

## Electronic Supporting Information (ESI)

### Peroxy radical isomerization in the oxidation of isoprene

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#### 1 CIMS sensitivity.

We estimate the CIMS sensitivity for the hydroxyhydroperoxides (ISOPOOH) and hydroperoxyaldehydes (HPALD) from the ion-molecule collision rate, calculated using the parameterization of Su and Chesnavich [1]. This requires knowledge of the average dipole moment and polarizability of the neutral species. We obtain these parameters for the species of interest from *ab initio* calculations. For accurate results, all conformers with significant populations at the temperature of interest must be considered. We calculate conformer-specific dipoles for all conformers with a relative population of >1% at T=298K, as estimated from a Boltzmann weighting to the conformer energies. The conformer-specific dipoles, weighted by their relative population, are averaged to yield the overall dipole moment for the species of interest. This methodology has been described in more detail by Garden *et al.* [2].

Table S1 lists the isomer-specific average dipole moments and polarizabilities for the four important ISOPOOH isomers and both

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HPALD isomers. In this work we use values calculated at the B3LYP/cc-pVTZ level. The same values calculated at the lower B3LYP/6-31G(d) level, used in the study of Paulot *et al.* [3], are listed for comparison.

The CIMS instrument measures the sum of isomers appearing at a specific mass. Thus to calculate the average CIMS sensitivity, we weight the four major ISOPOOH isomers according to the relative initial ISO<sub>2</sub> distribution (at 303 K) as calculated by Peeters *et al.* [4] (1-OH-2-OO: 0.45, Z-1-OH-4-OO: 0.21, 4-OH-3-OO: 0.23, 4-OH-1-OO: 0.11). We give the HPALD isomers equal weight. Weighting the ISOPOOH sensitivity by the near-equilibrium ISO<sub>2</sub> distribution predicted for our experimental conditions at 295 K (1-OH-2-OO: 0.67, Z-1-OH-4-OO: 0.04, 4-OH-3-OO: 0.27, 4-OH-1-OO: 0.02) [4] changes the inferred sensitivity by only ~3%. As both HPALD isomers have similar dipole moments, our determinations are insensitive to this weighting scheme.

Absolute sensitivities for both ISOPOOH and HPALD are determined from the calculated ion-molecule collision rates using the average between the ratios of the experimentally determined sensitivities for glycolaldehyde and hydroxyacetone to their respective calculated-collision rate:

$$\bar{R}_{\text{GH}} = \frac{\frac{s_{\text{expt}}^{\text{GLYC}}}{k_{\text{coll}}^{\text{GLYC}}} + \frac{s_{\text{expt}}^{\text{HAC}}}{k_{\text{coll}}^{\text{HAC}}}}{2}$$

$$S_{\text{calc}}^X = k_{\text{coll}}^X \times \bar{R}_{\text{GH}}$$

The sensitivity for the isoprene hydroxynitrates is determined relative to nitric acid following Paulot *et al.* [5].

## 2 Rate of 1,5-H-shift (from alcohol).

Fig. S1 shows CIMS observations of MVK+MACR and isoprene nitrates as a function of time for experiment #3 (main paper, Table 1, T=318 K). Also shown are results from a kinetic model simulation for this isoprene oxidation experiment for MVK+MACR and isoprene nitrates using several values for the 1,5-H-shift isomerization rate ( $k_{1,5\text{-isom}}$ ) within the model. Simulations were run using the rate for the 1,6-H-shift determined in this study, isomer-dependant nitrate yields from Paulot *et al.* [5], the temperature dependence

for nitrate yields from Carter and Atkinson [6], with several theoretical values for the 1,5-H-shift isomerization rates reported by Peeters *et al.* [4], da Silva *et al.* [7], Peeters and Muller [8]. The rate calculated by Peeters *et al.* [4] ( $k_{1,5\text{-isom}}^{318} = 0.026 \text{ s}^{-1}$ ) and increased by  $5\times$  in Peeters and Muller [8] ( $k_{1,5\text{-isom}}^{318} = 0.13 \text{ s}^{-1}$ ) predicts that the isoprene chemistry at the long  $\text{ISO}_2^\bullet$  lifetimes and elevated temperature in this experiment should be dominated by this mechanism. This however, is not consistent with the CIMS observations. The geometric average of the rates for the two 1,5-H-shift isomerization channels calculated by da Silva *et al.* [7] ( $k_{1,5\text{-isom}}^{318} = 0.005 \text{ s}^{-1}$ ) is consistent with our results, but also is not well constrained, as errors in the assumed  $\text{ISO}_2$  distribution,  $\text{ISO}_2 + \text{ISO}_2$  reaction rates, and isomer-specific nitrate yields, all can impact the modeled MVK+MACR and  $\text{ISONO}_2$ .

## References

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**Table S1** – Average dipole moments and polarizabilities for ISOPOOH and HPALD isoprene oxidation products, for  $T = 298$  K. Collision rates have units of  $10^{-9} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ .

Molecule	Structure	B3LYP/6-31G(d)			B3LYP/cc-pVTZ		
		Dipole (D)	Polarizability ( $\text{\AA}^3$ )	$k_{\text{coll}}^{\times}$	Dipole (D)	Polarizability ( $\text{\AA}^3$ )	$k_{\text{coll}}^{\times}$
$\beta$ 1-ISOPOOH		2.19	9.44	1.85	2.32	10.8	1.96
$\beta$ 4-ISOPOOH		2.20	9.44	1.85	2.29	11.0	1.95
$\delta$ 1-ISOPOOH		2.85	9.63	2.23	2.54	11.0	2.09
$\delta$ 4-ISOPOOH		3.34	9.66	2.49	3.22	11.06	2.47
HPALD1		2.51	9.5	2.03	2.54	10.9	2.10
HPALD2		1.90	9.6	1.70	2.36	10.9	2.00
Glycolaldehyde		2.3	4.5	2.0	2.33	4.64	2.06
Hydroxyacetone		3.1	5.5	2.5	3.08	6.40	2.49

**Figure S1** – CIMS observations (black circles) of MVK+MACR (top) and ISORO<sub>2</sub> (bottom) during isoprene oxidation experiment (#3 - main paper, T = 318 K). Kinetic model results are shown using a range of 1,5-H-shift isomerization rates.

