

Stereoselectivity in Atmospheric Autoxidation

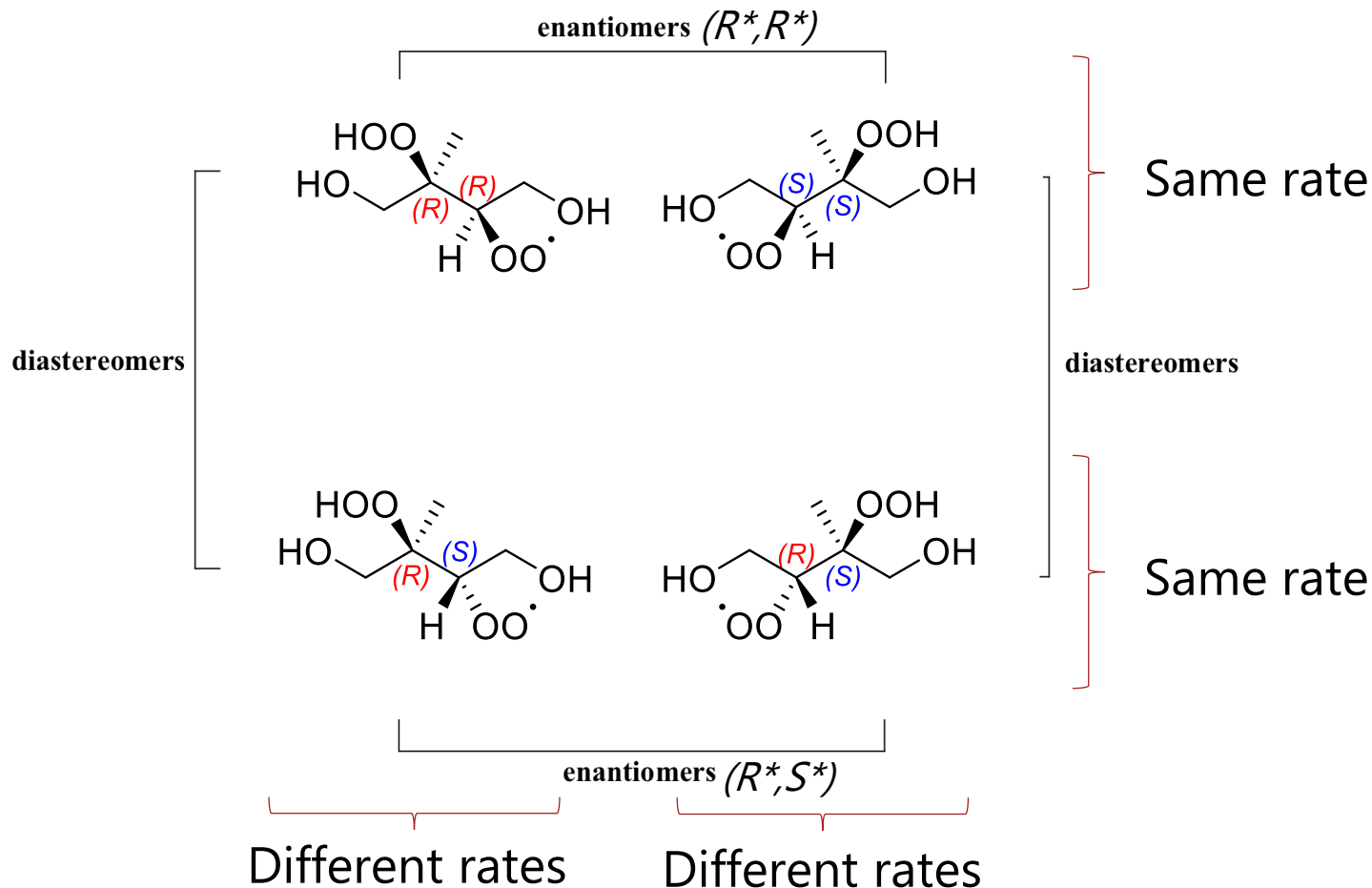
Kristian H. Møller,
Eric Praske, Lu Xu, John D.
Crounse, Kelvin H. Bates, Paul O.
Wennberg, Henrik G. Kjaergaard

EGU General Assembly 2020

UNIVERSITY OF COPENHAGEN



Stereoisomerism

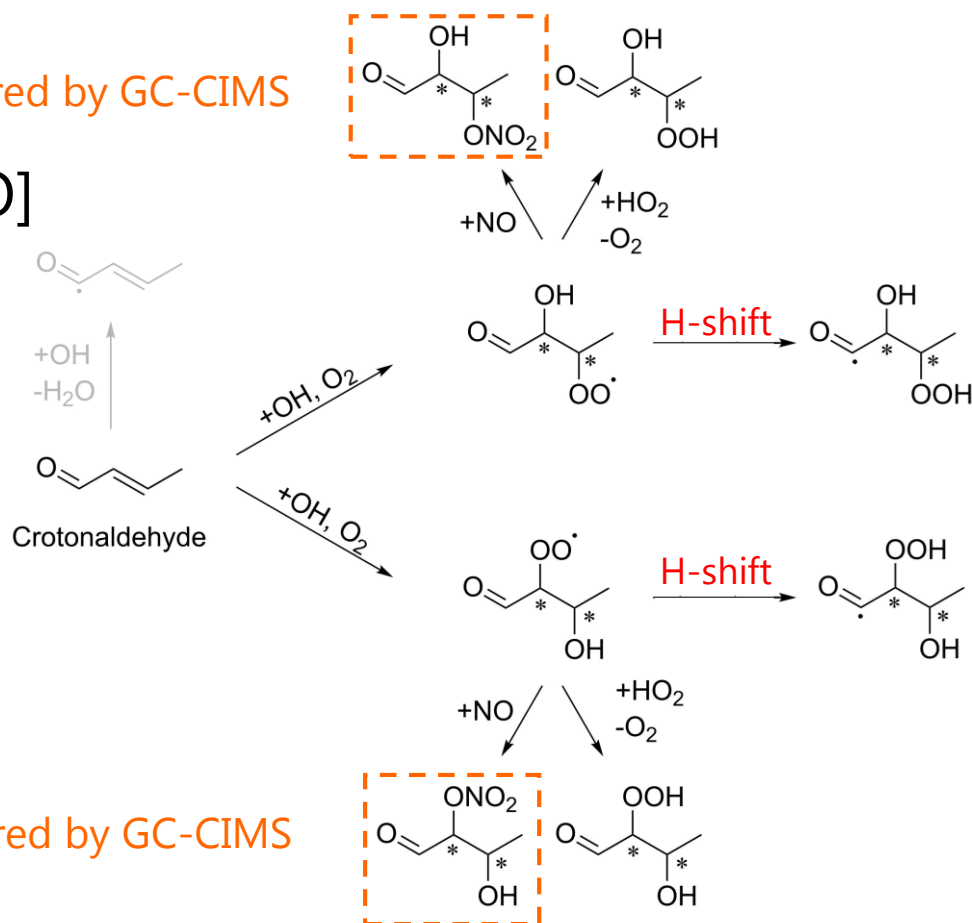


- Many atmospheric peroxy radicals have 2 chiral centers and thus exist as 4 stereoisomers
- The diastereomers which differ at only one of the chiral centers react unimolecularly with different rate coefficients

Stereoselectivity in Crotonaldehyde Oxidation

Measured by GC-CIMS

$\Delta[NO]$

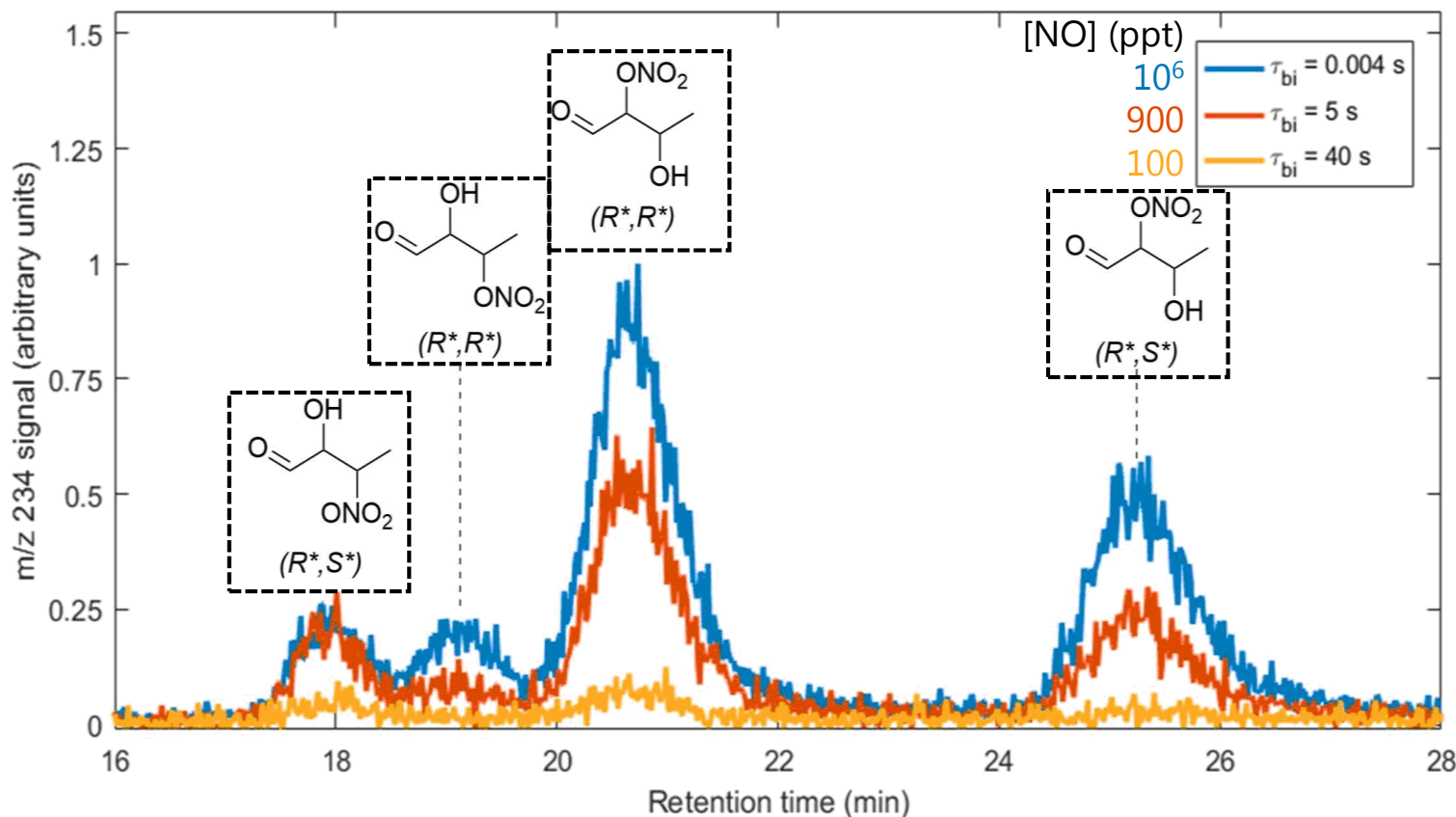
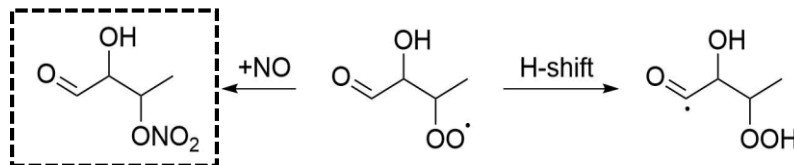


Measured by GC-CIMS

- We show the stereoselectivity experimentally for the **H-shifts** in crotonaldehyde hydroxy peroxy radicals
- We vary the NO concentration and measure the nitrate products of the competing bimolecular reaction using GC-CIMS
- The approach can distinguish the different stereoisomers

$$\tau_{bimolecular} = \frac{1}{k_{RO_2+NO}[NO] + k_{RO_2+HO_2}[HO_2]}$$

Gas Chromatograms and Bimolecular Lifetime



The nitrate peaks decrease to different extent with increasing bimolecular lifetime showing different unimolecular rate coefficients

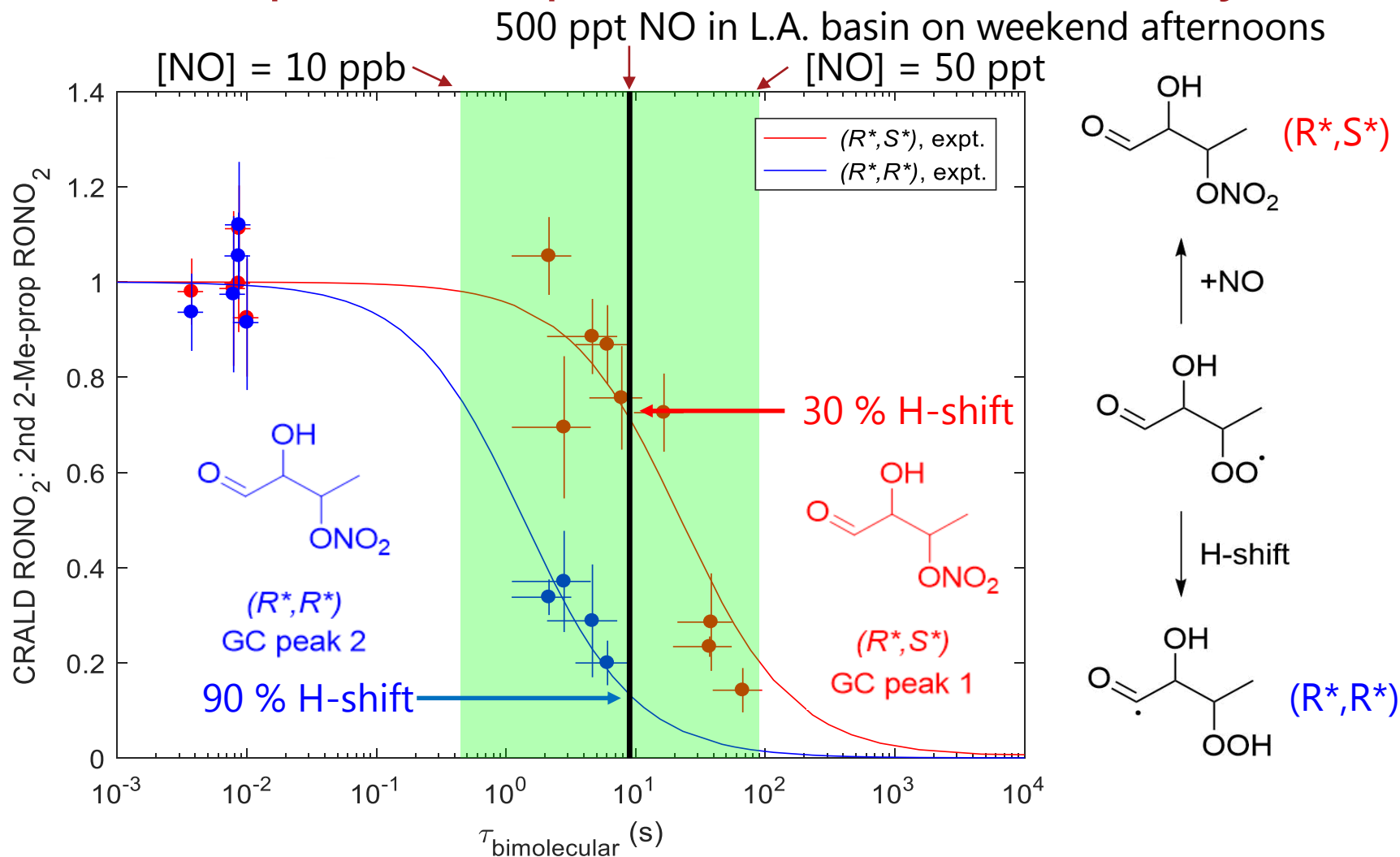
Reaction Rate Coefficients

Structure	Reaction	Stereoisomer	$k_{\text{calc.}} \text{ (s}^{-1}\text{)}$	$k_{\text{expt.}} \text{ (s}^{-1}\text{)}$	
	1,5 H-shift	(R^*, R^*)	0.25	0.7 (+1/-0.3)	× ~20
		(R^*, S^*)	0.021	0.04 (+0.03/-0.02)	
	1,4 H-shift	(R^*, R^*)	0.24	0.3 (+0.2/-0.1)	× 2
		(R^*, S^*)	0.82	0.6 (+0.4/-0.2)	

T = 296 K

- One structural isomer shows differences between diastereomers of about a factor of 20, the other about a factor of 2
- Theory predicted trends beforehand
- Agreement between calculations and experiments within a factor of 3

Atmospheric Impact of Stereoselectivity

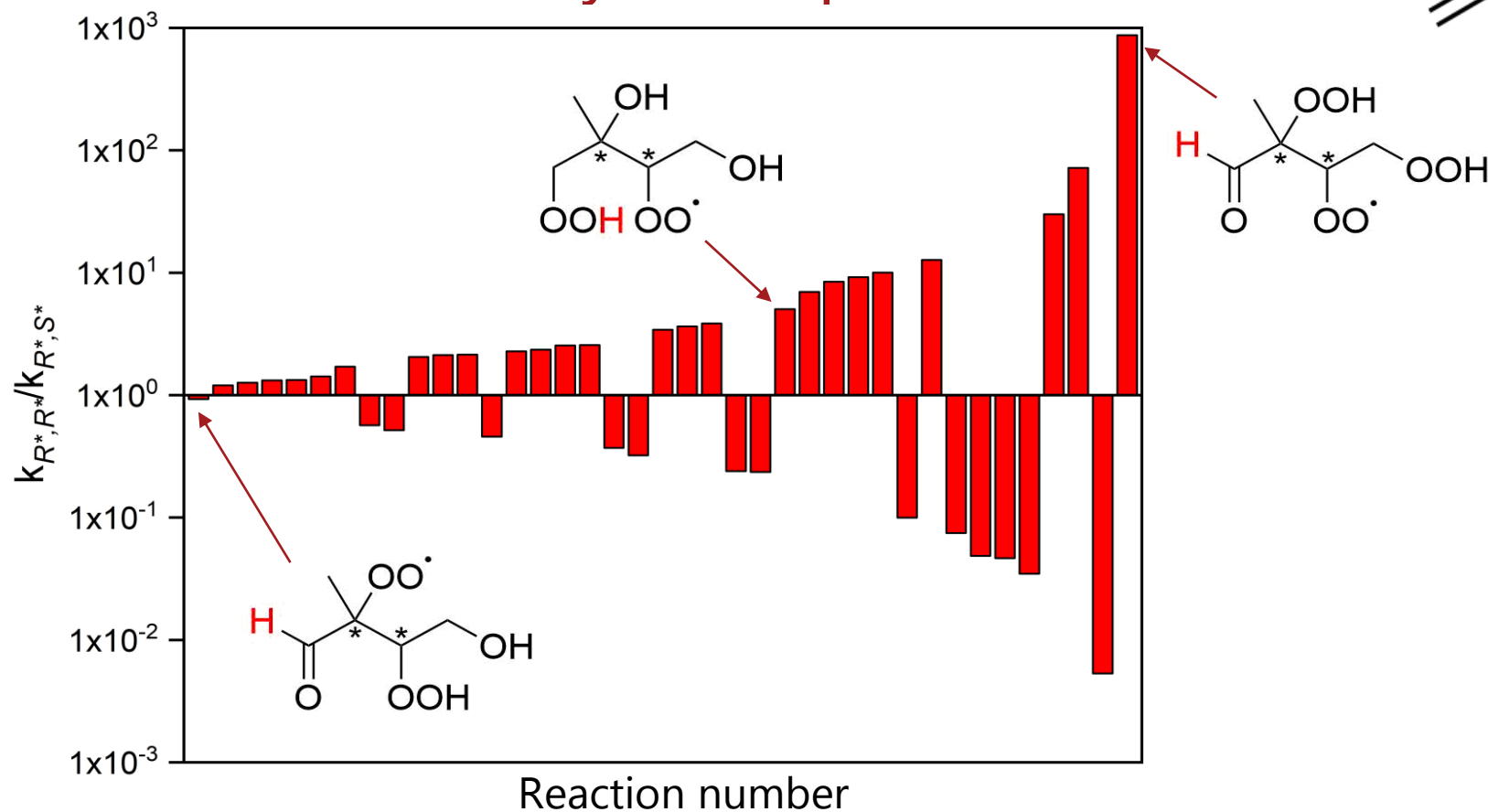
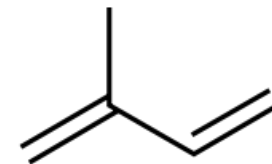


Under many atmospheric conditions, one diastereomer will react mainly unimolecularly and the other mainly bimolecularly leading to diastereomeric enhancements of products

Adapted with permission from Møller et al., *J. Phys. Chem. Lett.*, **2019** 10 (20), 6260-6266, DOI: 10.1021/acs.jpclett.9b01972.

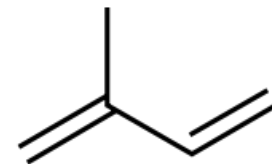
Copyright 2019 American Chemical Society.

Stereoselectivity in Isoprene Oxidation



- Much larger differences between diastereomers are possible in more oxidized systems
- In isoprene-derived peroxy radicals, differences of up to nearly a factor of 1000 have been calculated
- But it is seemingly very difficult to predict which systems display differences

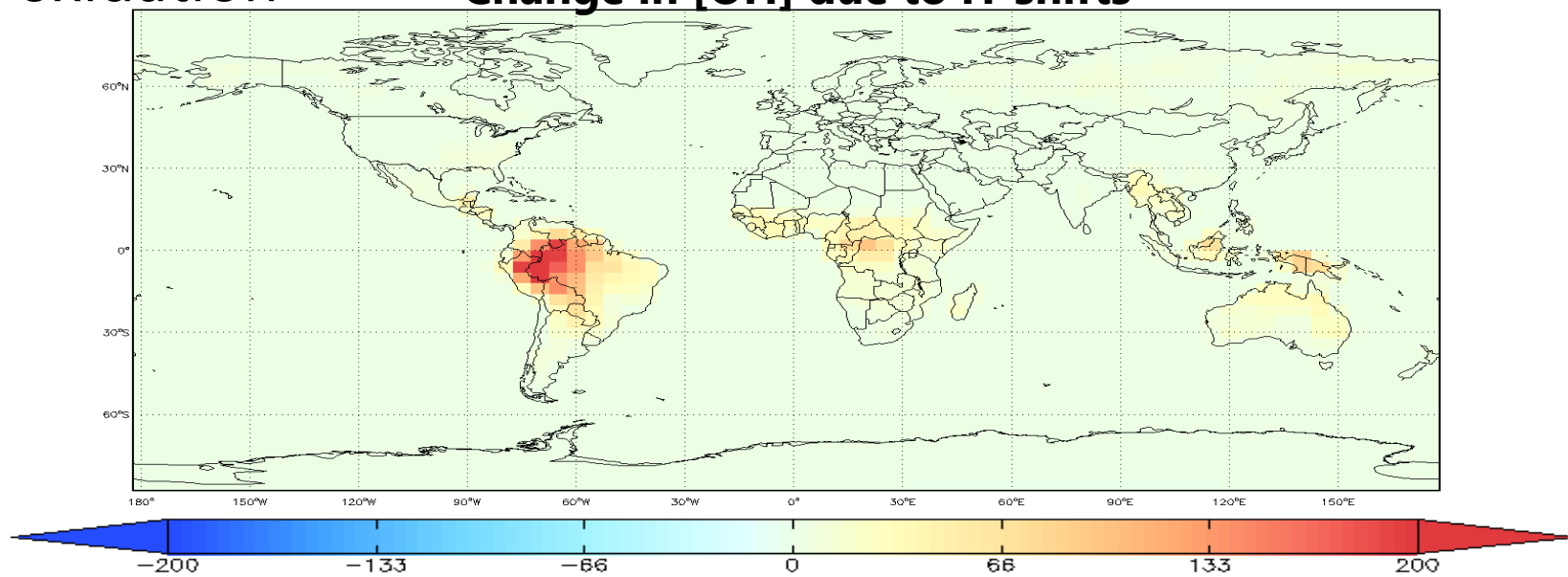
Atmospheric Modeling of H-shifts



GEOS-Chem modeling of H-shifts in isoprene oxidation:

- More than 30 % of all isoprene emitted undergoes a minimum of 1 H-shift
- H-shifts lead to 47 % OH-recycling in isoprene oxidation

Change in [OH] due to H-shifts



$\Delta[\text{OH}]$ (%) GEOS-Chem, Kelvin H. Bates

Acknowledgements



Kelvin H. Bates



Funding

