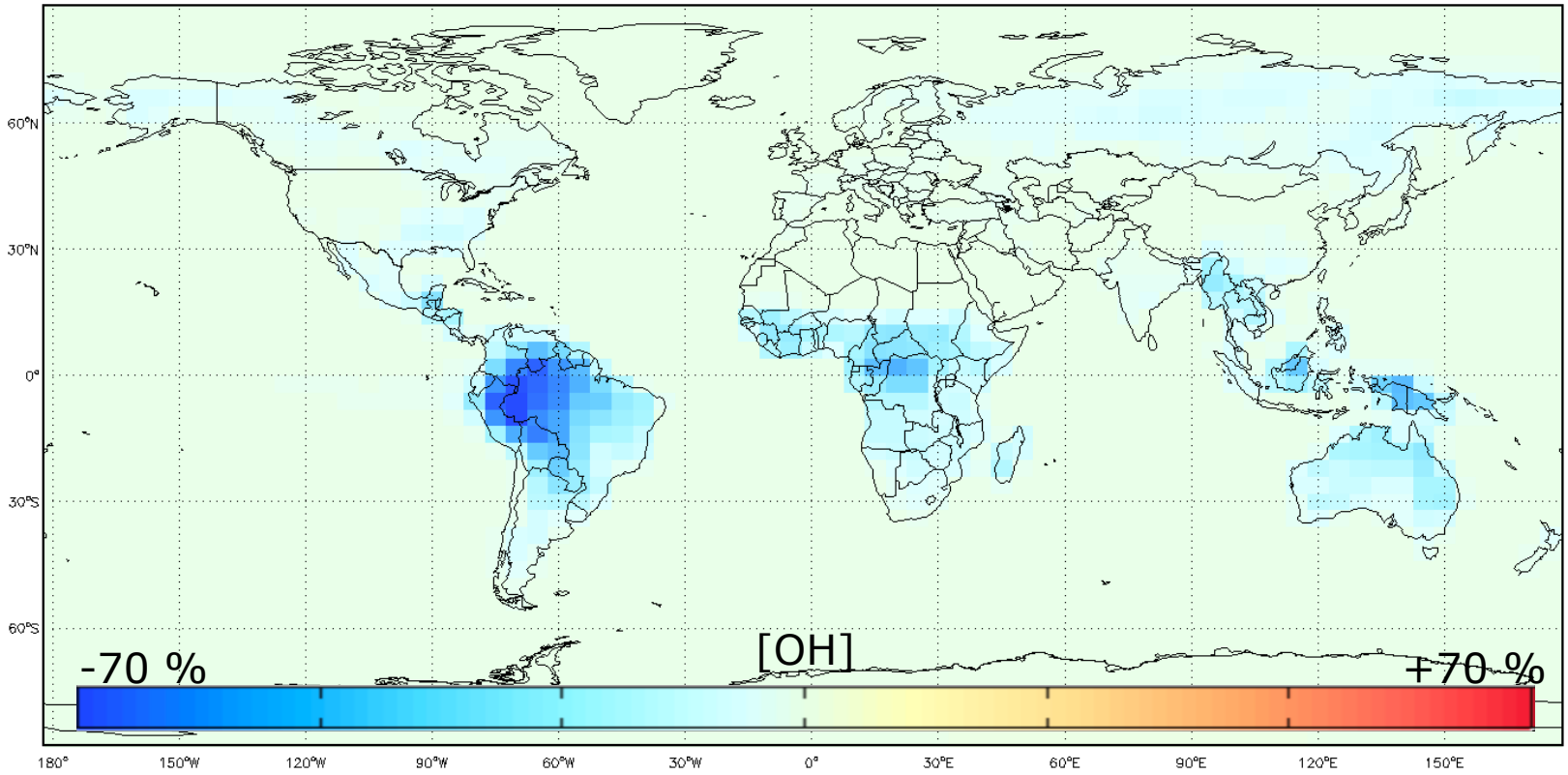


GEOS-Chem Modeling

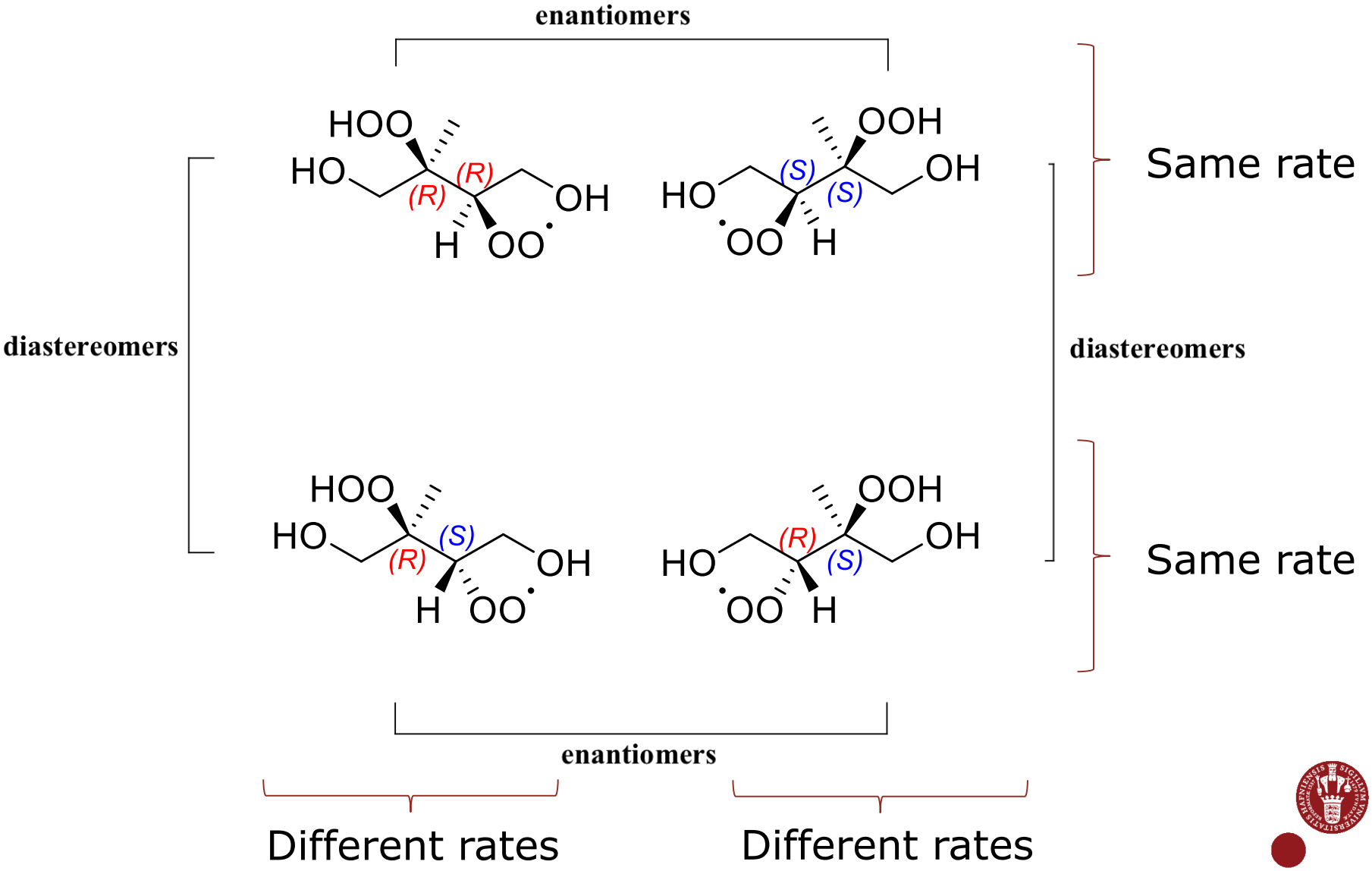
Yield of H-shift products for given peroxy radical: 10^{-5} - 1

Unique H-shifts: ≥0.30×isoprene (total 0.5×isoprene)

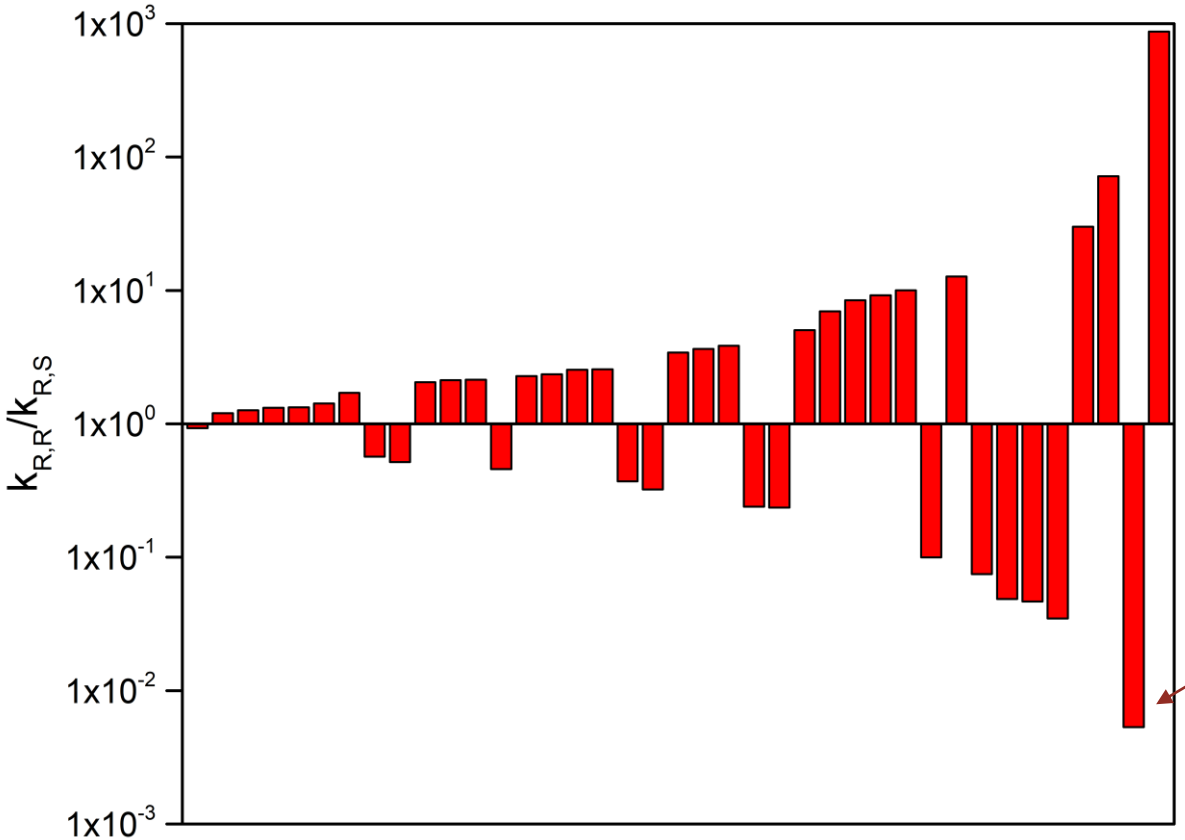
OH recycling: 0.47×isoprene

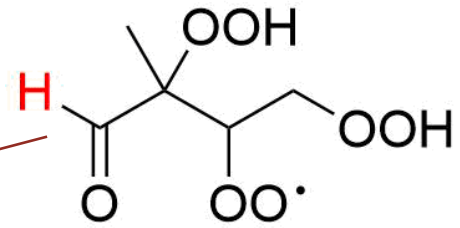


Stereoisomerism

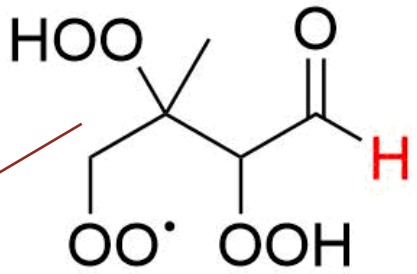


Stereoisomerism: Isoprene





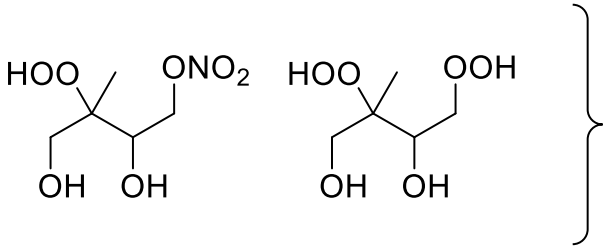
$$\frac{k_{R,R}}{k_{R,S}} = 874$$



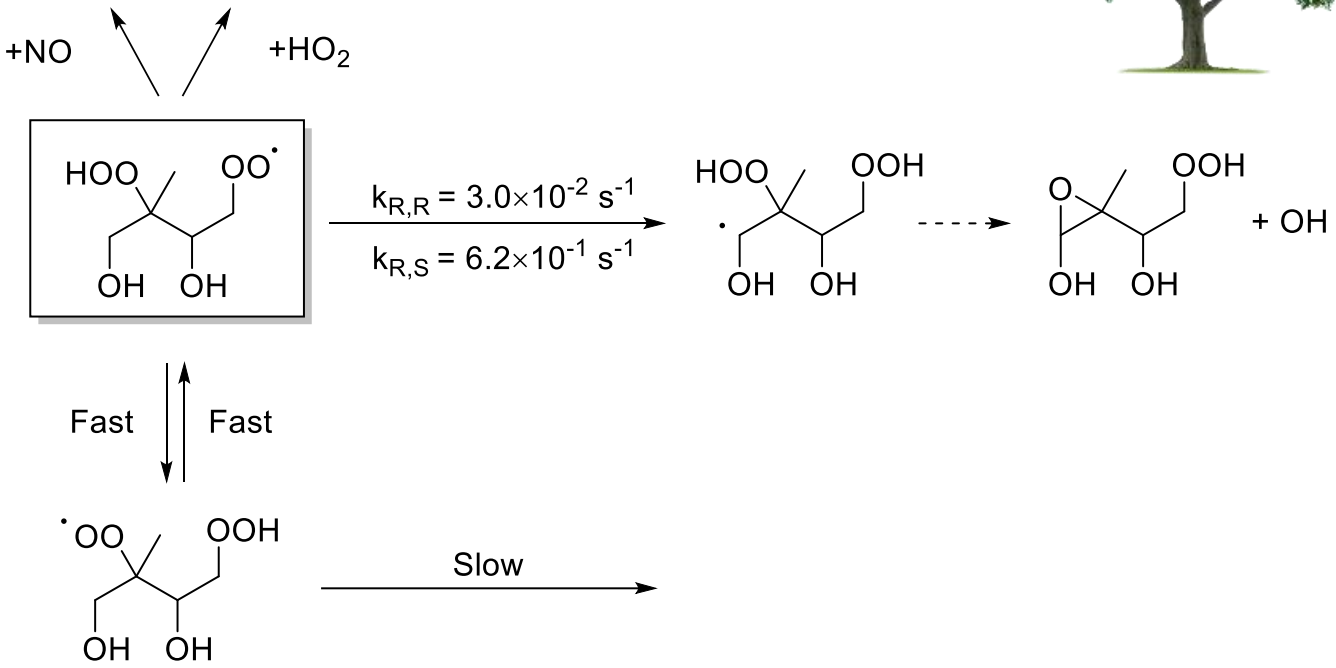
$$\frac{k_{R,R}}{k_{R,S}} = \frac{1}{188}$$

Møller *et al.*, J. Phys. Chem. A, **2017**, *121*, 2951-2959
Hazra *et al.*, J. Phys. Chem. A, **2011**, 115, 5294-5306

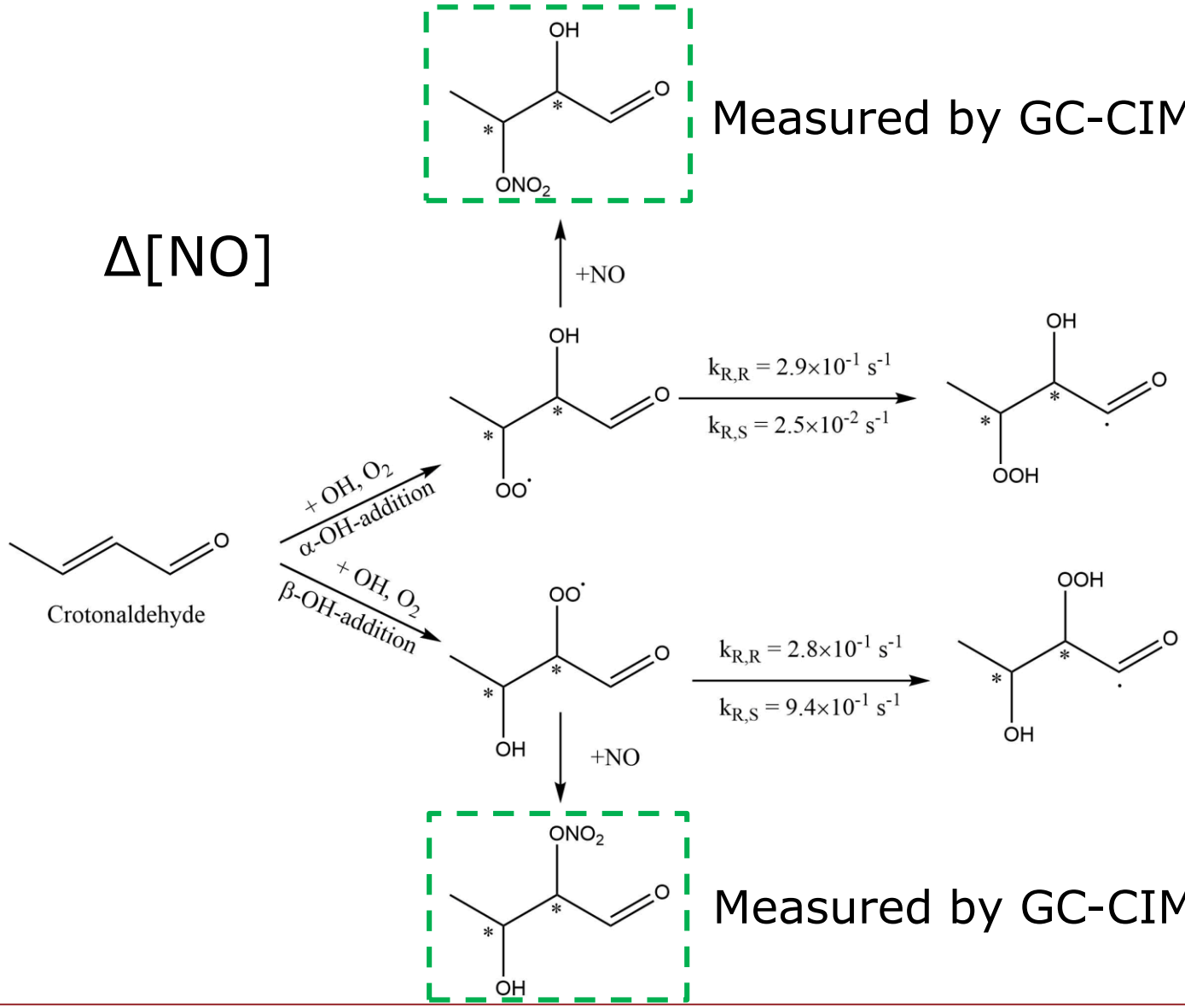
Chiral enhancement



R,R : R,S
12 : 1

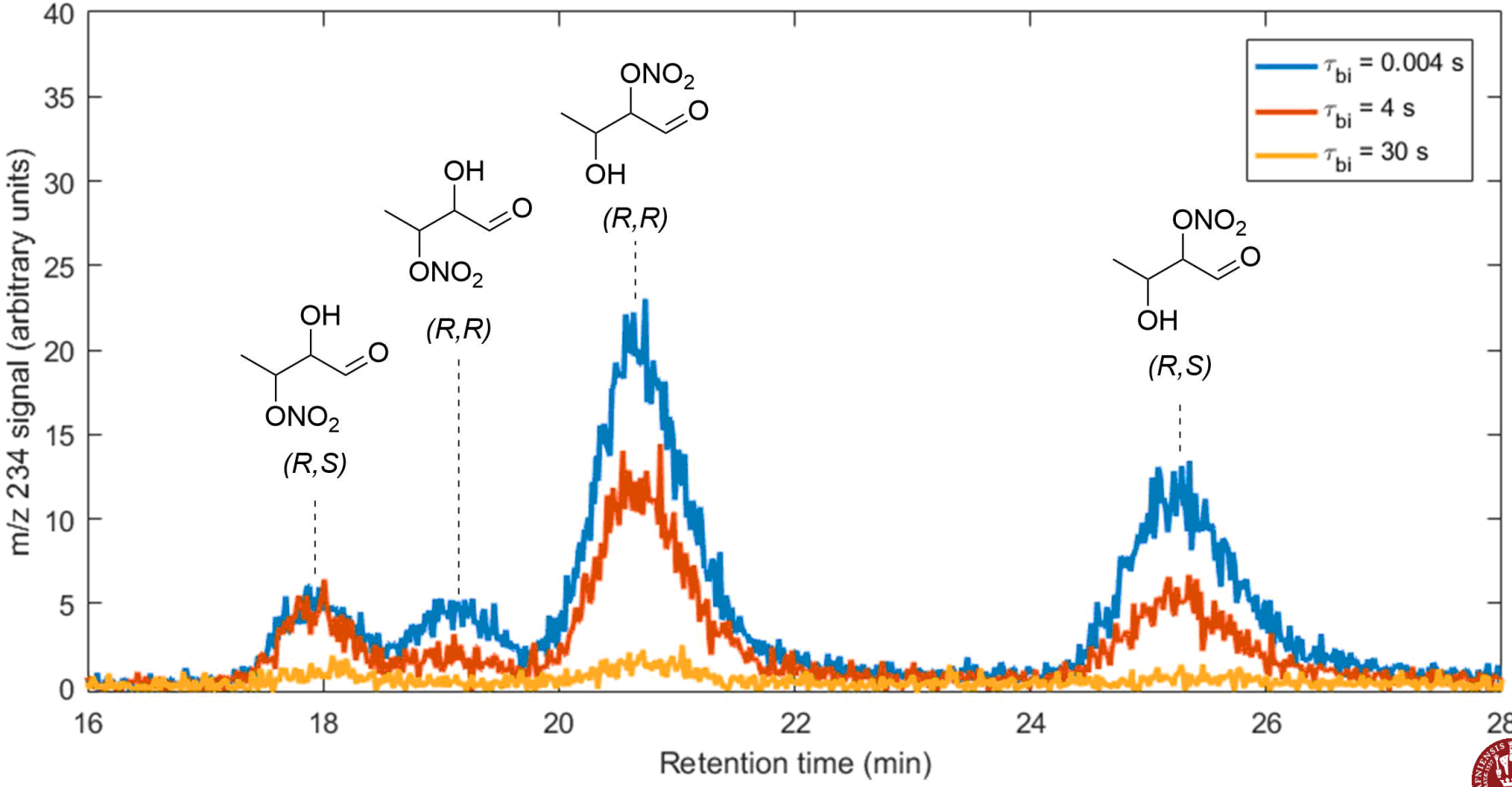


Stereospecificity in Crotonaldehyde Oxidation



Stereospecificity in Crotonaldehyde Oxidation II

Calcs: $k_{(R,R)} \sim 10 \times k_{(R,S)}$



Conclusions

- Calculated MC-TST rate constants for peroxy H-shifts in isoprene oxidation

- Large variation within reaction classes

- Modeling suggests that 30 % of isoprene undergoes H-shift

- Potentially large stereospecificity

Acknowledgements

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HARVARD
UNIVERSITY OF HELSINKI
Caltech
DCSC Danish Center for Scientific Computing
Ministry of Higher Education and Science – Denmark