

Hydroxyl Radical Regeneration in Isoprene Oxidation: the Upgraded Mechanism LIM1

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INTRODUCTION (1)

- ❖ In recent campaigns in isoprene-rich areas:
 - OH concentration often 5 (up to 10) times higher than model predictions
 - HO₂ also frequently underestimated
- ❖ Peeters et al. (PCCP, 2009, 2010)¹⁻³ proposed and theoretically quantified a new isoprene oxidation mechanism for low- and moderate NO levels that results in HO_x radical regeneration
 - ➔ LEUVEN ISOPRENE MECHANISM (LIM)

1. J. Peeters, T.L. Nguyen, L. Vereecken, *PCCP* 11, 5935-5939, 2009

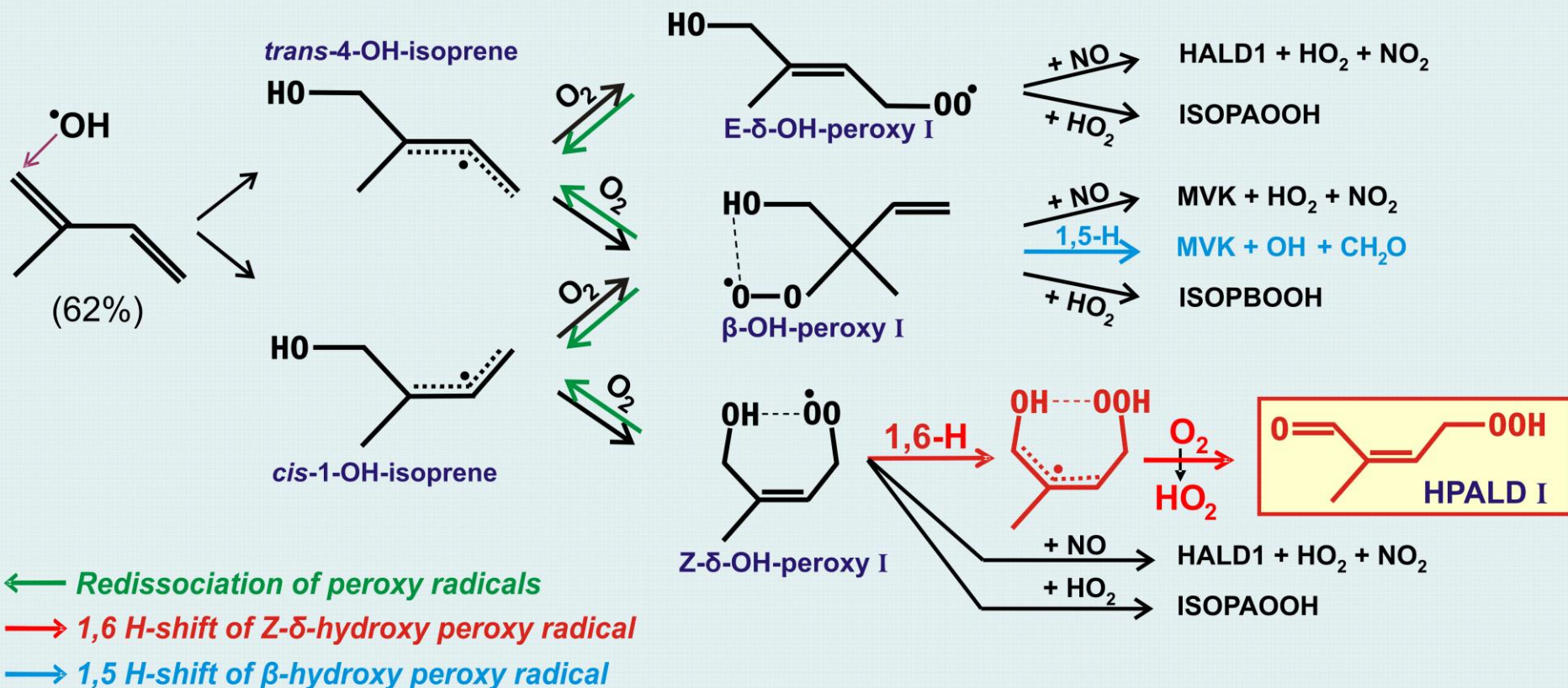
2. J. Peeters and J.-F. Müller, *PCCP* 12, 14227-14235, 2010.

3. T. Stavrou, J. Peeters, J.-F. Müller, *ACP* 10, 9863-9878, 2010

INTRODUCTION (2)

INITIAL STEPS

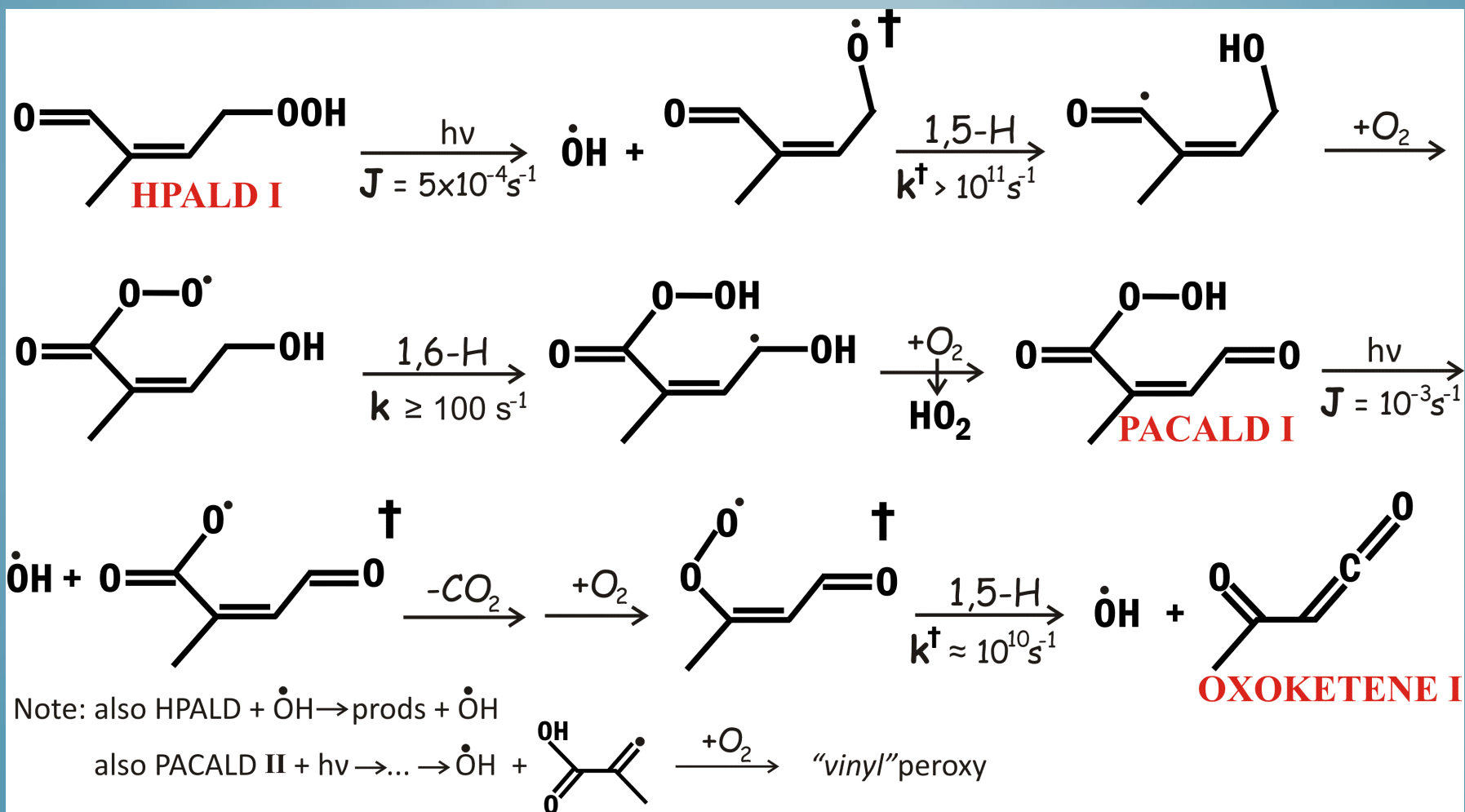
chemistry of OH-isoprene adducts I



INTRODUCTION (3)

SECONDARY CHEMISTRY : HPALD photolysis recycling OH

(Peeters and Müller, PCCP 2010; EGU meeting 2011)



UPGRADED MECHANISM LIM1

NEW ELEMENTS :

- Crouse et al. 2011: confirm HPALD formation, but report lower yield⁴ than LIM0 predictions
- Wolfe et al. 2012: confirm fast HPALD photolysis with unit quantum yield⁵
- Hofzumahaus et. al. 2009,⁶ Whalley et. al. 2011:⁷ invoke fast conversion $\text{HO}_2 + \text{X} \rightarrow \text{OH} + \dots$ in order to reproduce field observations, with X unknown

However, no (O)VOC known to react fast with HO_2 !

4. Crouse, J. D. *et al.*, Phys. Chem. Chem. Phys. 13, 13607, 2011.

5. Wolfe, G. M. *et al.*, Phys. Chem. Chem. Phys. 14, 7276, 2012.

6. Hofzumahaus, A. *et al.*, Science 324, 1702, 2009.

7. Whalley, L. K. *et al.*, Atmos. Chem. Phys. 11, 7223, 2011.

UPGRADED MECHANISM LIM1

(re-)Computation of isoprene peroxy isomerisation rate at much higher levels of theory

$$k_{(\text{isom})} = \sum_{i=\text{I,II}} B_i \times f(\text{Z}\delta) \times k^{\text{Z}\delta} (\text{1,6-H})$$

overall isom-rate
for **pool of peroxy**
(or “bulk” peroxy
rate)

Branching fraction
to initial OH-Adduct I or II

steady-state fraction
of **Z-δ peroxy**
isomers

isomer-specific rate
coefficient 1,6-H shift
of **Z-δ peroxy isomers**

Isomerisation rate of Z- δ peroxy

$$k^{Z\delta}(1,6H) = \kappa(T) \frac{k_B T}{h} \frac{\sum_7 Q_{TS}}{\sum_{22} Q_{Z\delta}} \exp \frac{-(E_{TS} - E_{Z\delta})}{k_B T}$$

Fraction of Z- δ peroxy at low NO :

$$f(Z\delta)_{(lowNO)} \cong K_{eq}^{Z\delta/\beta} = \frac{\sum_{22} Q_{Z\delta}}{\sum_{25} Q_{\beta}} \exp \frac{-(E_{Z\delta} - E_{\beta})}{k_B T}$$

- Multi-conformer Partition functions $\sum Q_{TS}$, $\sum Q_{Z\delta}$, $\sum Q_{\beta}$:
from **M06-2x/6-311++G(3df,2p)** level of QC theory
accounts properly for London-dispersion!

(while B3LYP method used for LIM0 does not)

- Energies of lowest conformers E_{TS} , $E_{Z\delta}$, E_{β} :
from very high-level **CCSD(T)/aug-cc-pVTZ** based on
QCISD/6-311G(d,p) geometries

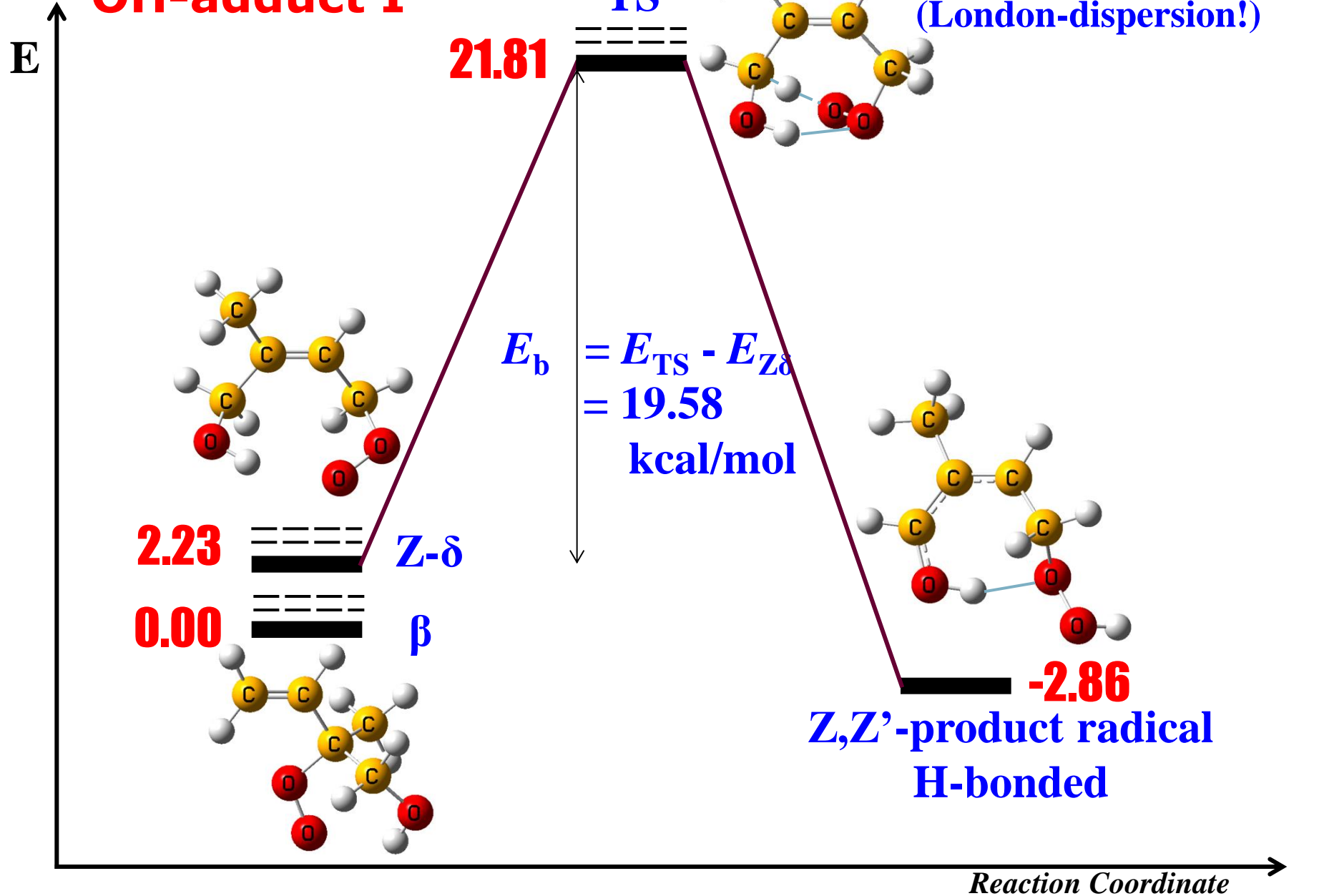
(the best level available: "gold standard")

expected error only ~ 0.3 kcal/mol

- $\kappa(T)$ tunneling factor: ZCT approach on asymmetric Eckart barrier
(for similar H-shifts in peroxy radicals: results close to high-level SCT approach, Zhang & Dibble, 2011)

RESULTS (a)

OH-adduct I



RESULTS: overall $k(\text{isom})$ by Z- δ 1,6 H shift

at 295 K

OH-adduct I		OH-adduct II	
$f(Z\delta)$	$k_{(1,6-H)}^{Z\delta}$	$f(Z\delta)$	$k_{(1,6-H)}^{Z\delta}$
1.3×10^{-2}	0.44 s^{-1}	2.6×10^{-3}	4.9 s^{-1}

lowNO
Overall $k(\text{isom}) = 7.5 \times 10^{-3} \text{ s}^{-1}$ at 295K

Compare to: $k(\text{peroxys} \rightarrow \text{HPALDs}) = (2 \pm 1) \times 10^{-3} \text{ s}^{-1}$ of Crouse;
but: isomerisation yields other products besides HPALDs

Note: $k(\text{isom})$: strongly T-dependent: $4.5 \times 10^9 e^{-8000/T} \text{ s}^{-1}$

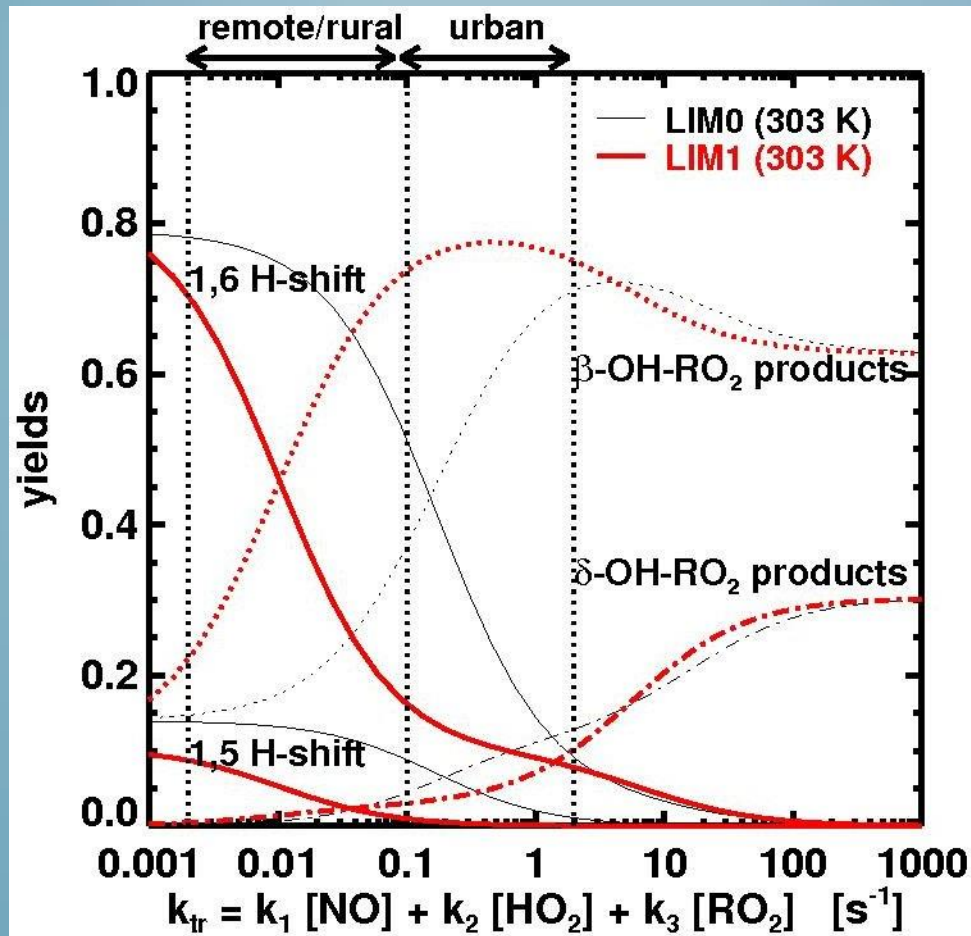
\Rightarrow at 303 K: $k(\text{isom}) = 1.5 \times 10^{-2} \text{ s}^{-1}$, i.e. about half the combined rate of traditional peroxy reactions at low NO

RESULTS: 1,5 H shift rate of β -hydroxyperoxys
(\rightarrow OH+CH₂O+MVK or MACR)

$$k_{(1,5-H)}^{\beta} = 1.04 \times 10^{11} \times \exp(-9746/T) \quad \text{OH-adduct I}$$
$$= 1.1 \times 10^{-3} \text{ s}^{-1} \quad \text{at 303 K}$$

$$k_{(1,5-H)}^{\beta} = 1.88 \times 10^{11} \times \exp(-9751/T) \quad \text{OH-adduct II}$$
$$= 2.0 \times 10^{-3} \text{ s}^{-1} \quad \text{at 303 K}$$

RESULTS : PRODUCT YIELDS



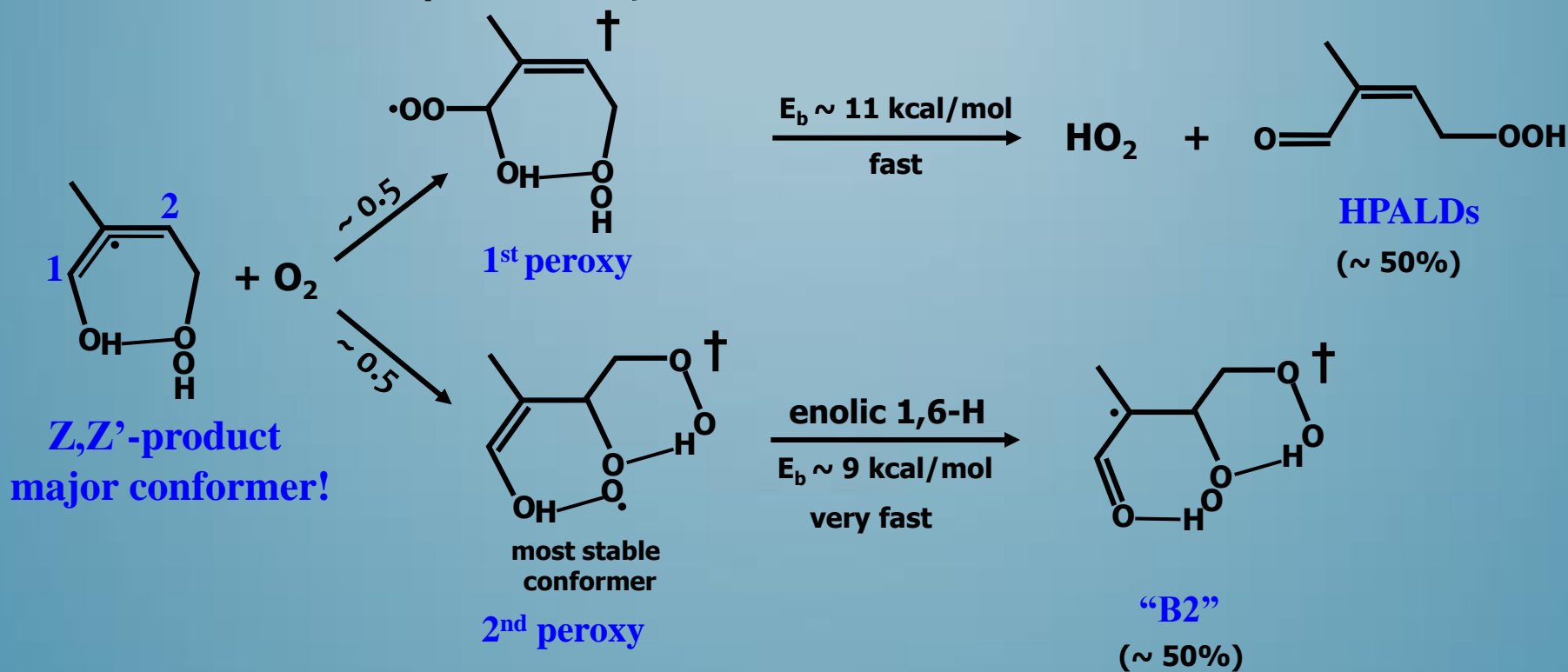
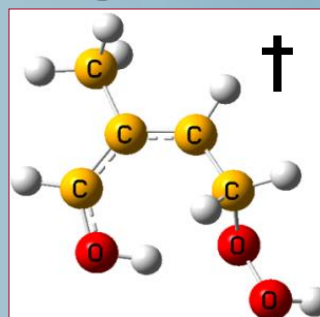
↓
Peroxy radical sink due to traditional (i.e. bimolecular) reactions, e.g. $\text{RO}_2 + \text{NO}$

PRODUCT CHANNELS Following Z- δ 1,6-H shift

❖ Stabilized allylic product radical :

adds O₂

Two main pathways:



refs. : GK21 Boulder June 2012, and IGAC Beijing, Sept 2012

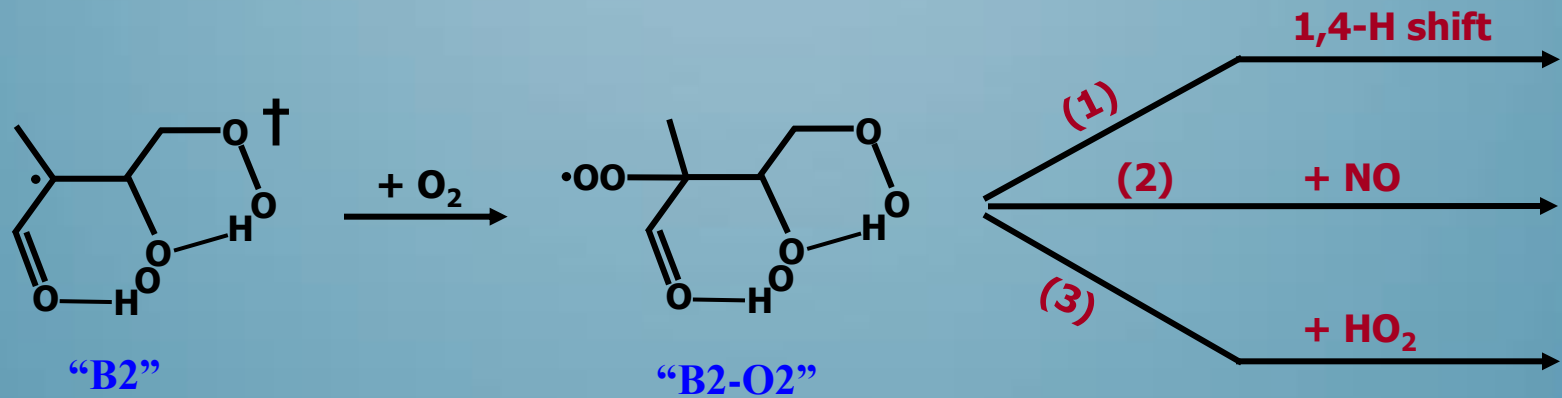
ACS meeting Philadelphia, Aug. 2012

PRODUCT CHANNELS (2)

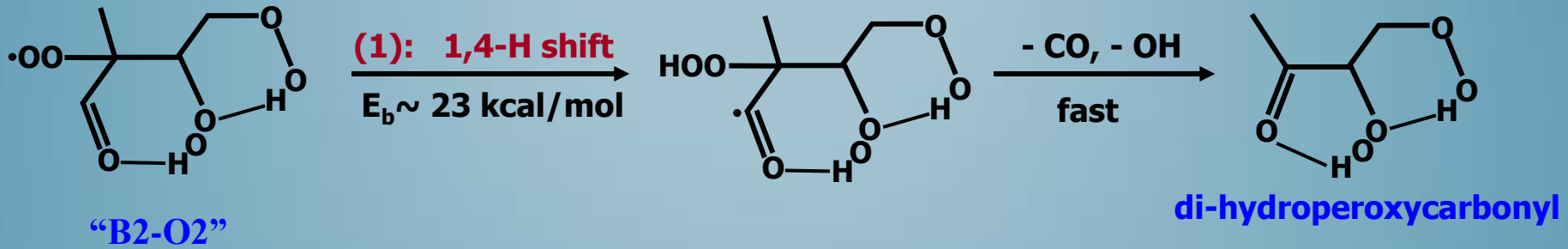
Fate of "B2⁺" radical:

a) Possibly chemically activated reactions (likely minor, still being explored)

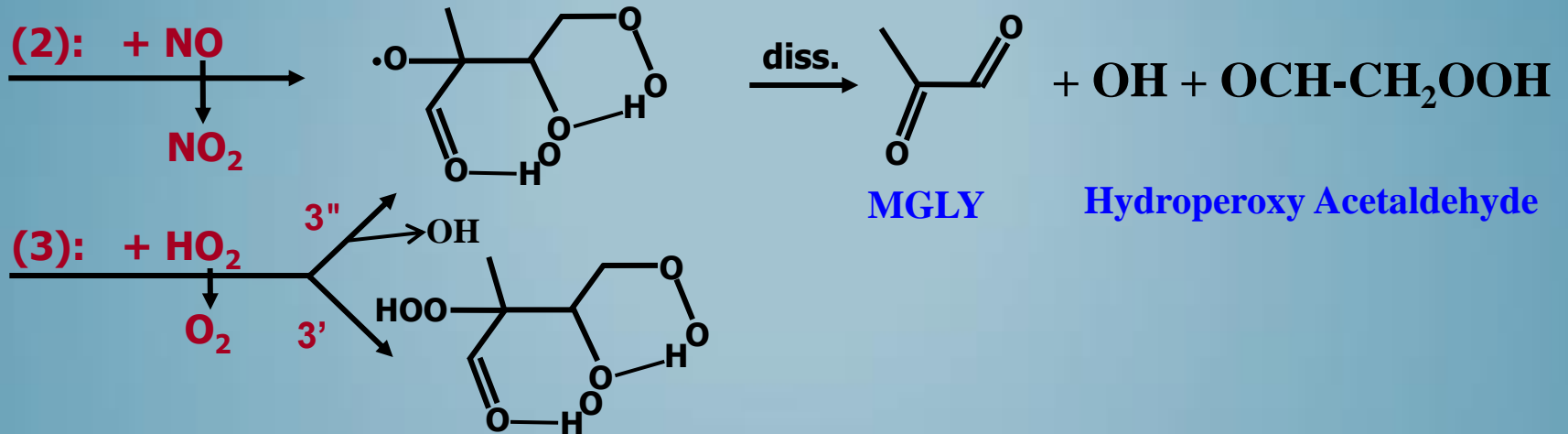
b) Collisionally stabilized B2: adds O₂



PRODUCT CHANNELS (3)



PRODUCT CHANNELS (4)

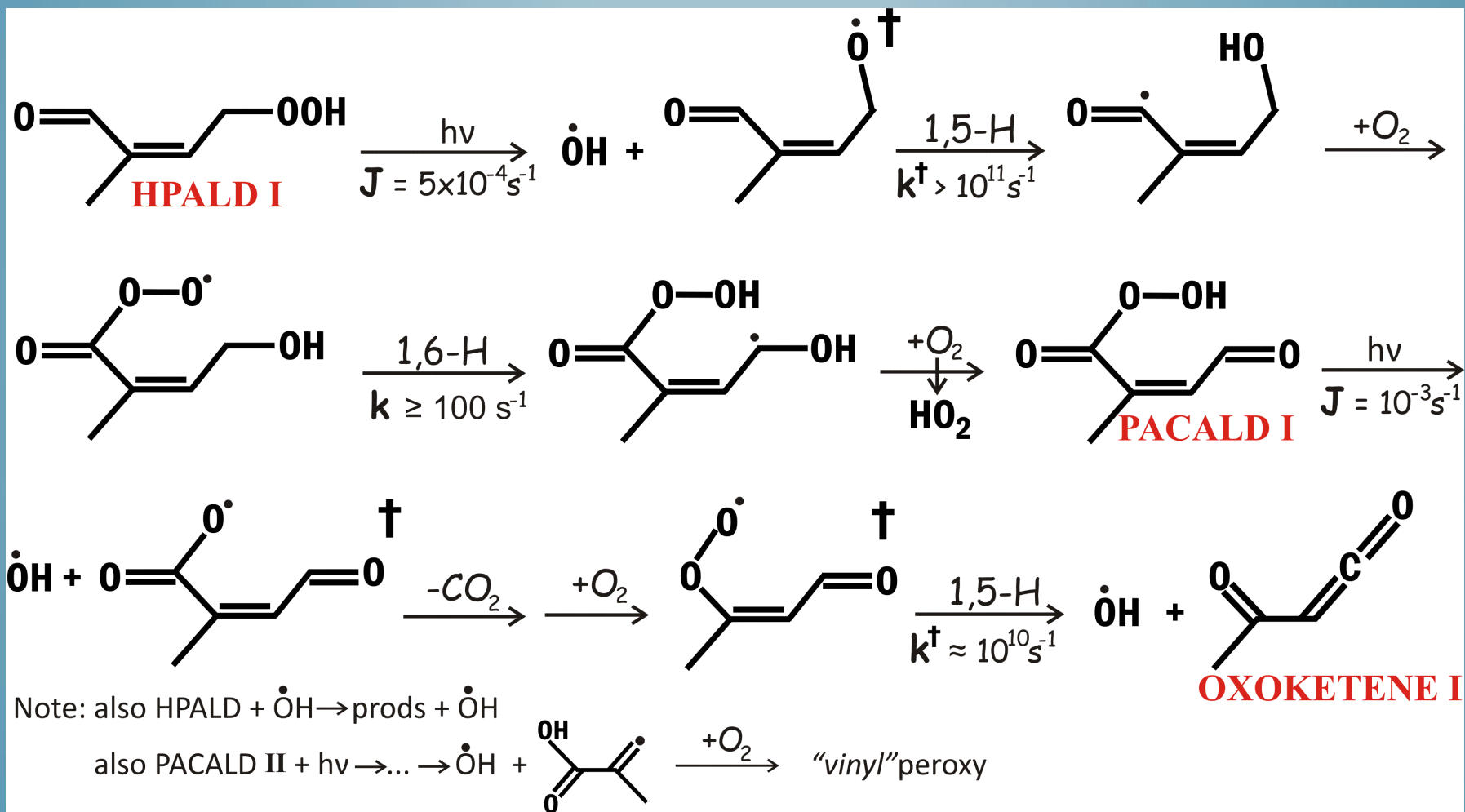


Hydroperoxy-acetaldehyde and counterpart from OH-adduct II: observed by Crouse et al. (Note in PCCP Sept. 2011) in yield of $\sim 25\%$ of HPALDs. Since routes (2) and (3'') from the 2nd peroxy should be minor in their conditions:

\Rightarrow channels through 2nd peroxy and B_2^\bullet / $\text{B}_2\text{OO}^\bullet$ at least as important as HPALD formation

Secondary chemistry of products from $\text{B}_2\text{OO}^\bullet$ reactions: complex sequences of competing photolysis and OH-reactions

OH REGENERATION BY SUBSEQUENT CHEMISTRY



Main fate of oxoketenes ?
OXOKETENE + HO₂

Very fast α -oxoketenes+HO₂ reactions

Recycling OH

- Through pre-reactive complex and submerged transition states



i.e. 10^4 to 10^5 x faster than e.g. $\text{CHOCHO} + \text{HO}_2$

- Including secondary chemistry: overall



⇒ ideal candidates for $\text{HO}_2 + \text{X} \rightarrow \text{OH} + \dots$ of Hofzumahaus and Whalley

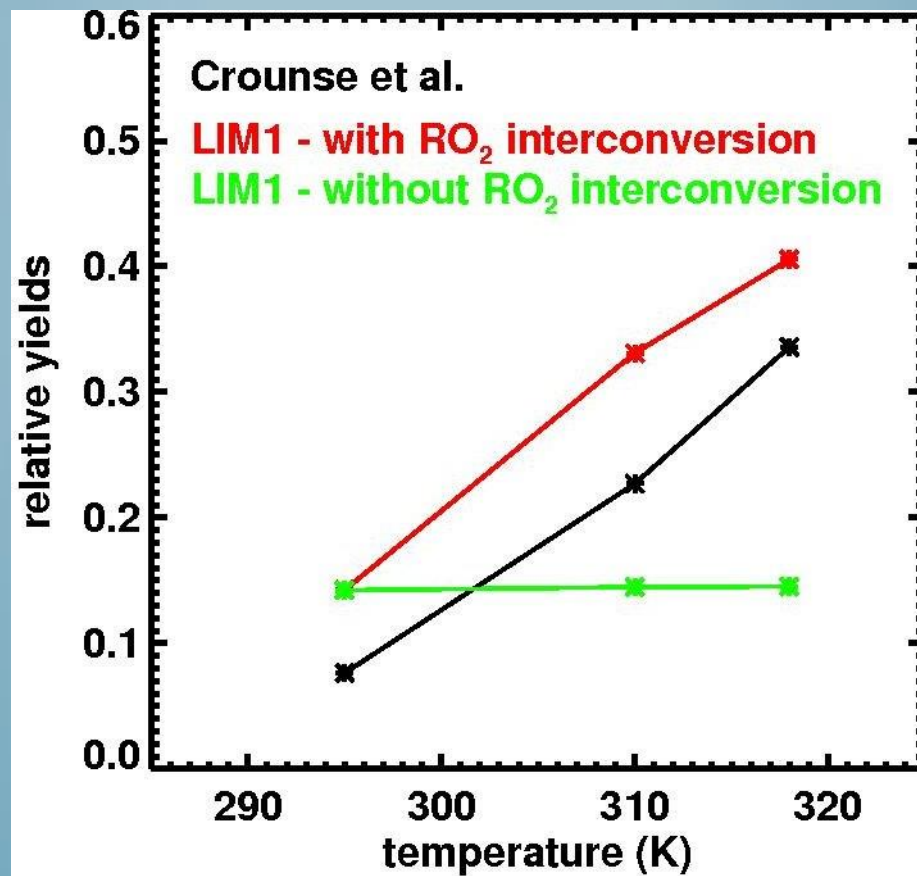
Comparison with Crouse et al. 2011

- LIM1 reproduces reasonably well the product yields observed by Crouse et al. 2011 at three different temperatures (factor of ~1.8 for HPALD). Note that
 - The reported HPALD measurement error is 50% (Crouse et al.)
 - The HPALD channel ratio is also uncertain

	Exp. # 1 T = 295 K		Exp. # 2 T = 310 K		Exp. # 3 T = 318 K	
	Obs.	LIM1	Obs.	LIM1	Obs.	LIM1
H ₂ O ₂	2.33	1.49	3.61	2.20	5.21	2.99
ISOPOOH	4.27	3.93	3.78	3.74	3.10	3.44
ISONO ₂	0.53	0.54	0.36	0.46	0.16	0.37
MVK+MACR	7.53	6.30	5.31	6.49	4.76	6.83
HPALD	1.02	1.79	2.78	4.65	4.06	7.26

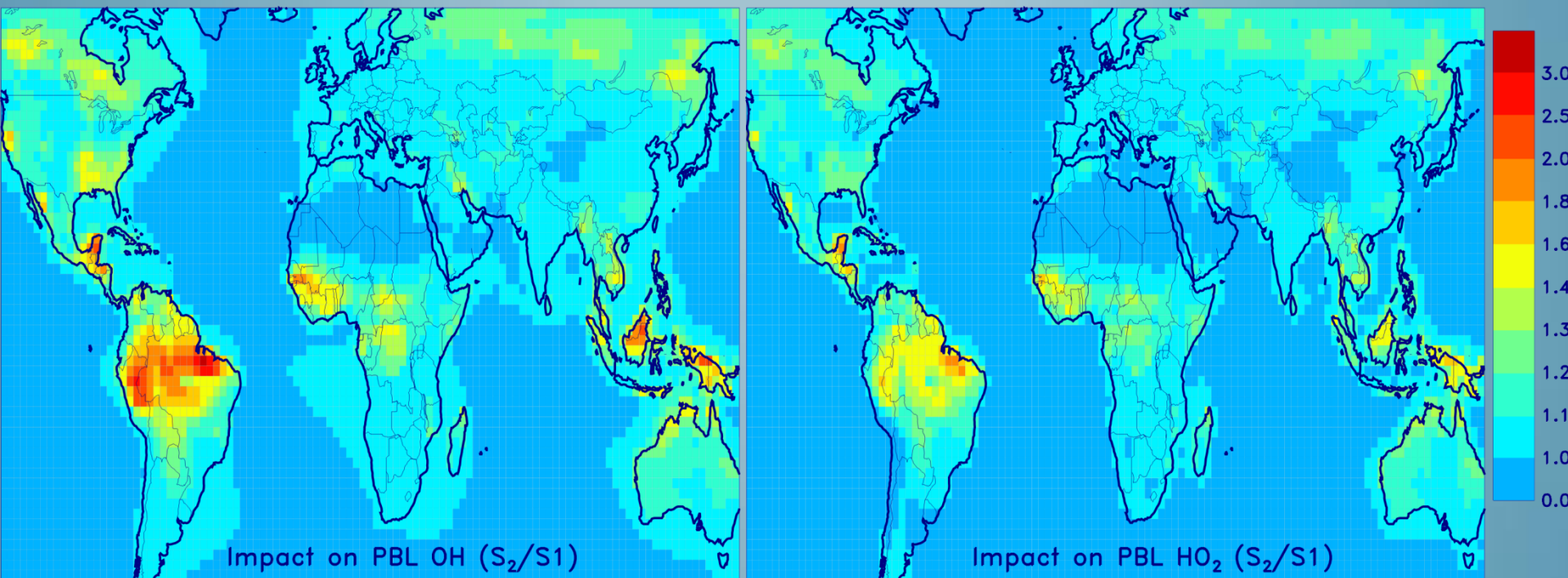
Product growth rates in pptv min⁻¹

Crouse et al. 2011 provide strong evidence for RO₂ interconversion



Without interconversion $\beta\text{-OH-RO}_2 \rightleftharpoons \text{Z-}\delta\text{-RO}_2$, the total product yield from 1,6-H shift would be limited to the $\sim 25\%$ Z- $\delta\text{-RO}_2$ initially formed

Impact of 1,6-H shift on HO_x in the IMAGESv2 CTM



Impact on PBL OH

Impact on PBL HO₂

- Globally averaged isomerisation yield = 28% in LIM1 (LIM0: 60%; Crouse *et al.* 2011: 10% HPALD yield)

Evaluation against field campaigns

S1: no isomerisation; S2: LIM1

GABRIEL, Oct. 2005
(Lelieveld et al., 2008)
PBL-averages, 9-17 LT

OP3-1, Borneo, Apr.
2008 (Whalley et al., 2011)
Averages, 9-17 LT

INTEX-A, Jul.-Aug.
2004 (Ren et al., 2008)
PBL-averages, 9-17 LT,
[ISOP]_{obs} > 300 pptv

	Obs.	S1	S2
NO (pptv)	20	22	20
OH (10 ⁶ cm ⁻³)	5.6	1.24	2.82
HO ₂ (10 ⁸ cm ⁻³)	-	3.1	7.1
HO ₂ * (10 ⁸ cm ⁻³)	10.5	5.84	10.6
ISOP (ppbv)	2.0	2.0	2.1
MVK+MACR (ppb)	~1	1.0	1.1
O ₃ (ppbv)	18.5	17.1	19.4

	Obs.	S1	S2
NO (pptv)	~40	59	40
NO ₂ (pptv)		152	136
OH (10 ⁶ cm ⁻³)	1.5	0.54	1.37
HO ₂ (10 ⁸ cm ⁻³)	1.7	1.96	3.8
ISOP (ppbv)	2.3	2.4	1.9

	Obs.	S1	S2
NO (pptv)	114	93	79
NO ₂ (pptv)	477	532	466
OH (10 ⁶ cm ⁻³)	6.5	3.8	5.0
HO ₂ (10 ⁸ cm ⁻³)	-	4.8	6.0
HO ₂ * (10 ⁸ cm ⁻³)	9.9	7.4	8.6
ISOP (ppbv)	0.94	1.27	0.93
(MACR+MVK)/ISOP (*)	2.2	2.1	2.0
O ₃ (ppbv)	53	63	62

(*) NEAQS, New England

$$[\text{HO}_2^*] = [\text{HO}_2] + \sum(\alpha[\text{RO}_2]) \quad (\text{Fuchs et al., 2012})$$

Fuchs, H. *et al.* Atmos. Meas. Tech. 5, 1611, 2012.

Lelieveld, J. *et al.* Nature

Ren, X. *et al.* J. Geophys. Res. 113, doi:10.1029/2007JD009166, 2008.

Whalley, L.K. *et al.*, Atmos. Chem. Phys. 11, 7223, 2011.

CONCLUSIONS

- Main features of LIM mechanism upgrade :
 - equilibrium ratio Z- δ -OH/ β -OH peroxy reduced by factor ~5;
 - isomerisation rate of Z- δ -OH-peroxy reduced by factor ~1.5
 - new routes besides HPALD formation
 - overall k(isom) compatible with observations Crouse et al. 2011
 - still, isomerisation yield = ca. 28% globally
 - secondary chemistry generates more OH, while keeping [HO₂] down
- α -Oxoketenes react very fast with HO₂ and convert it efficiently into OH → prime candidates for reactions X + HO₂ → OH invoked in recent studies
- Several secondary mechanisms and rates still remain uncertain, requiring refined theoretical quantification as already done for the primary steps