

## HO<sub>x</sub> Radical Regeneration in Isoprene Oxidation *via* Peroxy Radical Isomerisation.

### II: Experimental Evidence and Global Impact

#### - Electronic Supporting Information (ESI) -

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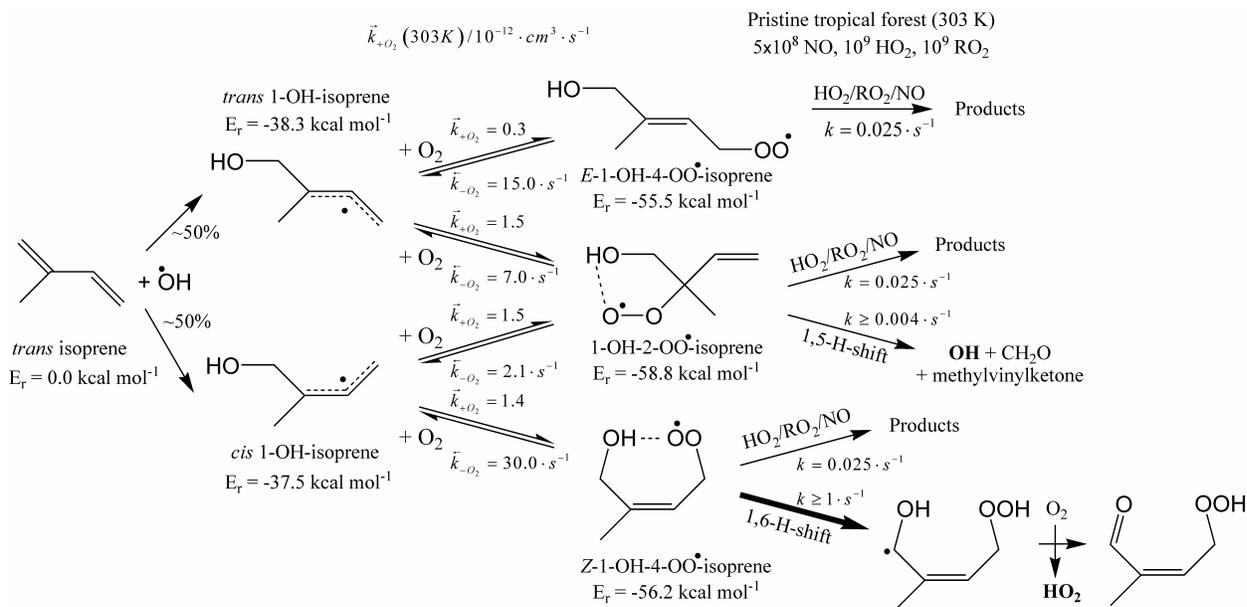
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#### Table of contents

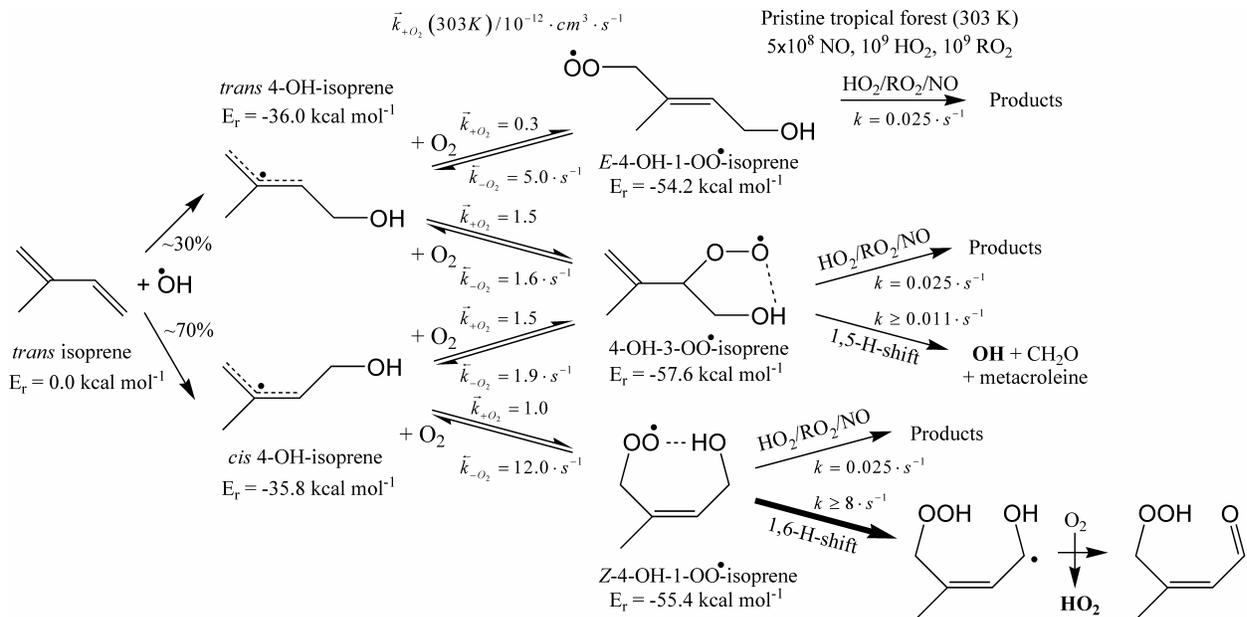
- p. 2: Revised isoprene oxidation mechanism for low to moderate NO<sub>x</sub> conditions as proposed earlier (Peeters et al., *PCCP*, 2009), with 303 K rate coefficients from first principles; Figs. S1 and S2
- p. 3: Temperature-dependent rate coefficient expressions for the unimolecular reactions of isoprene hydroxyperoxy radicals, T = 280 to 320 K, as used in this work; Table S1
- p. 4: Effects of allyl-stabilisation of products in peroxy radical H-shifts
- p. 5: Sensitivity analysis; Figs S3 - S6
- p. 8: Fate of substantial fraction of formed isoprene hydroxyperoxy radicals not accounted for in work of Paulot et al, *Science*, 2009; Table S2
- p. 10: Fast photolysis of hydroperoxy-methyl-butenals (HPALDs): mechanism and rate; Table S3 and Fig. S7
- p. 17: Reactions of HPALDs with OH: reaction channels, channel rate constants and OH-regeneration mechanisms
- p. 19: Fast PACALDs photolysis and (slow) PACALDs + OH reactions

Pages 2-3 and 8-20 constitute a first outline of the *Leuven Isoprene Mechanism (LIM)*

## Revised isoprene oxidation mechanism for low to moderate NO<sub>x</sub> conditions proposed earlier (reference 1) with 303 K rate coefficients from first principles



**Figure S1** : Reaction scheme for OH and HO<sub>2</sub> radical formation following 1-OH addition to isoprene (60%). Rate coefficients from first principles as originally reported (ref. 1), for T = 303 K. The NO, HO<sub>2</sub> and RO<sub>2</sub> levels are for the pristine forest BL conditions of the Gabriel campaign.<sup>2</sup>



**Figure S2** : Reaction scheme for OH and HO<sub>2</sub> radical formation following 4-OH addition to isoprene (30%). Rate coefficients from first principles as originally reported (ref. 1), for T = 303 K. The NO, HO<sub>2</sub> and RO<sub>2</sub> levels are for the pristine forest BL conditions of the Gabriel campaign (ref. 2).

reference 1 J. Peeters, T. L. Nguyen, and L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5935

reference 2 a) J. Lelieveld et al., *Nature*, 2008, **452**, 737; b) T. M. Butler, *Atmos. Chem. Phys.*, 2008, **8**, 4529

**Table S1. Temperature-dependent rate coefficient expressions,  $T = 280$  to  $320$  K, for the various unimolecular reactions of isoprene hydroxyperoxy radicals, as used in this work**

PN Relevant equilibrium constants as derived in reference 1 (and listed in ESI of ref 1)

$$K_{\text{eq}}(\text{cis-1-OH-isoprene} + \text{O}_2 \leftrightarrow \text{Z-1-OH-4-OO}^{\bullet}) = 1.79 \times 10^{-26} \exp(+8660/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{cis-1-OH-isoprene} + \text{O}_2 \leftrightarrow \text{1-OH-2-OO}^{\bullet}) = 3.57 \times 10^{-27} \exp(+9970/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{trans-1-OH-isoprene} + \text{O}_2 \leftrightarrow \text{1-OH-2-OO}^{\bullet}) = 4.00 \times 10^{-27} \exp(+9570/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{trans-1-OH-isoprene} + \text{O}_2 \leftrightarrow \text{E-1-OH-4-OO}^{\bullet}) = 9.80 \times 10^{-26} \exp(+7900/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{cis-4-OH-isoprene} + \text{O}_2 \leftrightarrow \text{Z-4-OH-1-OO}^{\bullet}) = 7.01 \times 10^{-27} \exp(+9110/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{cis-4-OH-isoprene} + \text{O}_2 \leftrightarrow \text{4-OH-3-OO}^{\bullet}) = 1.82 \times 10^{-27} \exp(+10216/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{trans-4-OH-isoprene} + \text{O}_2 \leftrightarrow \text{4-OH-3-OO}^{\bullet}) = 3.07 \times 10^{-27} \exp(+10116/T) \text{ cm}^3$$

$$K_{\text{eq}}(\text{trans-4-OH-isoprene} + \text{O}_2 \leftrightarrow \text{E-4-OH-1-OO}^{\bullet}) = 5.38 \times 10^{-26} \exp(+8405/T) \text{ cm}^3$$

1)  $T$ -dependent  $k(-\text{O}_2)$  expressions (280 - 320 K) for  $\text{O}_2$ -elimination from the given HO-isoprene-OO radicals. These  $k(-\text{O}_2)$  were derived from the theoretically derived equilibrium constants above (see also ESI ref 1) and the site-specific  $\text{O}_2$ -addition rate coefficients given in reference 1 and in Figs S1 & S2 above, assuming the latter independent of  $T$ .

$$k(-\text{O}_2)(\text{E-1-OH-4-OO} \Rightarrow \text{trans-1-OH} + \text{O}_2) = 3.1 \times 10^{12} \exp(-7900/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{1-OH-2-OO} \Rightarrow \text{trans-1-OH} + \text{O}_2) = 3.7 \times 10^{14} \exp(-9570/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{1-OH-2-OO} \Rightarrow \text{cis-1-OH} + \text{O}_2) = 4.2 \times 10^{14} \exp(-9970/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{Z-1-OH-4-OO} \Rightarrow \text{cis-1-OH} + \text{O}_2) = 7.8 \times 10^{13} \exp(-8660/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{E-4-OH-1-OO} \Rightarrow \text{trans-4-OH} + \text{O}_2) = 5.65 \times 10^{12} \exp(-8410/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{4-OH-3-OO} \Rightarrow \text{trans-4-OH} + \text{O}_2) = 5.0 \times 10^{14} \exp(-10120/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{4-OH-3-OO} \Rightarrow \text{cis-4-OH} + \text{O}_2) = 8.25 \times 10^{14} \exp(-10220/T) \text{ s}^{-1}$$

$$k(-\text{O}_2)(\text{Z-4-OH-1-OO} \Rightarrow \text{cis-4-OH} + \text{O}_2) = 1.4 \times 10^{14} \exp(-9110/T) \text{ s}^{-1}$$

2)  $T$ -dependent  $k(T)$  expressions for the Z- $\delta$ -OH-peroxy isomerisations by 1,6-H shifts

a) values derived from first principles (with WKB tunneling) as in reference 1:

$$k(\text{Z-1-OH-4-OO} \Rightarrow \dots \Rightarrow \text{HO}_2 + \text{hydroperoxy-aldehyde}) = 9.82 \times 10^8 \exp(-6303/T) \text{ s}^{-1}$$

$$k(\text{Z-4-OH-1-OO} \Rightarrow \dots \Rightarrow \text{HO}_2 + \text{hydroperoxy-aldehyde}) = 7.32 \times 10^8 \exp(-5556/T) \text{ s}^{-1}$$

b) the geometric average of the two expressions above as **adopted for both these 1,6-H shifts in this work** (see present paper)

$$k(1,6\text{-H})(T) = 8.48 \times 10^8 \exp(-5930/T) \text{ s}^{-1}, \text{ used for both Z-}\delta\text{-OH-peroxys}$$

3)  $T$ -dependent  $k(T)$  expressions for the  $\beta$ -OH-peroxy isomerisations by 1,5-H shifts,

a) the original expressions derived from first-principles (with WKB tunneling) as in reference 1:

$$k(\text{1-OH-2-OO} \Rightarrow \text{OH} + \text{H}_2\text{CO} + \text{MVK}) = 1.52 \times 10^{11} \exp(-9512/T) \text{ s}^{-1}$$

$$k(\text{4-OH-3-OO} \Rightarrow \text{OH} + \text{H}_2\text{CO} + \text{MACR}) = 6.08 \times 10^{10} \exp(-8893/T) \text{ s}^{-1}$$

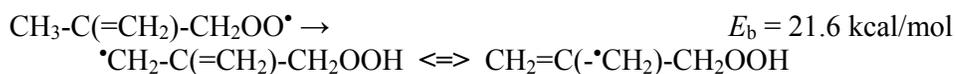
b) the geometric average of the above two  $k(T)$  **multiplied by 5 as adopted for both these 1,5-H shifts in this work** (see present paper):

$$k(1,5\text{-H})(T) = 4.81 \times 10^{11} \exp(-9203/T) \text{ s}^{-1}, \text{ used for both } \beta\text{-OH-peroxys}$$

reference 1 J. Peeters, T. L. Nguyen, and L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5935

### Effects of allyl-resonance stabilisation of products in peroxy radical H-shifts

Energy barriers  $E_b$  at the CBS-QB3 level have been computed for otherwise similar 1,5-H shifts in an alkyl- and an alkenylperoxy radical, showing the effect of the allyl-resonance product stabilisation in the latter, but also of the difference in geometries (T. L. Nguyen and J. Peeters, unpublished results, May 2008):

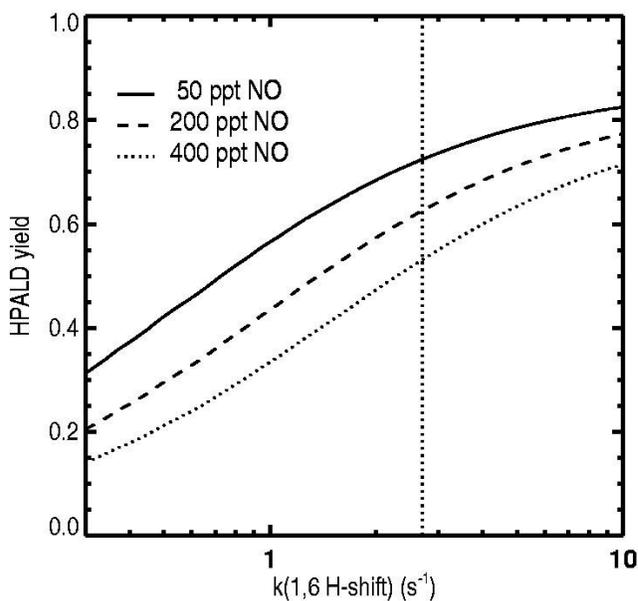


The allyl-resonance, which makes the reaction about 12 kcal/mol less endothermic, though somewhat off-set by the geometry change, lowers the CBS-QB3 barrier here by 1.9 kcal/mol, which on itself increases the 298 K rate coefficient by a factor  $\approx 25$ . The partition function ratios and hence the "conventional" pre-factors on the other hand should be rather similar.

Another difference however is the tunneling factor. As reported earlier (reference 1, p.2 and 3) The calculated tunneling factors for the allyl-resonance-assisted 1,6-H shifts in the Z-1-OH-4-OO and Z-4-OH-1-OO peroxy radicals from isoprene are high, about 25 - 30 (at 298 K) in the uni-dimensional WKB approximation based on CBS-QB3-computed IRCs. The high values are likely influenced considerably by the "late" allyl-resonance, which (i) lowers the energy of the product substantially (by 12 kcal/mol), hence increasing the range of energies through which tunneling can occur, but at the same time (ii) makes the barrier more narrow (at the products side), hence increasing the probability of tunneling for a given energy below the top.

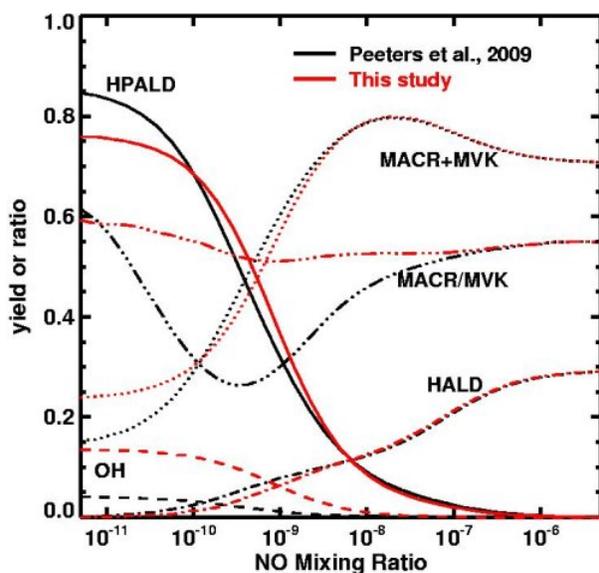
### Sensitivity analysis

Figure S3 shows the impact of changing the assumed rate coefficient of the 1,6 H-shifts of the  $\delta$ -isoprene-peroxys, at 303 K and at three NO levels (50, 200, 400 pptv). The rate adopted in this study (i.e. the geometrical average of the theoretical values for the two major  $\delta$ -isoprene-peroxys) at this temperature is indicated by the dotted vertical line. The figure illustrates the strongly non-linear dependence of the yields on the rates for the 1,6 H-shifts. As an example, at 50 ppt NO a 33-fold variation of the  $k(1,6\text{-H})$  from 0.3 to  $10\text{ s}^{-1}$  varies the HPALDs yield by a factor of only 2.6



**Figure S3:** Calculated yield of HPALDs in the oxidation of isoprene by OH, at 303 K and at three NO levels, depending on the assumed rate for the 1,6 H-shift.

The following figures compares the product yields obtained using the rate coefficients of this work (see Table S1; red curves) with those obtained when using the first-principles rate constants proposed in Peeters et al. (2009) (see Figs. S1 and S2; black curves), at a temperature of 303 K. The MACR/MVK yield ratio shows very little NO-dependence in the updated scheme. Its values (0.52-0.6) are very close to the traditional value (about 0.55) derived from laboratory measurements conducted at high  $\text{NO}^{10}$ , but they are slightly lower than the ratio of  $\sim 0.66$  derived in a laboratory study conducted at 200-600 pptv  $\text{NO}^2$ .

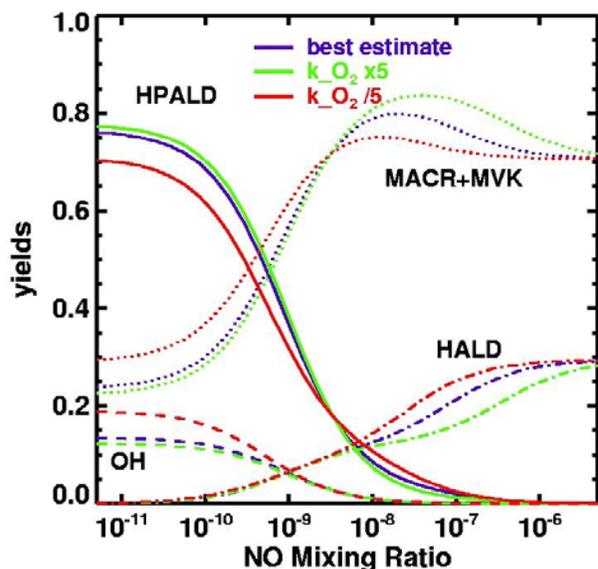


**Figure S4:** Primary yields of HPALD, OH, MACR+MVK and HALD, and ratio of MACR to MVK, at 303 K, using (i) the kinetic rates proposed in Peeters et al. (2009) (in black), (ii) the updated rates from this study (red).

**reference 1:** IUPAC subcommittee for Gas Kinetic Data Evaluation, <http://www.iupac-kinetic.ch.cam.ac.uk/> ; and references therein

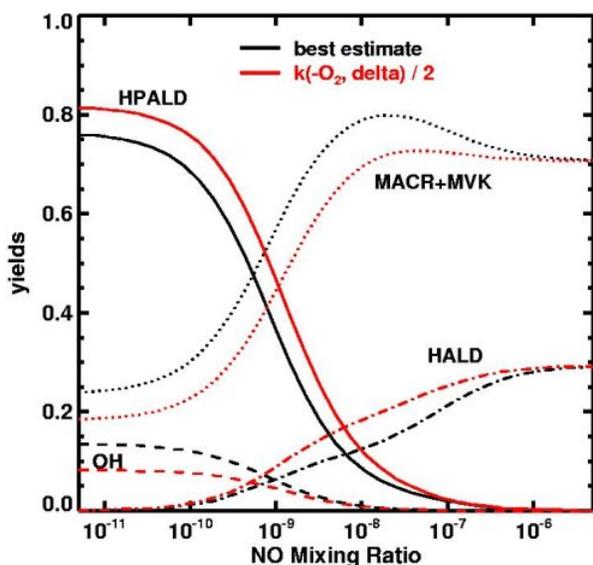
**reference 2:** M. Karl et al., H.-P. Dorn, F. Holland, R. Koppmann, D. Poppe, L. Rubb, A. Schaub, and A. Wahner, *J. Atmos. Chem.*, 2006, **55**, 167.

Figure S5 shows the impact of a 5-fold increase or decrease of all rates of  $O_2$  addition and elimination on the yields of the major products in the reaction of isoprene with OH. The impact of the 5-fold increase is found to be very small in the atmospherically relevant NO range ( $<1$  ppb). The 5-fold decrease of the rates is seen to decrease the HPALD+ $HO_2$  yield by up to  $\approx 5\%$ , and to increase the OH+MVK/MACR yield by approximately the same amount.



**Figure S5:** Primary yields of HPALD, OH, MACR+MVK and HALD, at 303 K, using (i) the best estimates for the  $O_2$  elimination and addition rates (in blue), (ii) these rates multiplied by 5 (green), or (iii) divided by 5 (red).

Figure S6 shows the impact of increasing the assumed stability of the  $\delta$ -isoprene-peroxys on these yields. The enhanced stability increases the HPALD yield by about 5% in the atmospherically relevant NO range, at the expense of MACR, MVK and OH. The HALD yield shows little sensitivity in the same NO range.



**Figure S6:** As previous figure, at 303 K, using either best estimate (in black) or halved  $O_2$  elimination rates for the  $\delta$ -isoprene-peroxys (in red).

### **Fate of substantial fraction of formed isoprene hydroxyperoxy radicals not accounted for in work of Paulot et al.<sup>1</sup> (*Science*, 2009): details of our analysis.**

Our analysis of the Paulot et al. data in their Fig. 1 show that the authors' interpretation leaves the fate of *ca* 25% of the formed ISOP-OH-OO peroxy radicals unexplained, this for larger reaction times *t* when over 50 ppbv isoprene is removed and the initial  $\approx 1$  ppbv NO<sub>x</sub> should be sequestered as nitrates. (Note that with  $J(\text{nitrates})$  of  $3 \times 10^{-6} \text{ s}^{-1}$ , the nitrate photolysis rate is three orders of magnitude below the isoprene removal rate of  $7 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1}$  at *t* = 4 hr).

Our analysis is based on the data of Paulot et al.<sup>1</sup> shown in Fig. 1 or given in either their paper or their Supporting online Material (SOM<sup>1</sup>). The various concentrations and rates of interest are listed in **Table S2**, below.

We took the ISOP-OH-OO **peroxy formation rate** equal to  $-0.96 \times d[\text{Isopr}]/dt$ , derived from the [isoprene] vs *t* profile in Fig. 1 of Paulot et al.<sup>1</sup>, the factor 0.96 allowing for  $\approx 4\%$  OH addition to a central carbon resulting directly in 4-penten-2-one.<sup>2</sup> The [OH] concentration was found from:

$$-d[\text{ISOP}]/dt = k_{\text{pr}} \times [\text{ISOP}] \times [\text{OH}] \quad \text{with } k_{\text{ISOP}+\text{OH}} = 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

The rate of ISOP-OH-OOH **hydroperoxide formation** by the ISOP-OH-OO + HO<sub>2</sub> reaction was obtained from the [ISOP-OH-OOH] vs *t* profile as:

$$d[\text{ISOP-OH-OOH}]/dt + 7.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \times [\text{OH}][\text{ISOP-OH-OOH}],$$

i.e. with  $k_{\text{ISOP-OH-OOH}+\text{OH}}$  slightly reduced compared to the experimental<sup>1</sup>  $k = 7.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , to account for  $\approx 7\%$  ISOP-OH-OO regeneration in this reaction (see their SOM<sup>1</sup>).

All other ISOP-OH-OO sinks considered by Paulot et al.<sup>1</sup> result in either:

- MVK or MACR, with reported summed yield of 12%,
- C<sub>5</sub>-diols, with measured reported yield of 2%,
- or C<sub>5</sub>-hydroxycarbonyls (HALD or isomer), with yield implied to be minor compared to that of MVK & MACR (SOM<sup>1</sup>) and assumed here as 3%;

with a combined yield of  $\approx 17\%$ . Their contribution to the ISOP-OH-OO removal rate is therefore taken as  $0.17 \times -d[\text{Isopr}]/dt$  (not listed in **Table S2**).

The fraction of ISOP-OH-OO peroxys formed not accounted for (**missing rate peroxys** in the table) is then obtained as:

$$\text{rate peroxy formation} - \text{rate hydroperoxide formation} - (0.17 \times -d[\text{Isopr}]/dt) \\ \text{i.e.: } -0.79 \times d[\text{Isopr}]/dt - \text{rate hydroperoxide formation}$$

and division by the ISOP-OH-OO **peroxy formation rate** yields the fraction of formed ISOP-OH-OO not accounted for, or the **fraction missing peroxys** (see **Table S2**).

In this way we find that consistently  $25 \pm 1\%$  of the formed peroxy radicals are not accounted for at times *t* = 3, 4 and 5 hr. We ascribe this to HPALD formation.

**Table S2 Calculation of fraction of formed ISOP-OH-OO radicals not accounted for**

<b><i>t</i> (hr)</b>	<b>[Isoprene] (10<sup>12</sup> cm<sup>-3</sup>)</b>	<b>-d[Isopr]/dt (10<sup>7</sup> cm<sup>-3</sup>s<sup>-1</sup>)</b>	<b>[OH] (10<sup>6</sup> cm<sup>-3</sup>)</b>	<b>rate peroxy formation (10<sup>7</sup> cm<sup>-3</sup>s<sup>-1</sup>)</b>	<b>rate hydro- peroxide formation (10<sup>7</sup> cm<sup>-3</sup>s<sup>-1</sup>)</b>	<b>missing rate peroxys (10<sup>7</sup> cm<sup>-3</sup>s<sup>-1</sup>)</b>	<b>fraction missing peroxys (%)</b>
<b>0.5</b>	2.04	14.9	0.73	<b>14.3</b>	<b>7.0</b>	<b>4.77</b>	<b>33%*</b>
<b>3.0</b>	1.02	8.4	0.82	<b>8.1</b>	<b>4.7</b>	<b>1.94</b>	<b>24%</b>
<b>4.0</b>	0.74	6.8	0.92	<b>6.5</b>	<b>3.75</b>	<b>1.62</b>	<b>25%</b>
<b>5.0</b>	0.52	5.8	1.10	<b>5.6</b>	<b>3.15</b>	<b>1.43</b>	<b>26%</b>

\*missing fraction larger at 0.5 hr because of reactions of peroxys with remaining NO at short times<sup>1</sup>

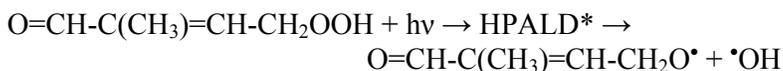
**reference 1:** F. Paulot, J. D. Crouse, H. G. Kjaergaard, A. Kurten, J. M. St. Clair, J. H. Seinfeld, and P. O. Wennberg, *Science*, 2009, **325**, 730

**reference 2:** E. E. Greenwald, *et al.*, *J. Phys. Chem.*, 2010, **114**, 904

## Fast photolysis of hydroperoxy-methyl-butenals (HPALDs): proposed mechanism and estimated rate.

### Mechanism

We propose that the hydroperoxy-methyl-butenals (HPALDs) resulting from the Z- $\delta$ -OH-peroxy 1,6-H shifts, undergo fast O--OH dissociation directly in the excited singlet state reached upon excitation of the  $S_0$  ground state ( $\approx 290 - \approx 360$  nm).



The excited singlet state results from  $n_1 \rightarrow \pi^*$  excitation of the conjugated  $\alpha,\beta$ -enone  $\text{O}=\text{C}-\text{C}=\text{C}-$  chromophore,  $S_0 + h\nu \rightarrow S_1$ , with  $S_1$  known to be 74 kcal/mol higher in energy than the  $S_0$  ground state (adiabatic energy difference), as experimentally determined for acrolein,<sup>1</sup> the smallest  $\alpha,\beta$ -enone homologue. Both MACR and MVK feature this same  $\text{O}=\text{C}-\text{C}=\text{C}-$  chromophore, and hence their known absorption cross sections can be adopted here. The  $n_1 \rightarrow \pi^*$  excitation leaves an unpaired non-bonding  $n_1$  electron on the carbonyl O while promoting its original partner to the anti-bonding  $\pi^*$  orbital, which extends over the  $\text{O}=\text{C}-\text{C}=\text{C}-$  conjugated system. Along the O--OH dissociation coordinate of interest here, the  $S_1$  surface is expected to connect to an excited alkoxy radical  $\text{RO}^*$  and ground state  $\text{OH}(^2\Pi)$  (see the schematic representation in Fig. S7).

However, for the HPALDs there is another singlet surface,  $S_2$ , which is reached by promotion of a lone pair  $n_2$ -electron of the O--OH group to the  $\sigma^*$  antibonding orbital of O--O. This  $S_2$  surface is therefore repulsive along the O--OH coordinate. *Vertical* excitation of the ground state of an RO--OH hydroperoxide to the repulsive  $S_2$  state has recently been computed at high *ab initio* levels of theory to require about 135 kcal/mol,<sup>2</sup> corresponding to  $\approx 210$  nm photons. This repulsive surface connects to the ground state alkoxy + OH radical fragments, and for a monofunctional ROOH hydroperoxide, direct  $n_2 \rightarrow \sigma^*$  photo-excitation is responsible for straight hydroperoxide photodissociation. However, as shown schematically in Fig. S7, for the HPALDS with their two chromophores, the  $(n_2, \sigma^*)$ -excited  $S_2$  surface, rapidly coming down along the O--O coordinate towards the asymptote of the ground state  $\text{RO}^\bullet + \text{OH}$  products, should cross the  $(n_1, \pi^*)$ -excited  $S_1$  surface that leads up to  $\text{RO}^* + \text{OH}$ . Lifting the HPALD  $C_s$  symmetry restriction will result in configuration interaction and hence an "avoided crossing" of  $S_1$  and  $S_2$ , so giving rise to two "new" singlet  $S_1/S_2$  states, with the maximum of the "new" lower curve becoming effectively a transition state for direct RO--OH dissociation into the ground state products on this lowest excited singlet surface.

First, the crossing point for the two original  $S_1$  and  $S_2$  states under  $C_s$  symmetry and its energy relative to the  $S_1$  zero-point level will be evaluated. For this, one needs to know (i) the excitation energy of the  $\text{O}=\text{C}-\text{C}=\text{C}-$  chromophore, i.e. the energy of the  $S_1$  minimum with respect to that of  $S_0$ , and (ii) the evolution of the potential energy of this molecule in its  $(n_1, \pi^*)$ -excited state as a function of the O-OH distance; the shape of this evolution as function of  $r(\text{O}-\text{OH})$  should be quasi identical to that for the ground state of a  $-\text{CH}_2\text{O}-\text{OH}$  hydroperoxide, as the (excited)  $\alpha,\beta$ -enone moiety is not affected by the  $r(\text{O}-\text{OH})$  bond lengthening (the O-OH being separated from the enone moiety by the  $\text{CH}_2$  group). Also needed is (iii) the energy of the lowest repulsive excited state ( $S_2$ ) of the  $-\text{CH}_2\text{O}-\text{OH}$  moiety

<sup>1</sup> A.D. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498.

<sup>2</sup> J. D. Watts and J. S. Francisco, *J. Chem. Phys.*, 2006, **125**, 104301.

likewise as a function of the O–OH distance. These data are available: the adiabatic excitation energy (i) was experimentally determined for the simplest  $\alpha,\beta$ -enone, acrolein, at 74 kcal/mol by Walsh,<sup>1</sup> while (ii) and (iii) can both be taken from the recent high-level computations by Watts and Francisco<sup>2</sup> for CH<sub>3</sub>O–OH, in combination with the vibration zero point energy (VZPE) data from Sun et al. for this same molecule and for its dissociation products.<sup>3</sup> Note that RO–OH hydroperoxide dissociation energies for allylic R—such as for the HPALDs—have been shown quasi identical to these for (any) alkyl R,<sup>4</sup> while the most recent experimental determination of  $D_e(\text{CH}_3\text{O-OH})$ , supported by high-level ab initio computations, gave a value of  $42.6 \pm 0.6$  kcal/mol.<sup>5</sup> All data required for the evaluation are thus available, either from experiment, or from recent high-level *ab initio* computations.

The potential energy data of Watts and Francisco<sup>2</sup> for CH<sub>3</sub>CO–OH were computed over the  $r(\text{O-OH})$  range 1.4 to 2.0 Å using the QCISD(T)/aug-cc-pVTZ level of theory for the ground state, and the EOM-CCSD level for the vertical excitation energies to the repulsive  $2^1\text{A}$  singlet state that we denote here as  $S_1$ . Note that the authors acknowledge that the EOM-CCSD vertical excitation energies are systematically somewhat too high compared with full configuration interaction computations; e.g. for the H<sub>2</sub>O<sub>2</sub> case, they found that the EOM-CCSD excitation energies are  $\approx 3.5$  kcal/mol too high compared to the much more reliable MSCASPT2 level (that was computationally too expensive to be applied to CH<sub>3</sub>OOH). The potential energy results of Watts and Francisco<sup>2</sup>,  $V_{\text{gst}}(r_{\text{O-O}})$  for the CH<sub>3</sub>OOH ground state, and the potential energies  $V_{\text{rep}}(r_{\text{O-O}})$  for the repulsive excited singlet state, corresponding here to  $S_2$ , are listed in Table S3, both relative to the  $V_{\text{gst}}(r_e)$  minimum. However, the vibration zero-point energies (VZPE), not computed by Watts and Francisco, have to be taken into account, or rather their changes with  $r(\text{O-O})$ , as well as the VZPE differences between the states involved. From the data of Sun et al.<sup>3</sup> and using  $\text{VZPE}(\text{OH}) = 5.34$  kcal/mol, the change in VZPE from the CH<sub>3</sub>O–OH equilibrium  $r_e(\text{O-O}) = 1.46$  Å to  $r(\text{O-O}) = \infty$ , i. e. for dissociation into CH<sub>3</sub>O• + •OH, is found to be  $-5.9$  kcal/mol. For intermediate  $r_{\text{O-O}}$ , the VZPE change can be taken isometric with the pure potential energy change. With the VZPE-corrected energies  $E_{\text{gst}}(r_{\text{O-O}})$  now relative to the zero-point vibration level of the ground state, one then has for the  $S_0$  ground state:  $E_{\text{gst}}(r_{\text{O-O}}) = V_{\text{gst}}(r_{\text{O-O}}) - 5.9 \times V_{\text{gst}}(r)/V_{\text{gst}}(\infty)$  (in kcal/mol), where  $V_{\text{gst}}(\infty) = 42.6 + 5.9$  using the recent experimental  $D_e$  of 42.6 kcal/mol for CH<sub>3</sub>O–OH from Matthews et al.<sup>5</sup> For the repulsive state, the ZPVE vibration energy can be taken as that of the ground state less the  $\approx 1$  kcal/mol for the O–O stretch contribution at equilibrium  $r_e(\text{O-O})$ . The VZPE-corrected energy for the repulsive  $S_2$  state, also relative to the VZP-level of the ground state, is then found as  $E_{\text{rep}}(r_{\text{O-O}}) = V_{\text{rep}}(r_{\text{O-O}}) - 1 - 4.9 \times V_{\text{gst}}(r)/V_{\text{gst}}(\infty)$ , i. e. with the VZPE change again isometric with the potential energy change of the ground state.

The energy of the  $\alpha,\beta$ -enone ( $n_1,\pi^*$ )-excited state,  $E(S_1)(r_{\text{O-O}})$ , is simply equal to  $E_{\text{gst}}(r_{\text{O-O}})$  increased by a constant 74 kcal/mol, the experimental adiabatic excitation energy of the  $\alpha,\beta$ -enone chromophore<sup>1</sup>. From these energy data for the  $S_1$  and  $S_2$  states in Table S3, the crossing of these states under  $C_s$  symmetry is found to occur at  $r_{\text{O-O}} = 1.71$  Å and 84.5 kcal/mol above the  $S_0$  VZP-level, i.e. 10.5 kcal/mol above the  $S_1$  VZP-level. Note that both these values are likely overestimates by at least 1 kcal/mol, since the EOM-CCSD-based  $S_2$  energies near the  $S_0$  equilibrium geometry are expected to be too high by about 3.5 kcal/mol<sup>1</sup> (see above). On the other hand, the  $S_1$  energies as derived here are adiabatic, i.e. for the minimum of the  $\alpha,\beta$ -enone ( $n_1,\pi^*$ )-excited state; vertical excitation from the  $S_0$  ground state ZPV-level to  $S_1$

<sup>3</sup> H. Sun, C.-J. Chen and J. W. Bozzelli, *J. Phys. Chem. A*, 2000, **104**, 8270.

<sup>4</sup> Sebbar, N.; Bockhorn, H.; Bozzelli, J. W. *Phys. Chem. Chem. Phys.*, 2002, **4**, 3691.

<sup>5</sup> J. Matthews, A. Sinha and J. S. Francisco, *J. Chem. Phys.*, 2005, **122**, 221101.

requires about 85 kcal/mol,<sup>1</sup> sizably more than the adiabatic 74 kcal/mol adiabatic<sup>1</sup> value. Therefore, instead of a crossing "point", one has an intersection of an up-sloping, fairly narrow S<sub>2</sub> valley with a broader S<sub>1</sub> well, but somewhat off the S<sub>1</sub> minimum ("narrow" or "broad" referring to the energy along the carbonyl C=O or C<sup>•</sup>-O<sup>•</sup> coordinate, respectively), giving rise to a crossing "seam". The lowest energy of the seam is estimated around 12 kcal/mol above the VZP-level of the S<sub>1</sub> well.

**Table S3. Potential energies, in kcal/mol, of CH<sub>3</sub>OOH ground state and repulsive singlet excited 2<sup>1</sup>A state;<sup>2</sup> and ZPVE-corrected Energies for the S<sub>0</sub>, S<sub>1</sub> and S<sub>2</sub> states relative to ZPVE-level of the ground state; as function of *r*(O-O)**

<i>r</i> (O-O)/Å	<i>V</i> <sub>gst</sub> ( <i>r</i> ) <sup>a</sup>	<i>V</i> <sub>rep</sub> ( <i>r</i> ) <sup>b</sup>	<i>E</i> (S <sub>0</sub> )( <i>r</i> ) <sup>c</sup>	<i>E</i> (S <sub>1</sub> )( <i>r</i> ) <sup>d</sup>	<i>E</i> (S <sub>2</sub> )( <i>r</i> ) <sup>e</sup>
1.46	0	135	0	74	134
1.5	1.0	124.4	0.9	74.9	123.3
1.6	5.0	101.6	4.4	78.4	100.1
1.7	11.4	87.6	10.1	84.1	85.4
1.8	18.6	78.8	16.3	90.3	75.9
1.9	25.8	73.6	22.7	96.7	70.0
2.0	33.6	71.2	29.5	103.5	66.8
∞	48.5 <sup>f</sup>	48.5 <sup>g</sup>	42.6 <sup>h</sup>	116.6	42.6 <sup>h</sup>

<sup>a</sup> from ref 2, relative to ground state minimum potential energy

<sup>b</sup> from ref 2, relative to ground state minimum potential energy

<sup>c</sup> *E*(S<sub>0</sub>)(*r*) relative to VZP-level of ground state; derived from *V*<sub>gst</sub>(*r*) by correcting for VZPE change

<sup>d</sup> *E*(S<sub>1</sub>)(*r*) = *E*(S<sub>0</sub>)(*r*) + 74 kcal/mol, the latter the experimental adiabatic excitation energy of the α,β-enone chromophore<sup>1</sup> (see text)

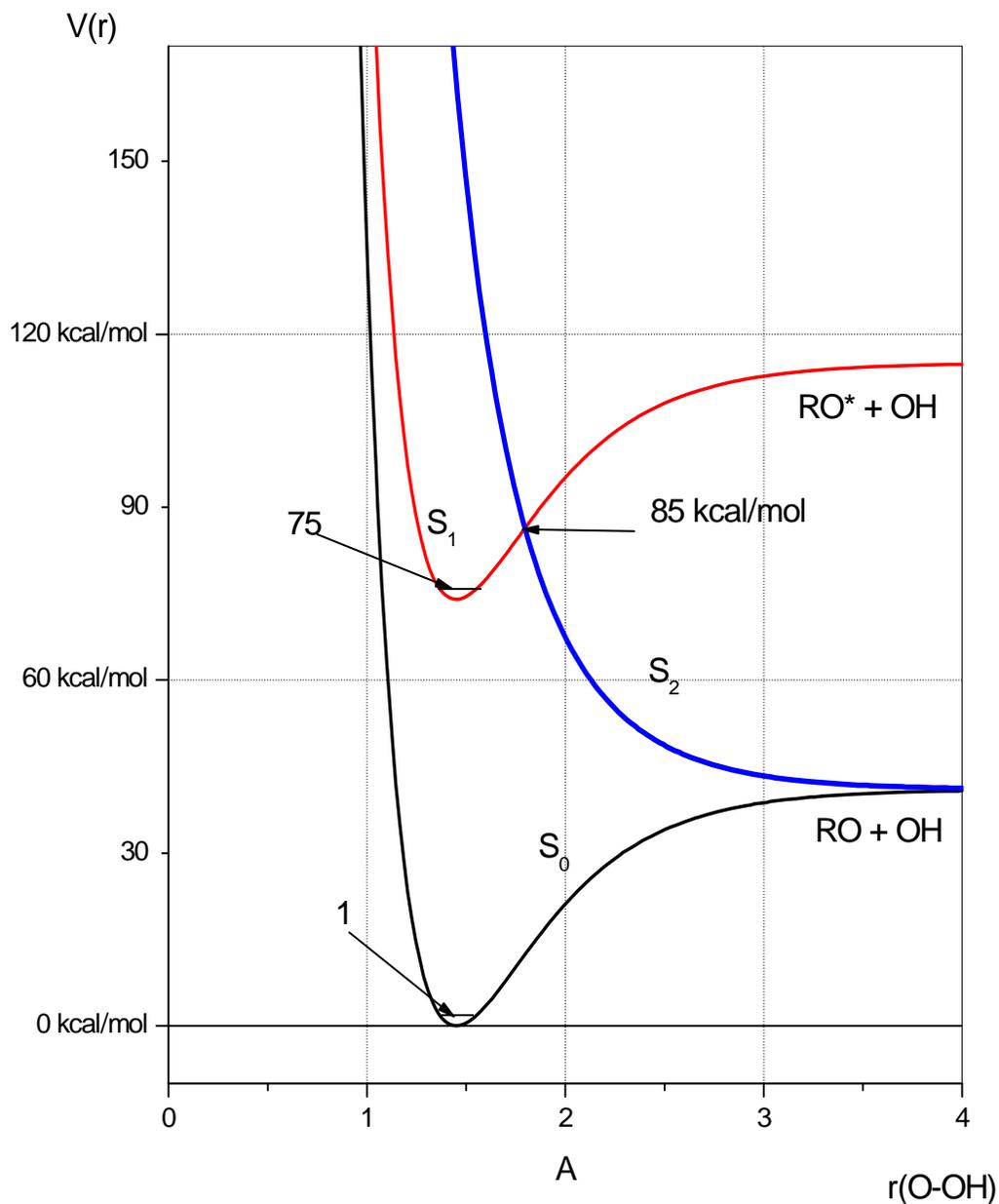
<sup>e</sup> *E*(S<sub>2</sub>)(*r*) relative to ZPVE-level of ground state; derived from *V*<sub>rep</sub>(*r*) by correcting for VZPE change

<sup>f</sup> equal to the experimental *D*<sub>e</sub> of 42.6 kcal/mol<sup>2</sup> plus the increase in ZPVE of 5.9 kcal/mol from *r*<sub>O-O</sub> = *r*<sub>e</sub> to ∞

<sup>g</sup> same RO + OH dissociation limit as ground state ; <sup>h</sup> experimental *D*<sub>e</sub> value<sup>5</sup>; same *E*<sub>∞</sub> limits for S<sub>0</sub> and S<sub>1</sub>.

Yet, when lifting the C<sub>s</sub> symmetry restriction implicit in all the above, for instance by allowing the carbonyl-O to move out of the HPALD symmetry plane, left or right, the S<sub>1</sub> and S<sub>2</sub> states become of the same species, such that their configuration interaction results in an avoided crossing. In other words, relaxation of the symmetry gives rise to a "conical intersection" instead of a single crossing point. Symmetry-relaxation can lower a reaction barrier drastically, as exemplified by the decomposition of H<sub>2</sub>CO into H<sub>2</sub> + CO with a much lower barrier under C<sub>s</sub> than C<sub>2v</sub> symmetry. For the case at hand, instead of two crossing curves, symmetry breaking gives two "new" excited S<sub>1</sub>/S<sub>2</sub> surfaces, with the maximum on the lower excited surface then constituting a transition state to direct HPALD\* dissociation into ground state RO<sup>•</sup> + <sup>•</sup>OH. For usual configuration interaction energies, the energy of this transition state is then expected to be somewhat less than 84 kcal/mol above the S<sub>0</sub> VZP-level, implying a barrier to dissociation of the (n<sub>1</sub>,π\*)-excited HPALD\* somewhat below 10 kcal/mol.

Note that this barrier is likely significantly lower, since without symmetry constraints the original S<sub>1</sub> curve for larger *r*<sub>O-O</sub> can lie lower than detailed above due to the strong stabilizing interaction between the leaving <sup>•</sup>OH and the excited-carbonyl C<sup>•</sup> site, amounting to a "missed" 1,5-OH shift in the singlet HPALD—a missed shift indeed, due to the avoided crossing with the repulsive S<sub>1</sub> state. On this basis, the energy barrier *E*<sub>b</sub> for O–OH homolysis on the symmetry-free excited singlet surface can be safely estimated at less than 10 kcal/mol, and likely around 8 kcal/mol.



**Figure S7.** Schematic representation of the Potential Energy Surfaces for the ground state ( $S_0$ ) and the two lowest excited singlet states  $S_1$  and  $S_2$  of  $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{OOH}$  (HPALD), for point group  $C_s$ .  $S_1$  is the ( $n_1, \pi^*$ ) excited state ( $\text{O}=\text{C}-\text{C}=\text{C}$  chromophore) whereas  $S_2$  is the repulsive ( $n_2, \sigma^*$ ) excited state ( $\text{O}-\text{OH}$  chromophore). RO is the ground state  $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{O}^\bullet$  radical, and  $\text{RO}^*$  its doublet excited state. Only the vibration zero point energy for the O-O stretch (circa 1 kcal/mol) is schematized here. Photodissociation to ground state  $\text{RO} + \text{OH}$  takes place by 290 - 360 nm  $S_0 \rightarrow S_1$  excitation and crossing from  $S_1$  to  $S_2$ . Under  $C_1$  point group, i.e. relaxing the planar symmetry, configuration interaction of the two states of the same species results in an avoided crossing and the effective barrier for dissociation on the excited singlet surface is lowered by configuration interaction ("conical intersection").

### Rate and approximate $J$ value

The nascent  $S_1^\dagger$  state as formed over most of the ( $n_1, \pi^*$ ) absorption band should thus have enough excess vibration energy to promptly dissociate in this way. The rate of the direct O--OH dissociation on  $S_1$  can be estimated using RRKM theory. [Whitten-Rabinovitch approximation. Details on inputs:  $s=42$ ;  $E_{ZPE} = 74$  and  $E_{ZPE}^\ddagger = 72$  kcal/mol;  $E_b \approx 8$  kcal/mol;  $\Pi v_i / \Pi v_j^\ddagger \approx 800 \text{ cm}^{-1} \times 10$ ;  $f_{\text{centrif}} = 1.5$ ; reaction path degeneracy = 2]. Thus it is found for the TS at 82 kcal/mol (= 74 + 8) above the  $S_0$  VZP-level:

$$k^\ddagger(93 \text{ kc/m})(320 \text{ nm}) \approx 5 \times 10^{11} \text{ s}^{-1}$$

$$k^\ddagger(88 \text{ kc/m})(340 \text{ nm}) \approx 1 \times 10^{11} \text{ s}^{-1}$$

$$k^\ddagger(84.3 \text{ kc/m})(355 \text{ nm}) \approx 1.5 \times 10^{10} \text{ s}^{-1}$$

(the energies are referred here to the  $S_0$  zero-point level; an average thermal contribution  $\langle E_{\text{therm}} \rangle$  of 3.5 kc/mol is added to the absorbed-photon energies).

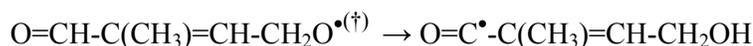
These very high rates are owed to the high *relative* excess internal energy; e.g. at 340 nm:  $E_{\text{int}}(S_1) = 88 - 74 = 14$  kcal/mol, which is 6 kcal/mol in excess of the 8 kcal  $E_b$ . These high rates of  $S_1$  removal by direct dissociation should be the fastest  $S_1$  removal processes by far. They can be compared for instance to the highest observed  $S_1$  removal rates for acetaldehyde upon 310 - 315 nm excitation, measured to be at most  $5 \times 10^8 \text{ s}^{-1}$  (at very low pressures), and ascribed to mainly intersystem crossing (ISC) to the  $T_1$  state and dissociation into  $\text{CH}_3 + \text{CHO}$  on the  $T_1$  surface.<sup>6</sup> The HPALD  $S_1$  dissociation rate also outruns collisional quenching, up to about 360 nm, meaning over almost the entire absorption band, which should ensure a high  $J$ , approaching  $5 \times 10^{-4} \text{ s}^{-1}$  for an overhead sun.

### Energy disposal

As straight O--O homolysis on a repulsive curve is involved here, most of the potential energy released from the TS (at  $\approx 82$  kcal/mol above the  $S_0$  VZP-level) to the products asymptote (at  $\approx 43$  kcal/mol), should dynamically go to relative energy of translation and rotation of the two separating fragments, while a smaller fraction ( $\approx 30\%$ ) can go to internal energy of the  $\text{RO}^\bullet$  fragment. The excess energy above the TS, about 8 kcal/mol on average, should be statistically distributed over all the modes of the fragmenting molecule, thus in part also going to the degrees of freedom of relative motion of the fragments. This means that the oxy radical fragment should not contain much internal energy,  $\approx 18$  kcal/mol on average.

### Subsequent chemistry

The  $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{O}^\bullet$  oxy fragment (whether still activated or not) should undergo a very fast 1,5-H shift



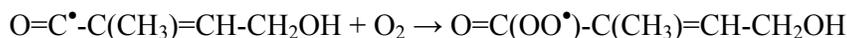
with barrier expected below 7 kcal/mol. Neither elimination of HCHO facing a barrier of 23 kcal/mol<sup>7</sup> (SAR), nor reaction with  $\text{O}_2$  are in any way competitive. The shift is exo-ergic for 17 kcal/mol, such that the resulting acyl radical may contain some 30-35 kcal/mol provided collisional energy loss prior to the shift remains limited. Subsequent prompt CO elimination is however not expected to be important given the high barrier of about 21 kcal/mol.<sup>8</sup> (For prompt CO elimination to really compete with collisional stabilisation, the acyl radical would

<sup>6</sup> G. H. Leu, C. L. Huang, S.H. Lee, I.C. Chen, *J. Chem. Phys.*, 1998, **109**, 9340

<sup>7</sup> L. Vereecken and J. Peeters, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9062-9074

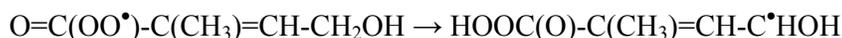
<sup>8</sup> R. Méreau, M. T. Rayez, J. C. Rayez, F. Caralp and R. Lesclaux, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4712.

have to contain at least 40-45 kcal/mol internal energy, i.e.  $\approx 10$  kcal/mol more than estimated above). Therefore, the acyl product is rather expected to stabilise and add  $O_2$  to form an acylperoxy:



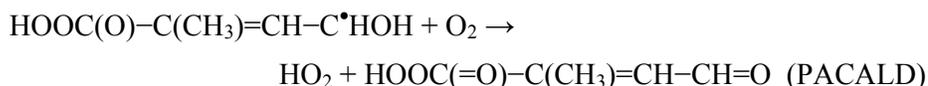
Important to stress is that the fate of this acyl radical would however be quite different if the HPALD photolysis were to occur as we originally suggested, that is by fast internal conversion of the excited  $S_1$  state into highly vibrationally excited electronic ground state  $S_0^{\dagger}$ , which then would promptly dissociate into ground state  $RO^{\bullet} + \bullet OH$ . In that case all the energy above the 43 kcal/mol dissociation limit would be available for statistical distribution over the internal modes, with therefore about  $(90 - 43) \times (36/42) = 40$  kcal/mol ending up as internal energy of the  $RO^{\bullet}$  fragment. For such an highly activated oxy radical, the (17 kcal/mol exoergic) 1,5-H shift would undoubtedly be prompt, thus resulting in an acyl radical with an energy content of 57 kcal/mol. With such a high internal energy, the acyl radical should promptly eliminate CO at a rate of  $\approx 5 \times 10^{10} s^{-1}$  (a hundred times faster than for the mechanism above), easily outrunning collisional stabilisation. Hence, for this earlier proposed HPALD photolysis mechanism, one would rather end up with  $\bullet OH + CO + \bullet C(CH_3)=CH-CH_2OH$  instead of  $\bullet OH$  plus the acyl radical as for the mechanism newly put forward here.

The resulting acylperoxy radical above, a *Z* conformer too, should undergo a very similar 1,6-H shift as the *Z*-4-OH-1- $OO^{\bullet}$  peroxy precursor ( $H_2C(OO^{\bullet})-C(CH_3)=CH-CH_2OH$ ) of one of the HPALDs:



One difference is a stronger internal H-bond in the reactant (between the hydroxy-H and the carboxyl-O; 7-ring) of  $\approx 4$  kcal/mol, that has to be broken for the H-shift, instead of the  $\approx 1.3$  kcal/mol internal H-bond (8-ring) we computed for the *Z*-4-OH-1- $OO^{\bullet}$  reactant. Yet, this is most likely overcompensated by the peroxy-acid H-OO bond formed here being 4-5 kcal/mol stronger<sup>9</sup> than the hydroperoxide H-OO bond formed in the *Z*-4-OH-1- $OO^{\bullet}$  case. Therefore, we expect a barrier  $\approx$ equal to (or somewhat lower than) the average 17 kcal/mol barrier we computed for the 1,6-H shifts in *Z*-4-OH-1- $OO^{\bullet}$  and *Z*-1-OH-4- $OO^{\bullet}$ . As the reaction is similarly allyl-assisted, we expect also a similar tunneling factor of 25 as our WKB-computed factor for the *Z*-4-OH-1- $OO^{\bullet}$  and *Z*-1-OH-4- $OO^{\bullet}$  cases, such that the 298 K rate constant can be estimated at  $\geq 2 s^{-1}$ , i.e. nearly two orders of magnitude faster than the combined rate ( $0.045 s^{-1}$ ) of the acylperoxy reactions with  $HO_2$ ,  $NO_2$ ,  $NO$  and  $RO_2$  in Gabriel conditions, and in any case outrunning the traditional  $HO_2$  and  $NO_x$  reactions in all atmospheric conditions with low- to moderate NO levels.

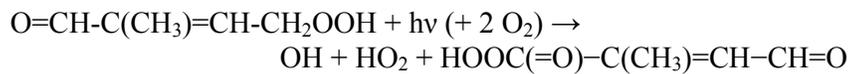
The product radical of the 1,6-H shift will rapidly react with  $O_2$



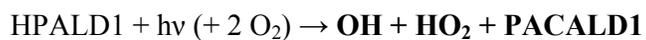
forming another highly photolabile species.

The HPALD photolysis mechanism proposed here will therefore result in the overall reaction:

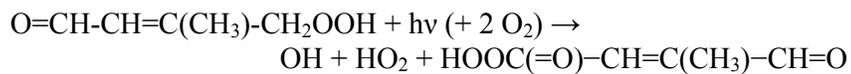
<sup>9</sup> M. Jonsson, *J. Phys. Chem.*, 1996, **100**, 6814



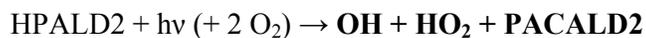
or:



And similar for the other HPALD formed via 1,6-H shift from the Z-4-OH-1-OO• radical:



or:

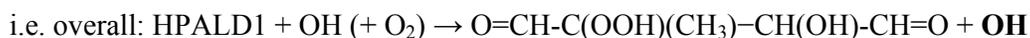
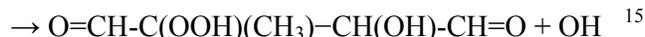
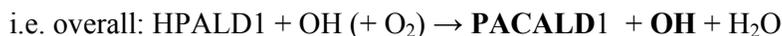
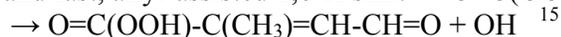
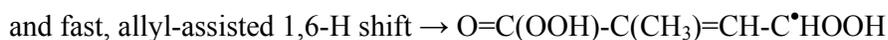
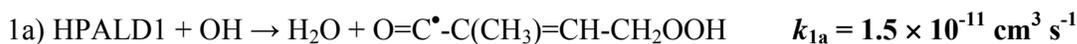


## Reactions of hydroperoxy-methyl-butenals (HPALDs) with OH: reaction channels, channel rate constants and likely, OH-regenerating mechanisms

Rate constants (298 K) for the various OH + HPALDs reaction channels are essentially based on (i) the IUPAC-recommended overall rate constants for OH reactions with analogous unsaturated carbonyls featuring O=C-C=C conjugation (MACR, MVK, acrolein, crotonaldehyde),<sup>10</sup> and (ii) their primary-product distributions as derived from the high-NO experiments of Orlando et al.<sup>11</sup> These data and results are consistent with a 298 K rate constant for the aldehydic-H abstraction equal to  $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  as for CH<sub>3</sub>CHO, whereas, due to the e<sup>-</sup> withdrawing CHO group, both the OH addition rates to >C=C< are reduced by a factor 4.0 as compared to the predictions of our SAR for OH-addition to (poly-)alkenes,<sup>12</sup> however with the *ratio* for the site-specific rate constants maintained at the predicted 0.45:3:5.5 for resulting primary, secondary and tertiary radicals, respectively. (Note, for MVK, the CH<sub>3</sub>CO group reduces both OH-addition rates by only a factor 1.75; this is due to compensation by the CH<sub>3</sub> group which satisfies much of the e<sup>-</sup> appetite of the carbonyl-O).

In addition, H-abstraction also occurs from the -CH<sub>2</sub>OOH group (hydroperoxide α-H), with rate coefficient estimated at  $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  based on the  $0.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for the similar CH<sub>3</sub>CH<sub>2</sub>OOH case,<sup>13,10</sup> but increased here by a factor 1.6 for the allyl-resonance in the product here, taking into account the dependence of this effect on the C-H bond energy.<sup>14</sup>

Thus, for O=CH-C(CH<sub>3</sub>)=CH-CH<sub>2</sub>OOH + OH, (denoted as HPALD1), the following major product channels with their rate constants (298 K) are expected, all likely regenerating OH:



<sup>10</sup> IUPAC subcommittee for Gas Kinetic Data Evaluation, <http://www.iupac-kinetic.ch.cam.ac.uk/>; and references therein

<sup>11</sup> a) J. J. Orlando and G. S. Tyndall, *J. Phys. Chem. A*, 2002, **106**, 12252; b) J.J. Orlando, G. S. Tyndall and S. E. Paulson, *Geophys. Res. Lett.*, 1999, **26**, 2191.

<sup>12</sup> a) J. Peeters, W. Boullart, and J. Van Hoeymissen, in P. M. Borrell, *et al.* (Eds.), Proc. Eurotrac Symp '94, SPB Academic Publishers, The Hague, p. 110 (1994); b) J. Peeters, W. Boullart, V. Pultau, S. Vandenberg, and L. Vereecken, *J. Phys. Chem. A*, 2007, **111**, 1618

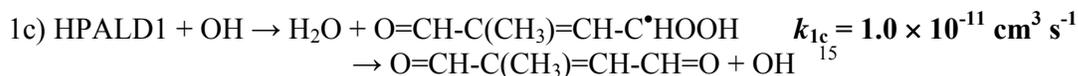
<sup>13</sup> C. Wang, C. and Z. Chen, *Atmos. Environ.*, 2008, **42**, 6614; note that in their experiments, net hydroperoxide removal occurs only upon abstraction of the hydroperoxide α-hydrogens, CH<sub>3</sub>CH<sub>2</sub>OOH, indicated here in bold.

<sup>14</sup> L. Vereecken and J. Peeters, *Chem. Phys. Lett.*, 2001, **333**, 162-168

<sup>15</sup> R-C<sup>•</sup>HOOH radicals are unstable and decompose spontaneously into R-CHO and OH: L. Vereecken, T. L.

Nguyen, I. Hermans, and J. Peeters, *Chem. Phys. Lett.*, 2004, **393**, 432

<sup>16</sup> 1,5-H shift assisted by double H-bonding: between carbonyl-O and alcohol-H, and between hydroperoxide-H and alcohol-O (two 6-rings with a common C-O bond), resulting in estimated k(1,5-H)(298 K) of  $\approx 5 \text{ s}^{-1}$

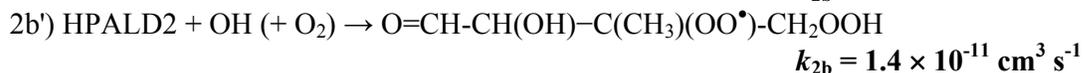
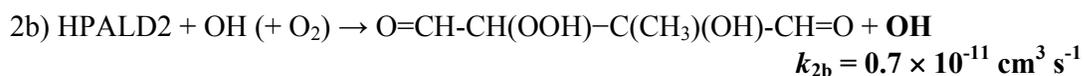
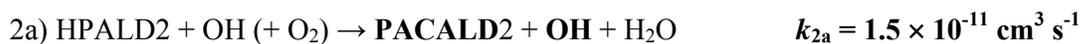


i.e. overall:  $\text{HPALD1} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{O} + \text{OH}$

minor channel: OH-addition to  $\alpha$ -carbon  $k_{1b'} = 0.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$   
 with fate of resulting peroxy radical uncertain

(channel 1d, not considered further: abstraction of OO-H  $k_{1d} = 0.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$   
 which, counting also HPALD photolysis, should be minor (<10%), and can either regenerate HPALD1 in high  $[\text{HO}_2]$  conditions, or, more likely, yield OH + PACALD1 via consecutive 1,6-H shifts of peroxy radicals.)

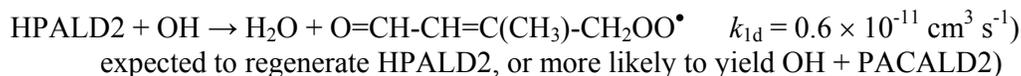
For the other HPALD, i.e.  $\text{O}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2\text{OOH} + \text{OH}$ , similar major reaction channels are expected, and similar overall reactions (given here without details):



(note: further mechanism of peroxy radical still uncertain)



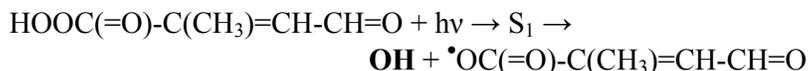
(note: channel 2d, not considered further:



## Fast PACALD photolysis

### Mechanism

The unsaturated peroxy-acid-aldehydes (PACALDs) are bi-conjugated O=C-C=C-C=O systems, similar to butenedial and Z-4-oxo-2-pentenal, which feature n→π\* absorption maxima around 340 - 345 nm and have measured J values of (1 to 2) × 10<sup>-3</sup> s<sup>-1</sup>.<sup>17</sup> Given that the peroxy-acid O--O bond strength is also only ≈40 kcal/mol, we can expect again a very efficient direct PACALD dissociation in its initially excited S<sub>1</sub> state, via a similar mechanism as the HPALDs, above.



The J value is likely about double that for the HPALDs, as the absorption cross sections are somewhat higher and the curve is shifted more towards longer wavelengths, i.e. for an overhead sun:  $J \approx 1 \times 10^{-3} \text{ s}^{-1}$ .

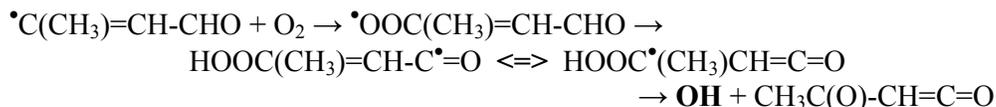
### Energy disposal and suggested subsequent chemistry

For the HPALDs, the potential energy decrease from the S<sub>1</sub>/S<sub>2</sub> (avoided) crossing to the oxy + OH dissociation fragments involves only the repulsive O--O homolysis. Yet for the PACALDs, the repulsive O--O breaking is accompanied at the end of the process by another electronic structure change, i.e. electron delocalization in the resulting acyloxy function,  $\bullet\text{OC(=O)-C=}$   $\Leftrightarrow$   $\text{O=C(O}\bullet\text{)-C=}$ , affording a resonance stabilization energy of *ca* 13 kcal/mol, which should go entirely to vibrational energy of the acyloxy product. Adding a conservative 20% of the repulsive energy release (here minus the dedicated 13 kcal/mol specified), one estimates an average total internal energy of the nascent acyloxy fragment around 27 kcal/mol.

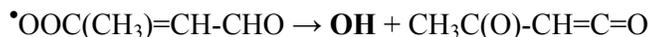
The RRKM estimate (W-R approximation) for the rate of CO<sub>2</sub> elimination from the activated acyloxy product radical, for a barrier of 7 kcal/mol,<sup>7</sup> at nascent internal energy of 25 kcal/mol, is ≈3 × 10<sup>12</sup> s<sup>-1</sup> (and ≈0.5 × 10<sup>12</sup> s<sup>-1</sup> for the PACALD2-acyloxy, with barrier 10 kcal/mol<sup>7</sup>), which far outruns collisional energy loss (and also the competing 1,5-H shift of the aldehyde-H to the acyloxy site, with estimated rate ≈5 × 10<sup>10</sup> s<sup>-1</sup> for a barrier of 6 kcal/mol):



The vinyl-type radical then adds O<sub>2</sub>, after which a 1,5-H shift of the aldehyde-H can occur, with estimated barrier (below) 18 kcal/mol, resulting in a resonance-stabilized radical that is unstable as it can spontaneously expell OH:



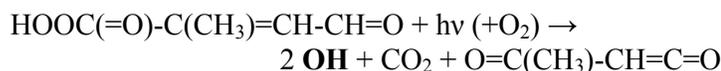
The 1,5-H shift and OH elimination might occur in a concerted process:



<sup>17</sup> M. P. O'Connor, J. C. Wenger, A. Mellouki, K. Wirtz and A. Munoz, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5236

For a barrier of 18 kcal/mol, and with a tunneling factor of  $\approx 25$  as for the 1,6-H shift in the initial Z- $\delta$ -OH-peroxys, the estimated rate is  $\approx 1 \times \text{s}^{-1}$  at 298 K, i.e. far faster than the traditional reactions with HO<sub>2</sub> and NO in low- to moderate NO<sub>x</sub> conditions.

PACALD1 photolysis can then be represented as a single reaction:



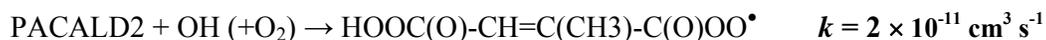
The thus suggested product from PACALD1 photolysis is acetylketene, while that from the analogous PACALD2 is formyl-methylketene:



These products, conjugated  $\alpha$ -oxo-ketenes, are quite labile structures that should readily photolyze and react rapidly with OH, likely products among other being hydroxyacetone and acetaldehyde.

**PACALD + OH reactions:** only one channel of importance, and slow compared to photolysis

For the reactions of HOOC(O)-C(CH<sub>3</sub>)=CH-CH=O (PACALD1) and HOOC(O)-CH=C(CH<sub>3</sub>)-CH=O (PACALD2) with OH, only one channel is of importance, i.e. the aldehyde-H abstraction, with expected channel rate constant  $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (as generally for aldehyde functionalities in larger molecules). OH addition to  $>\text{C}=\text{C}<$  is slowed down to quasi negligible rates due to the presence of **two** e<sup>-</sup> withdrawing substituents, the formyl O=CH group on the right, and the (per)acid group O=C(OOH) on the left, together thus reducing the summed addition rate constant by a factor  $\approx (4 \times 4)$ , i.e. to  $(1/16) \times (5.5 + 3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \approx 0.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .<sup>1,12</sup> Moreover, the rate of OH reaction with the peroxy-acid functionality proper, as for peracetic acid, is generally considered slow ( $k \approx 0.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ). Thus, for PACALDs + OH, the total rate constant at 298 K can be estimated to be around  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , with aldehyde-H abstraction dominating:



Thus, given the PACALD photolysis rate estimate of  $J = 1 \times 10^{-3} \text{ s}^{-1}$  for an overhead sun, the OH + PACALD reaction should be minor, even for an [OH] as high as  $10^7 \text{ cm}^{-3}$ .

**CONCLUSION:** As a result, for the HPALD photolysis mechanism newly proposed here and the subsequent PACALD photochemistry, one can expect overall regeneration of up to 3 OH. It must be stressed that this would not be the case for the originally suggested HPALD photolysis mechanism (Peeters et al., PCCP 2009), as this does not result in the photolabile PACALDS.