

Supporting information for: Autoxidation of Organic Compounds in the Atmosphere

John D. Crounse,^{*,†} Lasse B. Nielsen,[‡] Solvejg Jørgensen,[‡] Henrik G. Kjaergaard,[‡]
and Paul O. Wennberg^{*,†,¶}

*Division of Geological and Planetary Sciences, California Institute of Technology,
Pasadena, USA, 91125, Department of Chemistry, University of Copenhagen, DK-2100
Copenhagen Ø, Denmark, and Division of Engineering and Applied Science, California
Institute of Technology, Pasadena, USA, 91125*

E-mail: crounjd@caltech.edu; wennberg@caltech.edu

Phone: 626-395-8655. Fax: 626-395-8535

*To whom correspondence should be addressed

†Division of Geological and Planetary Sciences, Caltech.

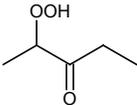
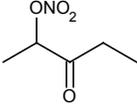
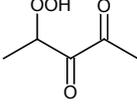
‡University of Copenhagen

¶Division of Engineering and Applied Science, Caltech.

Calibrations

The chemical ionization signals for C₅-hydroperoxy carbonyl (HPC), C₅-carbonyl nitrate (CN), and C₅-hydroperoxy di-carbonyl (HPdC) were converted into mixing ratios using sensitivity factors estimated from ion–molecule collision rates, using the parameterization of Su and Chesnavich.^{S1} The conformationally-averaged dipole moment (weighted average of the dipoles for all conformers which contain >1% of the population at $T = 298$ K) and polarizability of the neutral molecule are needed for the collision rate calculation. These parameters are obtained using theoretical methods,^{S2} and shown in Table S1.

Table S1: Conformationally averaged dipole moments and polarizabilities for 3-pentanone oxidation products, for $T = 298$ K . Collision rates have units of 10^{-9} cm³ molec⁻¹ s⁻¹.

Molecule	Structure	B3LYP/cc-pVTZ		
		Dipole (D)	Polarizability (Å ³)	k_{coll}^x
HPC		3.36	10.6	2.53
CN		2.25	12.1	1.88
HPdC-1		2.78	10.7	2.17

Products of 3-pentanone + OH oxidation experiment.

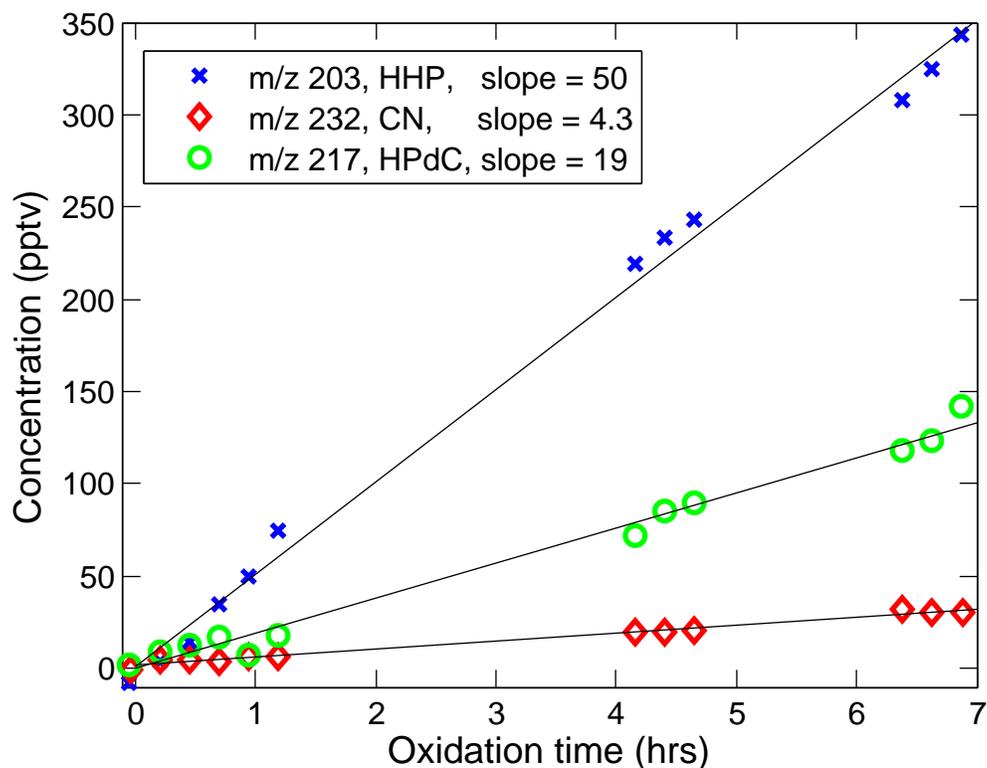


Figure S1: Time traces for C₅-hydroperoxy carbonyl (HPC), C₅-carbonyl nitrate (CN), and C₅-hydroperoxy di-carbonyl (HPdC) for a slow 3-pentanone + OH oxidation experiment. Data gaps are present when sampling from the reaction bag was ceased in order to prolong reaction time.

H-shifts at increasing length from RO₂ group.

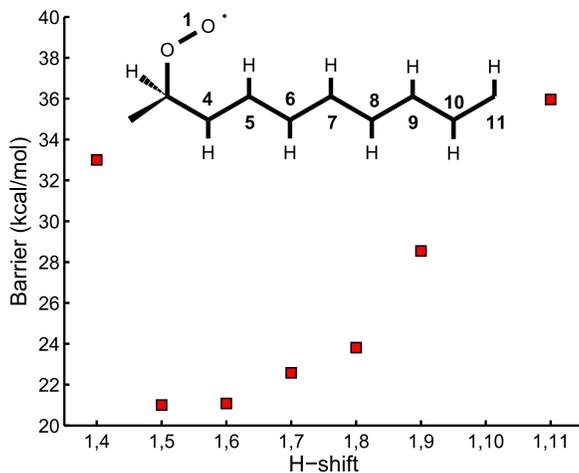


Figure S2: The ZPVE corrected forward barrier in kcal/mol for H-shifts in 2-peroxy-decane at B3LYP/6-31+G(d,p).

We have investigated H-shifts in 2-peroxy-decane at increasing length from the peroxy group. All the calculations were done with UB3LYP/6-31+G(d,p). A straight 2-peroxy-decane carbon chain was used as the reactant for all of the calculated reaction barriers. We selected the lowest energy conformers based on chemical intuition, as investigation of all possible conformers of the C₁₀ carbon chain would be prohibitive. Transition states were verified solely by visualization of the imaginary frequency. The H-shift reactions are labeled by the number of heavy atoms between the peroxy group and the reacting hydrogen.

We plot the energy barriers for the H-shifts in figure S2, except for the 1,10 H-shift which we could not find. We conclude that the 1,5 to 1,8 H-shifts may all be important in the oxidation of organic species in the environment, and deserving of additional study.

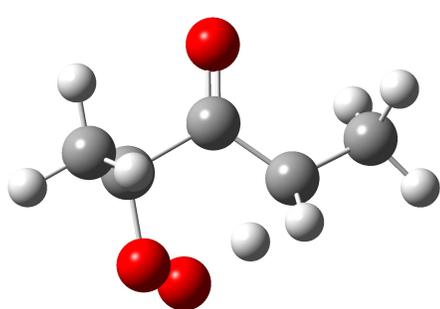
Stereo selectivity of H-shift reactions.

We find differences in the rate constants calculated for the different stereo isomers, see table S2. The (2S,4R) stereo isomer generally give H-shift rate constants that are up to an order of magnitude bigger than the (2R,4R) counterpart. This imply that the atmosphere may select one stereo isomer over the other and that is an aspect that has not been considered before. We expect that the observed energy difference between the (2S,4R) and (2R,4S) stereo isomers of less than 1 kcal/mol is due to the slightly difference in the two conformers of the "same" transition state structure. For example, the transition state structures of βO (2R,4S) and βO (2S,4R) differ in the orientation of the $-\text{CH}_2\text{CH}_3$ group, this group is slightly bend in the transition state structure βO (2R,4S) leading to higher energy than the energy of the transition state structure βO (2S,4R). (See figure S3) We expect that the (2S,4R) isomer and its mirror image (e.g. (2R,4S)) should have identical structures and energies. We verified this by optimization of the transition state structure of βO (2R,4S) stereo isomer created as a perfect mirror image of the transition state structure of βO (2S,4R) isomer, and find that the two isomers have the exact same energies.

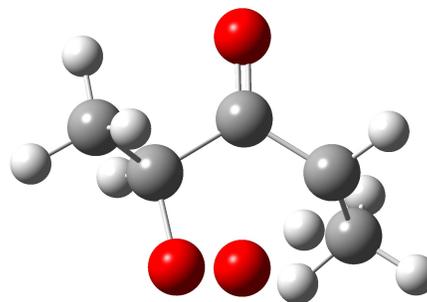
Table S2: Forward barrier (F) and forward rate constant for different stereo isomers. Energies are calculated with UB3LYP/aug-cc-pVTZ.

Name	Isomer	F ^a (kcal/mol)	k(→) s ⁻¹	Name	Isomer	F ^a (kcal/mol)	k(→) s ⁻¹
Alkane	(2R,4R)	21.10	4.77×10 ⁻³	βO	(2R,4R)	21.78	5.33×10 ⁻²
	(2S,4R)	19.91	2.76×10 ⁻²		(2S,4R)	21.60	5.36×10 ⁻²
	(2R,4S)	20.58	1.67×10 ⁻²		(2R,4S)	22.33	1.28×10 ⁻²
γOH	(2R,4R)	17.41	2.74×10 ⁰	γOOH	(2R,4R)	16.54	2.79×10 ¹
	(2S,4R)	15.97	2.46×10 ¹		(2S,4R)	17.83	3.55×10 ¹
	(2R,4S)	16.19	2.04×10 ¹		(2R,4S)	17.03	2.46×10 ¹

^a Forward barrier ($\text{RO}_2 \rightarrow \text{QOOH}$).



β O (2S,4R)



Mirror image of β O (2R,4S)

Figure S3: Transition state structures that correspond to the β O (2S,4R) and (2R,4S) values reported in table S2. The (2R,4S) isomer has been mirror inverted, so that it is easy to compare with the (2S,4R) structure.

Hydrogen abstraction by OH in 3-pentanone.

We carried out calculations for the hydrogen abstraction from 3-pentanone initiated by hydroxyl radical. At the BH&HLYP/6-31+G(d,p) level we find that H abstraction by OH from the -CH₂- and -CH₃ groups are 87 and 13%, respectively. This indicates that RO₂-1 (Scheme 1) is the dominant peroxy radical produced in the first step 3-pentanone oxidation by OH.

Additional calculated RO₂ 1,5-H-shift rates

Table S3: B3LYP/aVTZ calculated parameters for the RO₂ 1,5-H-shift reactions. The imaginary frequency ($\tilde{\nu}_{\text{IMAG}}$), forward (F) and reverse (R) isomerization barriers, Eckart tunneling factors (κ), and forward [$k(\rightarrow)$] and reverse [$k(\leftarrow)$] reaction rate constants at T=298 K.

Name	TS	$\tilde{\nu}_{\text{IMAG}}^a$ (cm ⁻¹)	F ^b /R ^c (kcal mol ⁻¹)	κ	$k(\rightarrow)$ (s ⁻¹)	$k(\leftarrow)$ (s ⁻¹)	$F_{\text{isom}}^d/F_{\text{isom}/25}^e$
$\beta\text{O-CH}_3$		1863	19.29/17.70	254	6.97×10^{-1}	1.22×10^1	0.97/0.58
$\delta\text{O-CH}_3$ (2S,4R)		1752	14.31/14.86	71	1.15×10^3	4.47×10^2	1.00/1.00
$\delta\text{O-OOH}$ (2R,4S)		1806	16.05/22.84	197	2.85×10^2	-D ^f	1.00/1.00
$\delta\text{O-OH}$ (2R,4S)		1649	11.92/21.69	39	3.76×10^4	3.24×10^{-3}	1.00/1.00

^aImaginary frequency. ^bForward barrier (RO₂ → QOOH). ^cReverse barrier (QOOH → RO₂). ^dFraction undergoing H-shift isomerization followed by O₂ addition ($k_{\text{O}_2} = 1 \times 10^{-12}$ cm³ molec.⁻¹ s⁻¹), or decomposition in the case of α -hydroperoxy alkyl radicals (-D-, assumed to be prompt^{S3}), when the traditional RO₂ reactivity is set to 2×10^{-2} s⁻¹ (equivalent to gas phase reactivity in presence of ~ 100 pptv NO) in 1 atm of air. ^eFraction calculated undergo H-shift isomerization using *ab initio* forward ($k(\rightarrow)$) and reverse ($k(\leftarrow)$) H-shift rates reduced by a factor of 25. ^f In the case of α -hydroperoxy alkyl radicals decomposition (-D-) is assumed to outrun the reverse H-shift.^{S3}

References

- (S1) Su, T.; Chesnavich, W. J. Parameterization of the Ion-molecule Collision Rate-constant by Trajectory Calculations. *J. Chem. Phys.* **1982**, *76*, 5183–5185.
- (S2) Garden, A. L.; Paulot, F.; Crouse, J. D.; Maxwell-Cameron, I. J.; Wennberg, P. O.; Kjaergaard, H. G. Calculation of Conformationally Weighted Dipole Moments Useful in Ion-molecule Collision Rate Estimates. *Chem. Phys. Lett.* **2009**, *474*, 45–50.
- (S3) Vereecken, L.; Nguyen, T. L.; Hermans, I.; Peeters, J. Computational Study of the Stability of α -Hydroperoxyl- α -alkylperoxyl Substituted Alkyl Radicals. *Chem. Phys. Lett.* **2004**, *393*, 432–436.