



The impact of the aldehyde-hydrogen shift on the OH radical budget in the isoprene oxidation mechanism in pristine environments.

A. Novelli¹, L. Vereecken¹, B. Bohn¹, H.-P. Dorn¹, A. Hofzumahaus¹, F. Holland¹, X. Li^{1,*}, M. Kaminski^{1,#}, Z. Yu¹, S. Rosanka¹, D. Reimer¹, G. I. Gkatzelis¹, D. Taraborrelli¹, F. Rohrer¹, R. Tillmann¹, R. Wegener¹, A. Kiendler-Scharr¹, A. Wahner¹ and H. Fuchs¹.

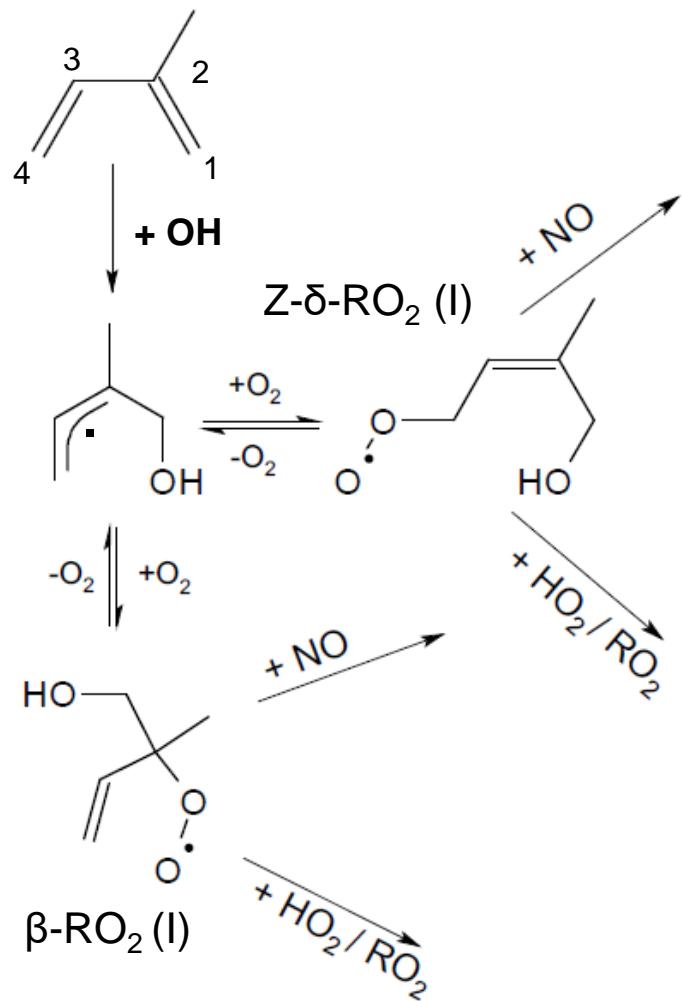
¹ Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

* now at: College of Environmental Sciences and Engineering, Peking University, Beijing, China

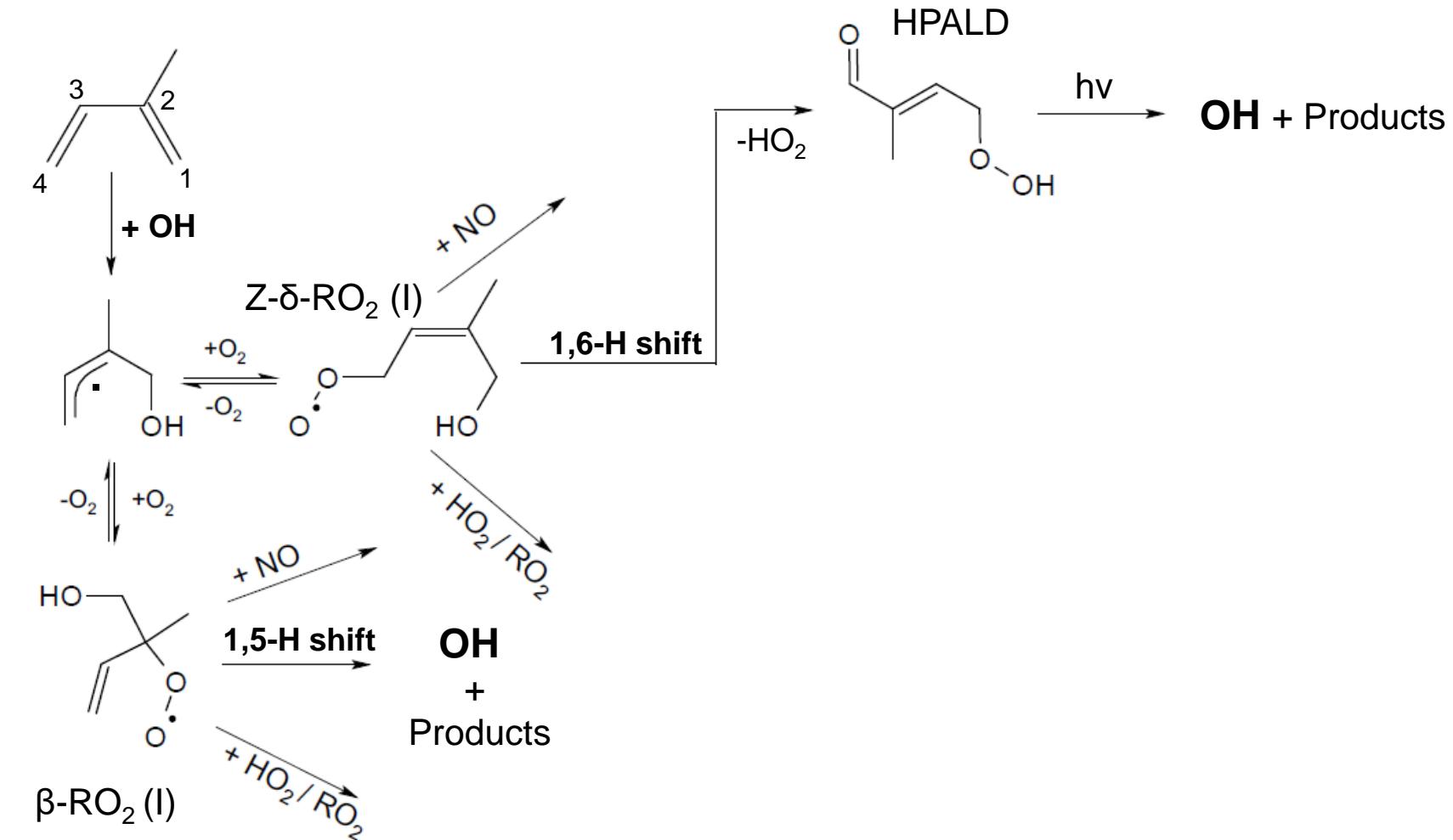
now at: Bundesamt für Verbraucherschutz, Abteilung 5, Berlin, Germany

Mitglied der Helmholtz-Gemeinschaft

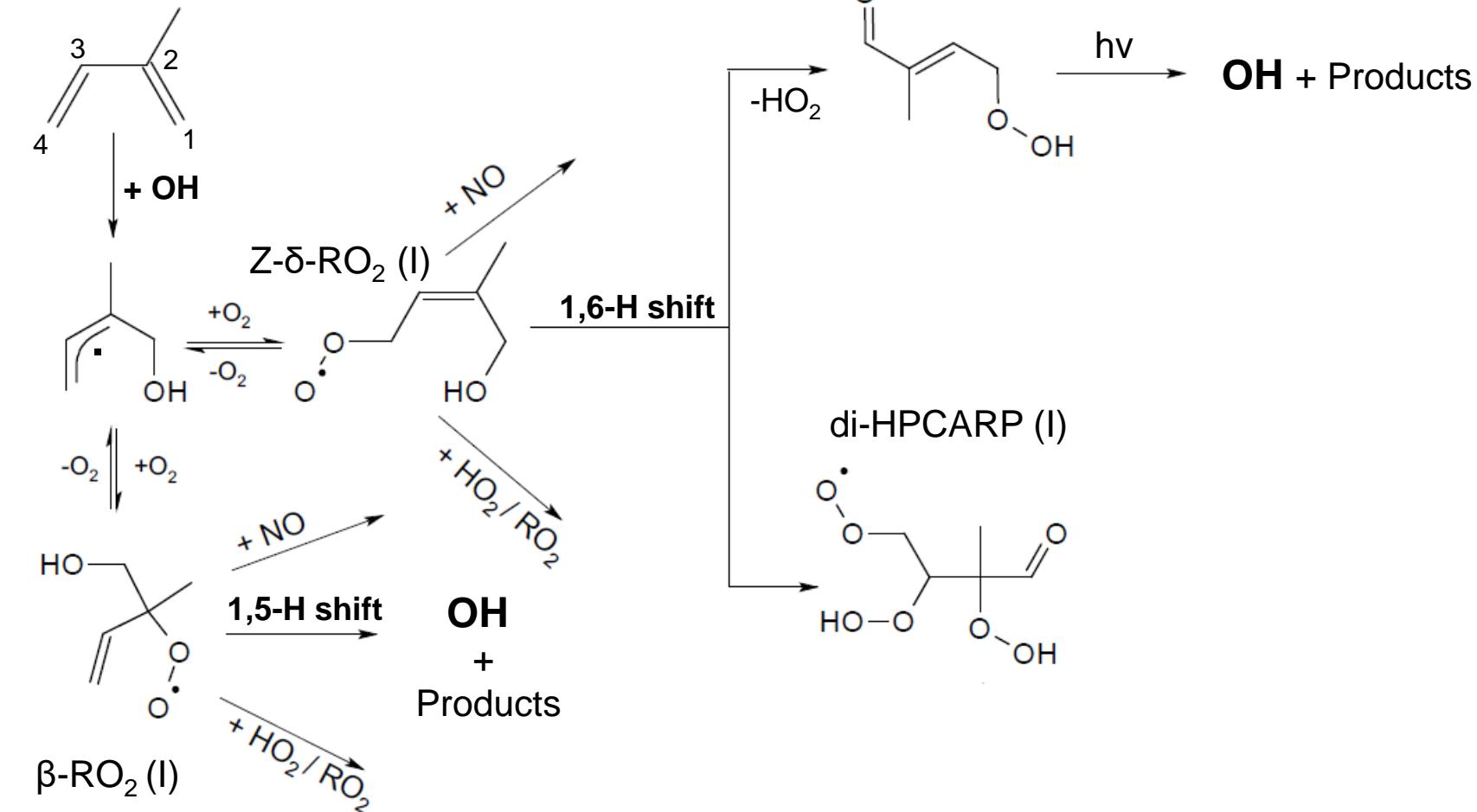
Isoprene oxidation mechanism



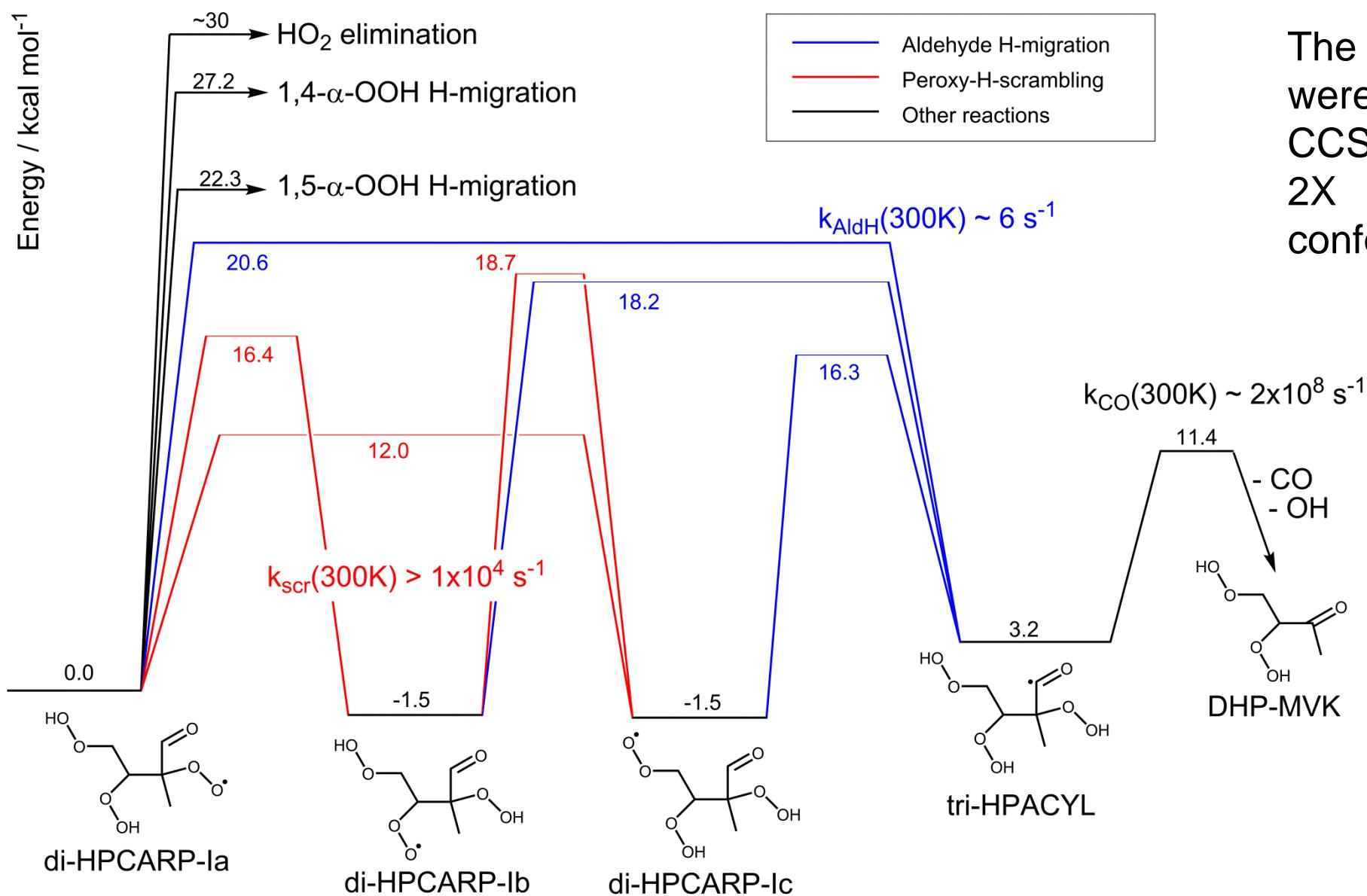
Isoprene oxidation mechanism



Isoprene oxidation mechanism

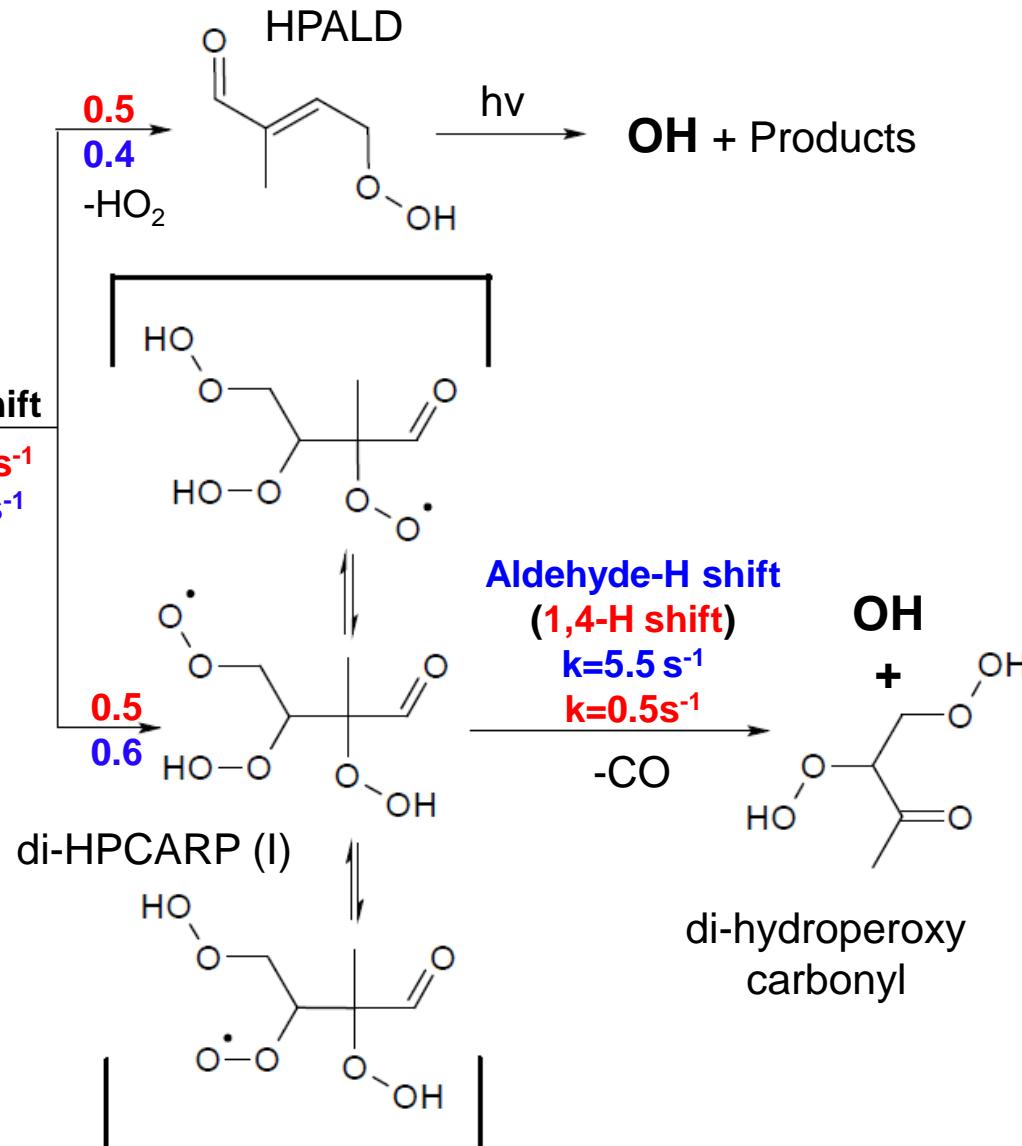
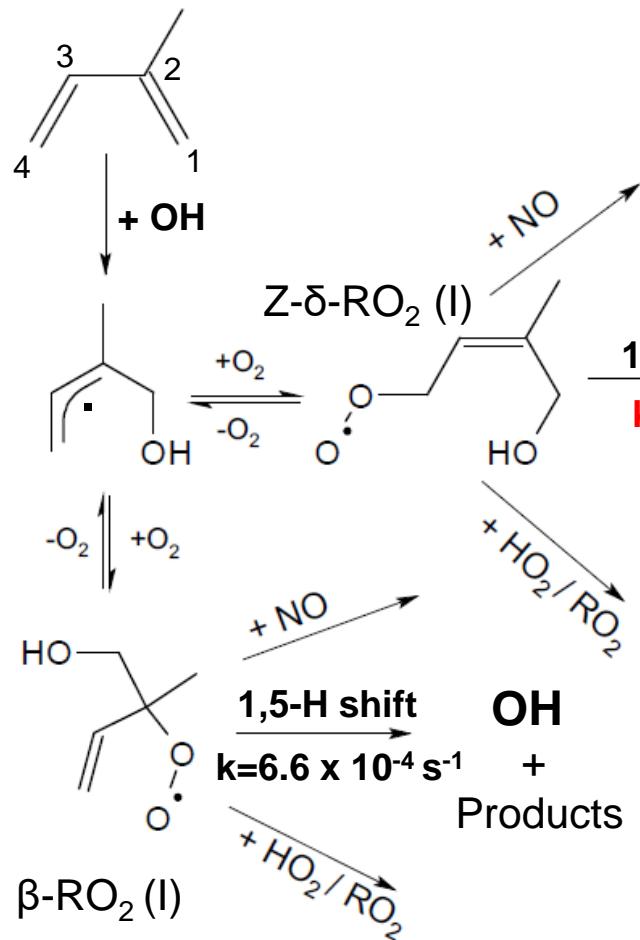


Theoretical calculation



The H-migration reactions were studied at the high-level CCSD(T)/aug-cc-pVTZ//M06-2X level of theory (all conformers).

Isoprene oxidation mechanism



Summary of the modifications for the isoprene chemistry following the OH-addition on C-1 ($Y \sim 0.3$).

Same rates and yields are used for the chemistry of the $Z\text{-}\delta\text{-OH peroxy II}$ which originates from the addition on C-4 ($Y \sim 0.2$).

Rate coefficient are calculated for 298 K.

Peeters et al. 2014
Jenkin et al. 2015
Teng et al. 2017

Goal of this study

- Test new mechanisms in chamber experiments by comparing measured OH and HO₂ radicals, isoprene concentrations together, measured products over a range of NO values (1.5 ppbv > NO > 0.1 ppbv)
- Three mechanisms will be compared:
 - MCM 331
 - MCM 331 no H-Shift (without the isomerization reactions)
 - MCM 331 Best (with the aldehyde-H shift from this work and with a fast 1,6-H shift and yield towards di-HPCARP of 0.6 as suggested by Teng et al. 2017)

Atmospheric simulation chamber SAPHIR



- Volume 270 m³
- Walls made of Teflon film (high UV transmission)
- Light source: solar radiation
- 1-min mixing time

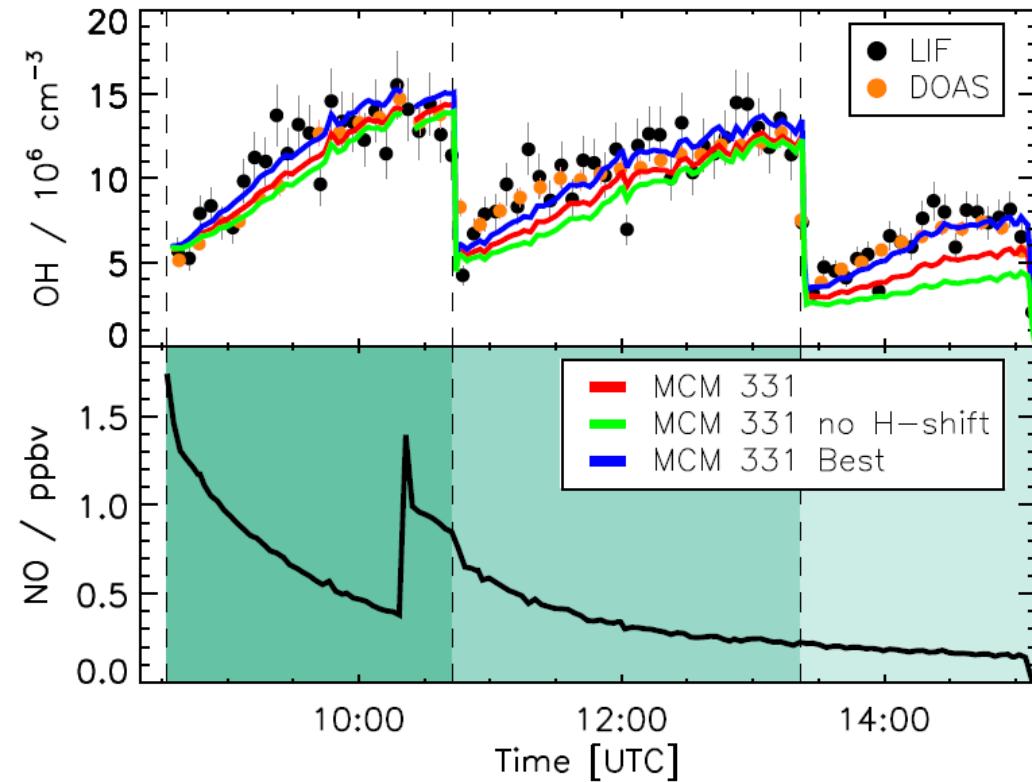
Radical source



Instrumentation:

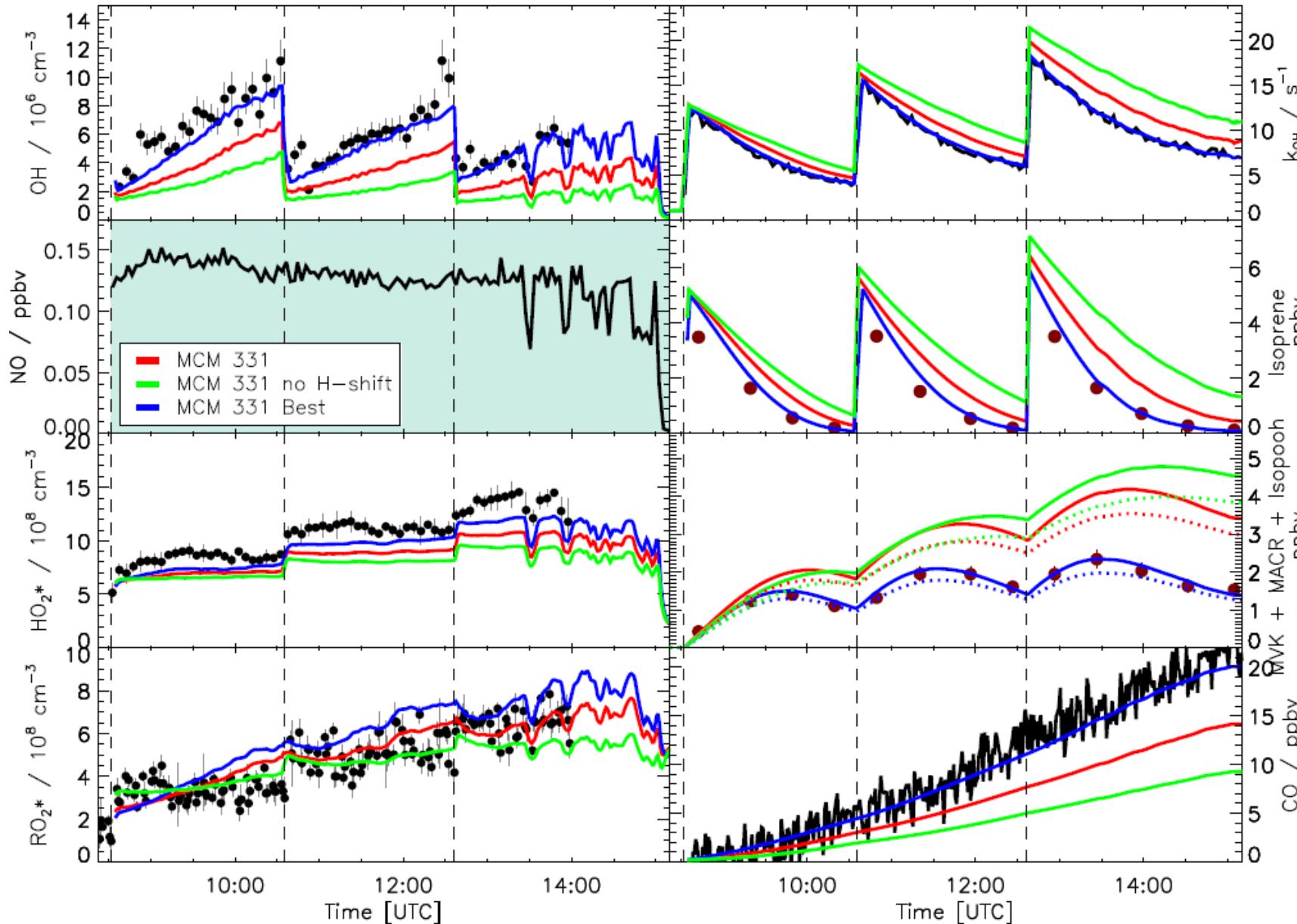
- OH, HO₂, RO₂, k(OH): Laser-induced fluorescence (LIF)
- OH: Differential Optical Absorption Spectroscopy (absolute technique) (DOAS)
- ISOPRENE, MACR, MVK: GC-FID and PTR-TOF-MS
- HONO: Long Path Absorption Photometer (LOPAP)
- NO, NO₂, O₃: Chemiluminescence detectors

From high (1.5 ppbv) to low NO (0.2 ppbv)



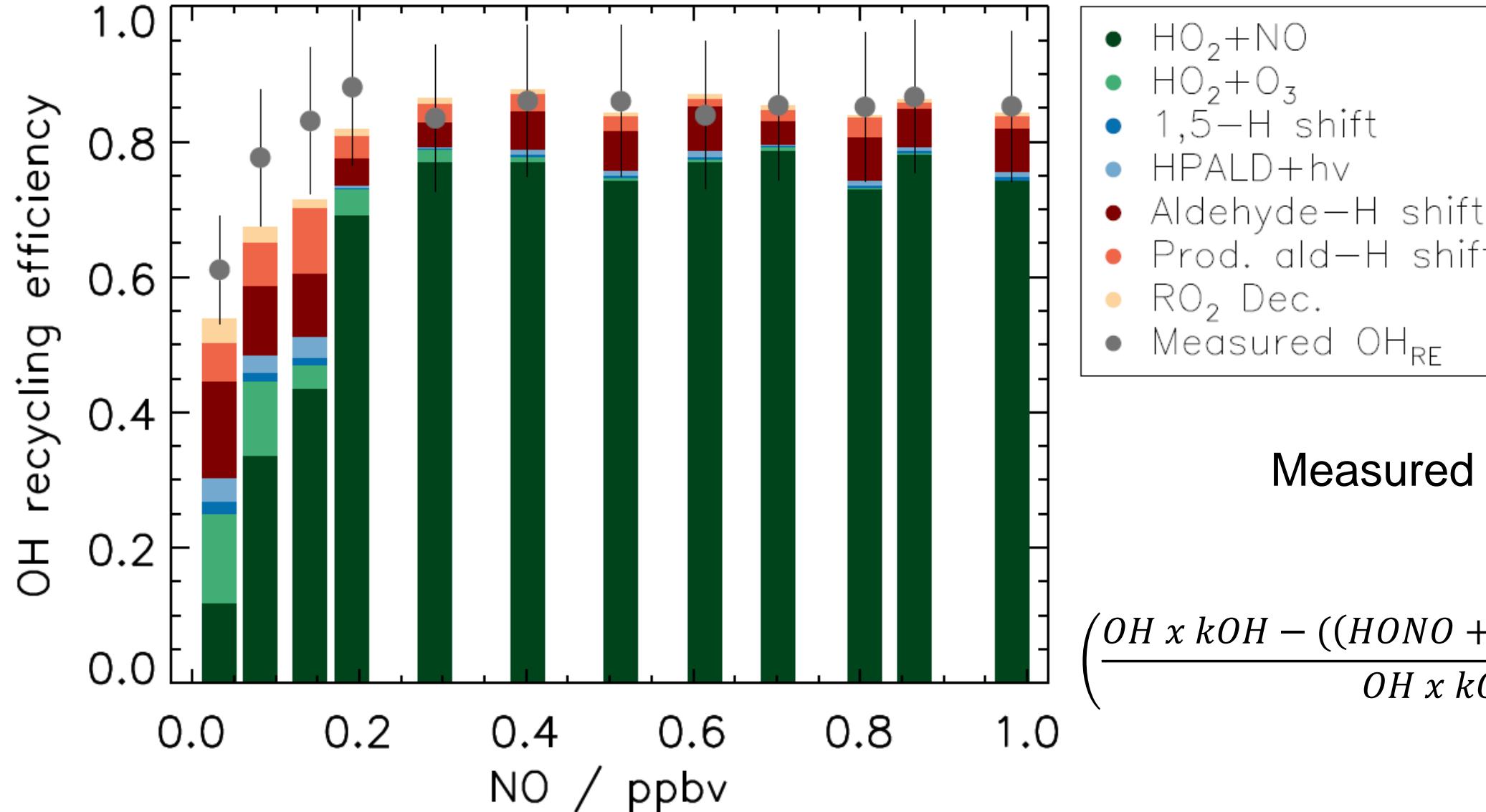
- Three injections of isoprene.
- Good agreement between measured radical species and all mechanisms at $\text{NO} > 200 \text{ pptv}$.
- For $\text{NO} < 200 \text{ pptv}$ MCM 331 underestimates the OH radical concentration.

Low NO (< 0.2 ppbv)

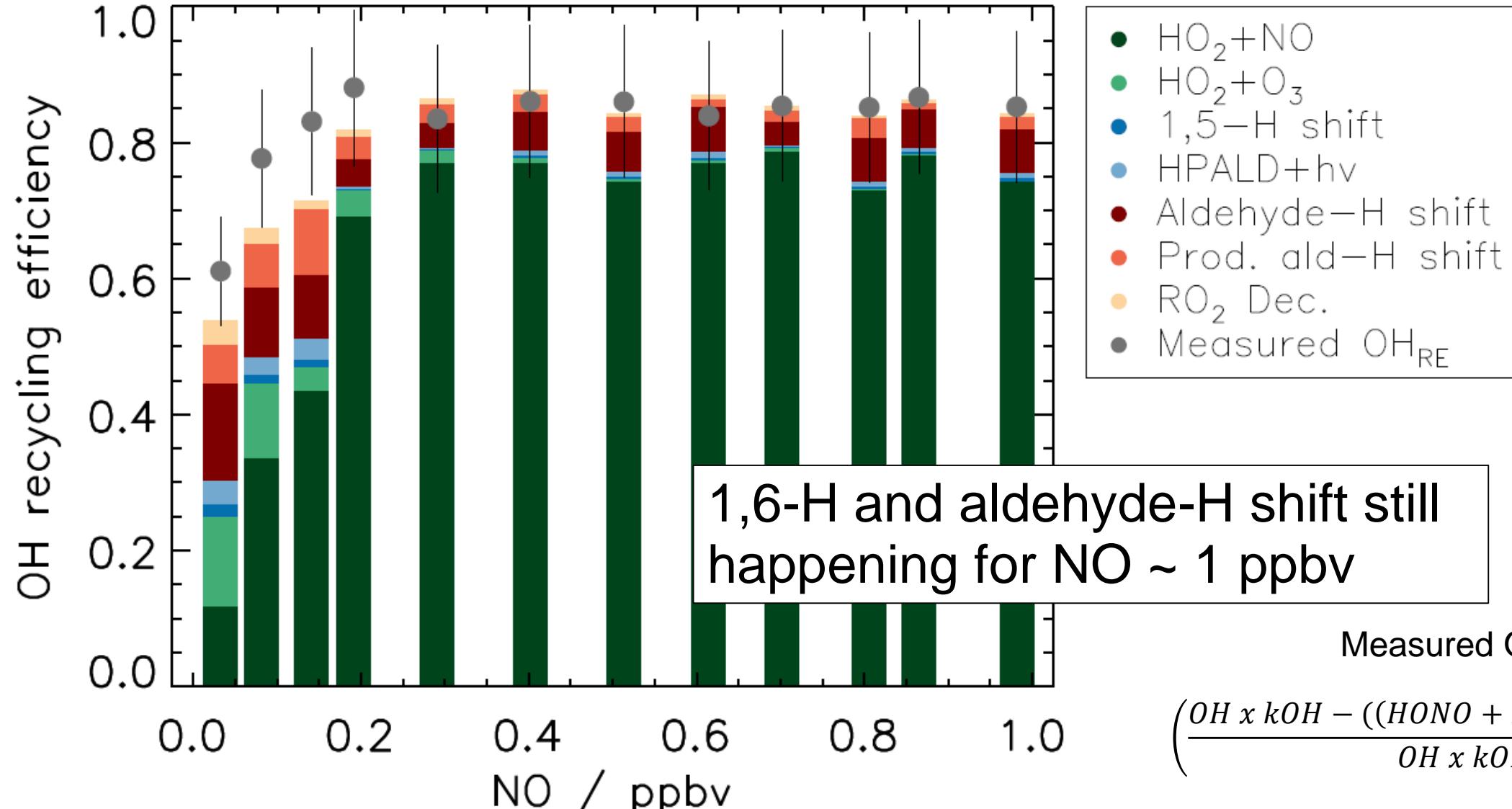


- Three injections of isoprene.
- MCM 331 underestimates the OH radical concentration up to a factor of 2.
- MCM 331 Best can reproduce the measured trace gases within their uncertainties (15%).

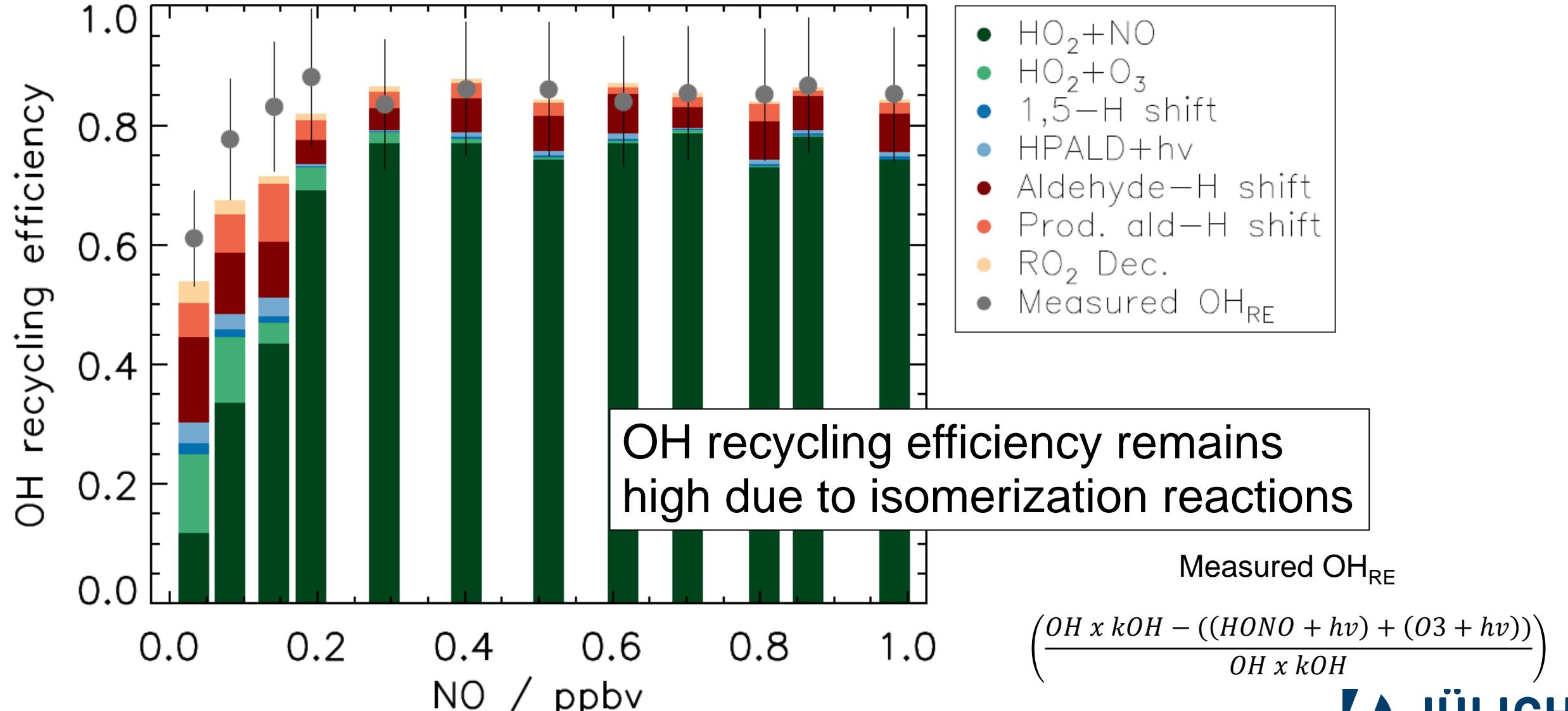
OH recycling efficiency over a range of NO levels



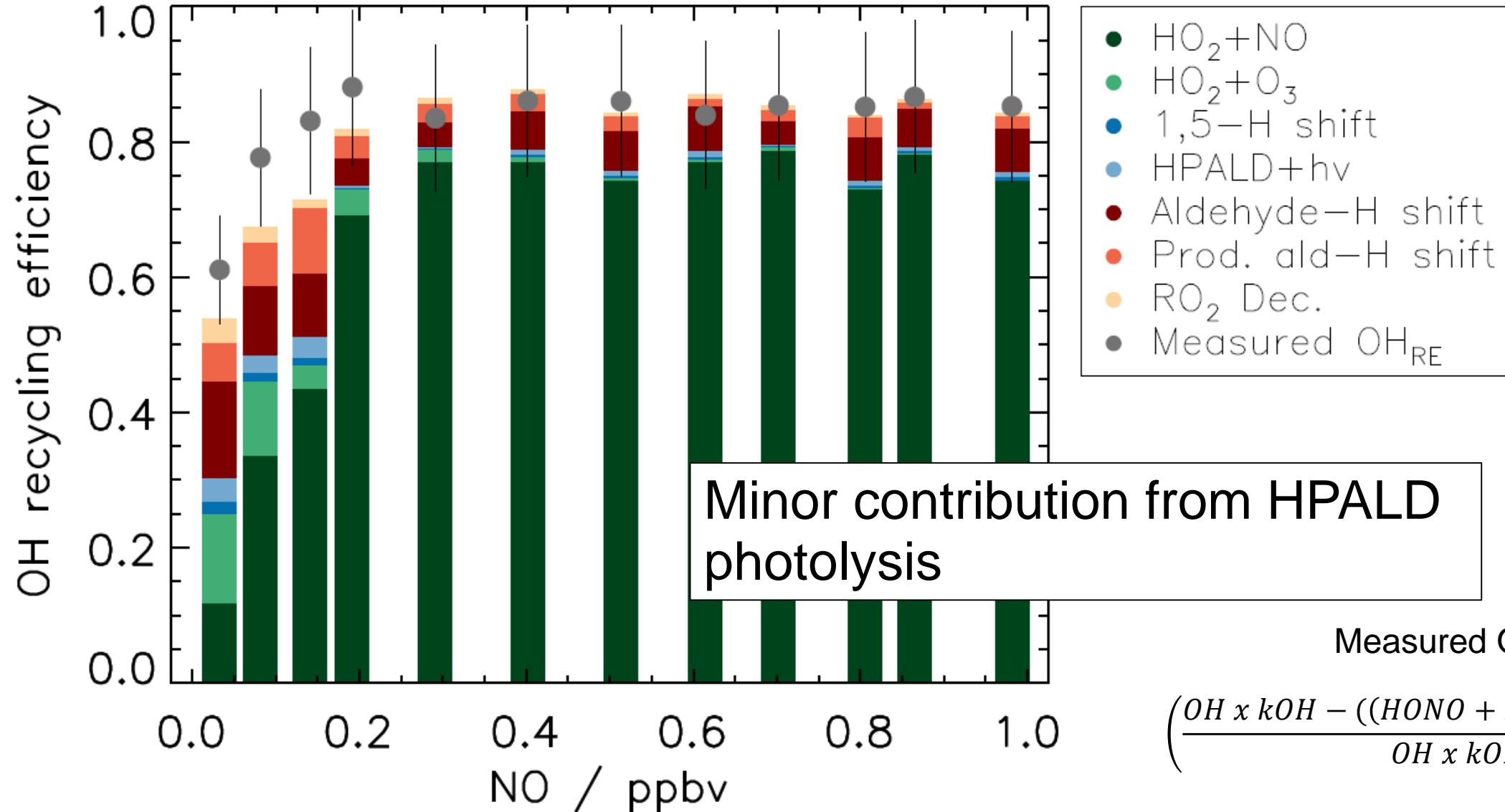
OH recycling efficiency over a range of NO levels



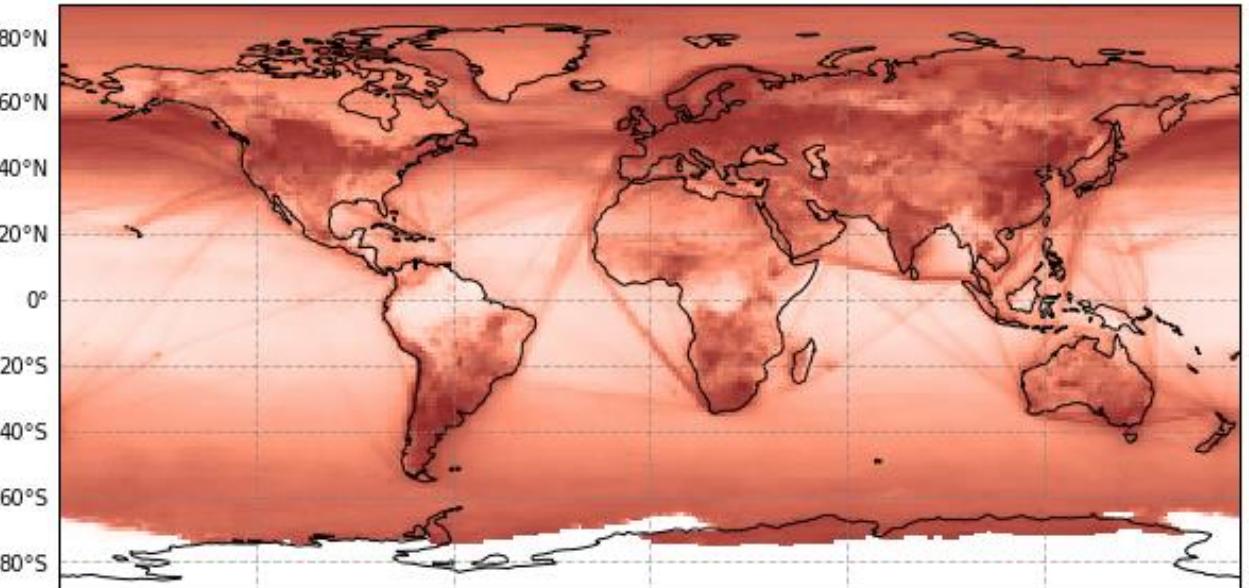
OH recycling efficiency over a range of NO levels



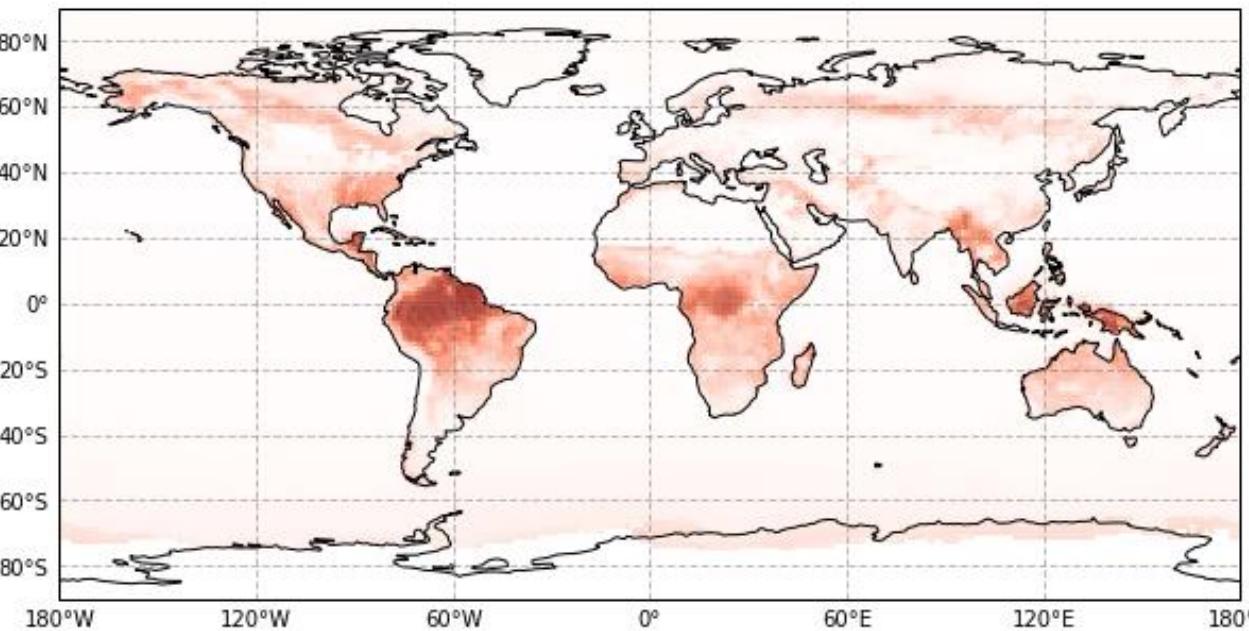
OH recycling efficiency over a range of NO levels



Global model

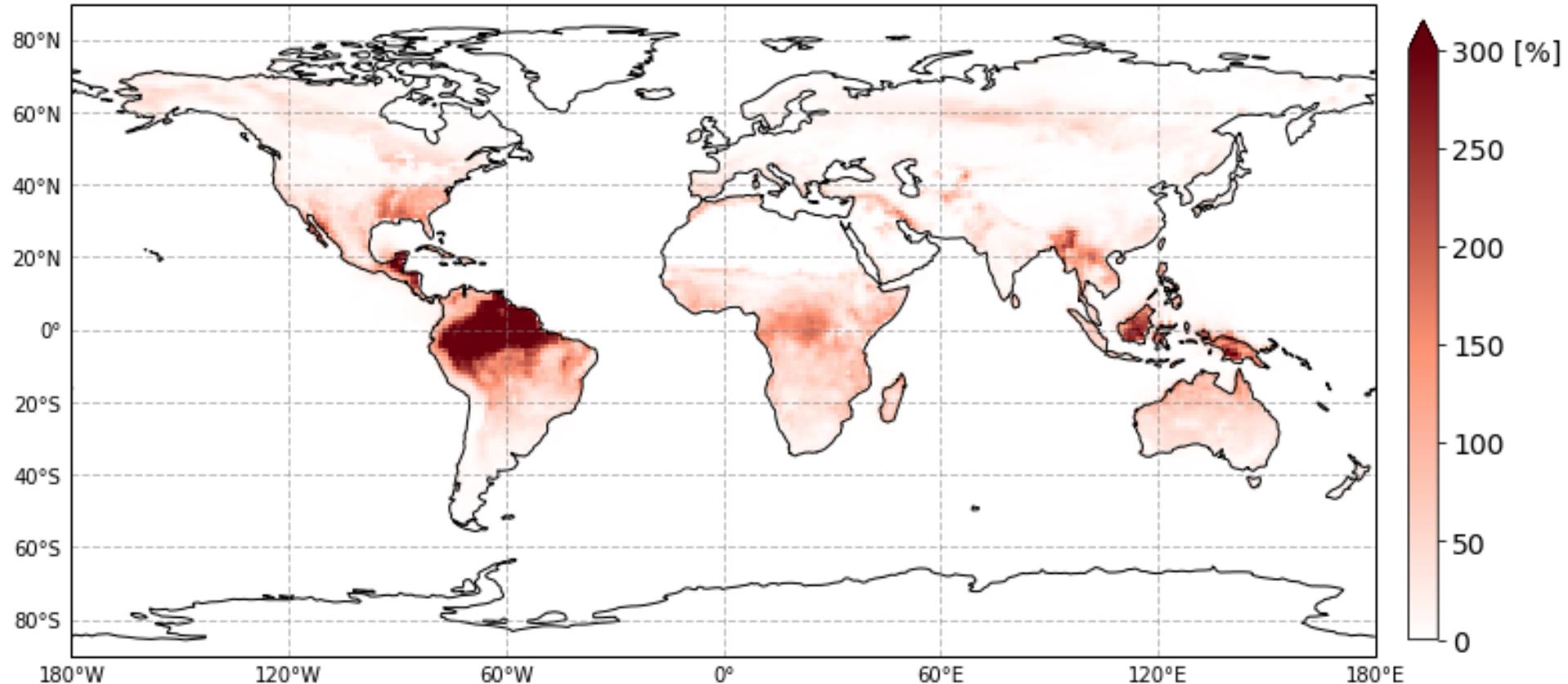


OH recycling efficiency from $\text{HO}_2 + \text{NO}$
and $\text{HO}_2 + \text{O}_3$



OH recycling efficiency from
isomerization reactions

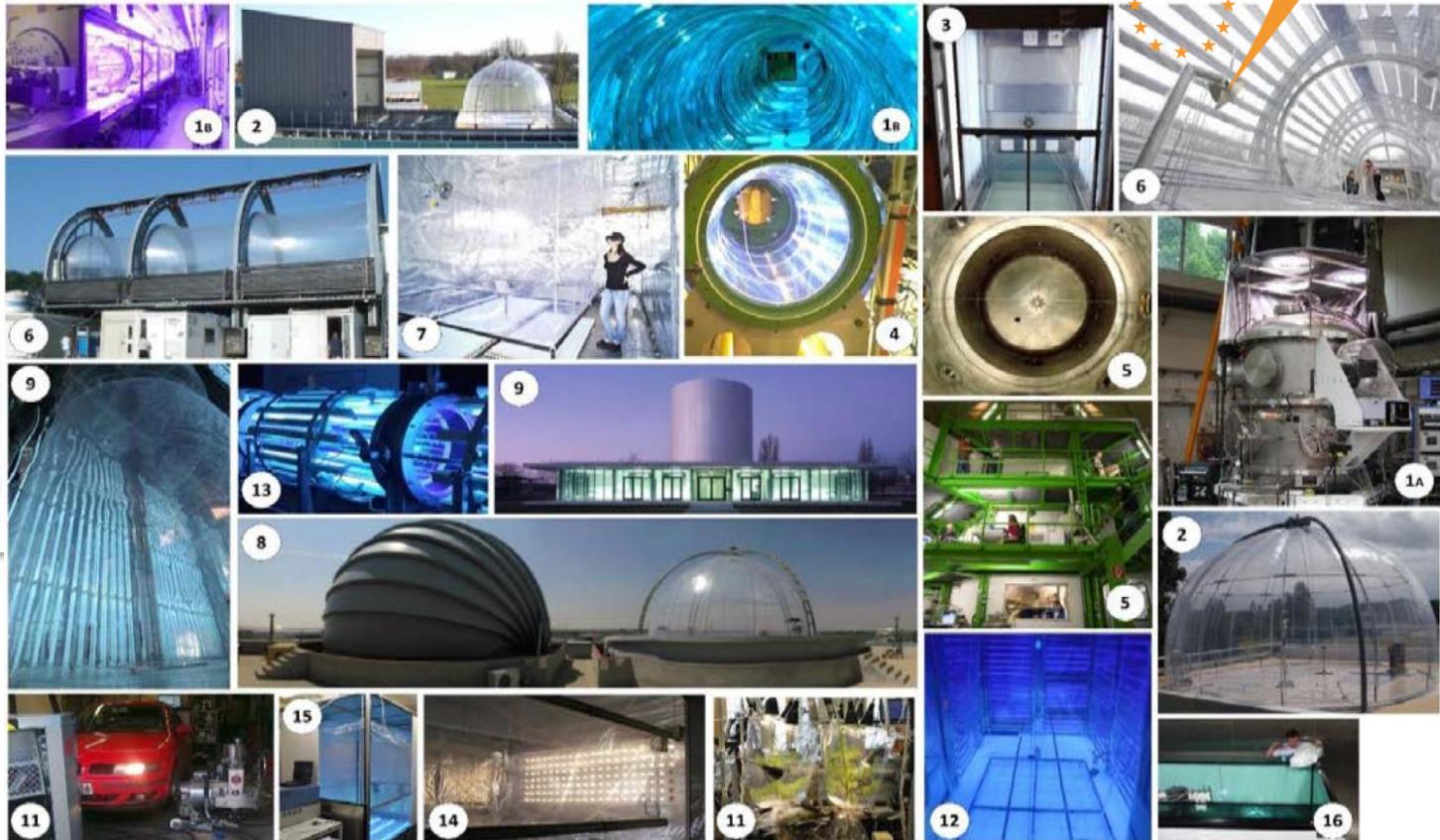
Relative OH concentration increase



Conclusions

- Mechanisms with and without isomerization reactions are able to reproduce the OH radicals concentration for NO values larger than 0.3 ppbv.
- The MCM 3.3.1 is not able to reproduce the measured trace gases for NO < 0.2 ppbv.
- Best agreement observed when the MCM 3.3.1. is implemented with a faster 1,6-Hydrogen shift.
- Contribution from photolysis of HPALD to the OH radical concentration at low NO is small and most of the regenerated OH radical originates from the aldehyde-H shift and its products.
- The isomerization reactions maintain the OH recycling efficiency to a value above 60% at low NO sustaining a larger than expected OH radical concentration (up to a factor of 3).
- The implementation of a fast 1,6-H shift and the aldehyde-H shift in a global model shows a large increase (> 300%) of OH radical concentration in environments with high isoprene emissions and confirms the need for a better understanding of the chemistry of the products following the aldehyde-H shift.

TRANSNATIONAL ACCESS TO EUROPEAN ENVIRONMENTAL CHAMBERS



Eurochamp offers:

- Free access to chambers
- Travel support

→ Application: www.eurochamp.org