Supplement of Atmos. Chem. Phys., 23, 10517–10532, 2023
https://doi.org/10.5194/acp-23-10517-2023-supplement

Atmospheric Chemistry and Physics Open Access

Supplement of

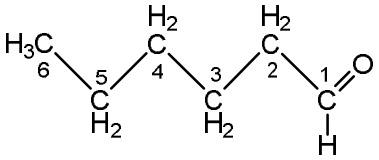
An aldehyde as a rapid source of secondary aerosol precursors: theoretical and experimental study of hexanal autoxidation

Shawon Barua et al.

Correspondence to: Shawon Barua (shawon.barua@tuni.fi) and Matti Rissanen (matti.rissanen@tuni.fi)

S1: Rate coefficients of H-abstractions predicted by SAR

To place the calculated H-abstraction rate coefficients of hexanal + OH reaction in perspective, we compare them to a structure-activity relationship (SAR) data reported in the literature.[1,2] The SAR rate coefficients are calculated by using the formula, $k_{SAR} = k_{abs} \times F(X) \times F(Y)$ and the resulting values are shown in Supplementary Table S1. Here, k_{abs} indicates the rate coefficient associated with the group (–C(=O)H), –CH_2–, –CH_3) from which the H atom is being abstracted, where, F(X) and F(Y) are the substituent group factors. For aldehydic H-abstraction on C1, the substituent group factor F(X) corresponds to a –CH_2– group. Accordingly, for non-aldehydic H-abstraction from the secondary carbon C2, the substituent group factors F(X) and F(Y) correspond to –C(=O)H and –CH_2– groups respectively.



Supplementary Table S1. Calculated rate coefficients of different H-abstraction reactions in hexanal + OH reaction predicted by SAR.

H-abstraction channels	k_{abs} [a] (10^{-12} cm^3 $molecule^{-1}$ s^{-1})	F(X) [b]	F(Y) [b]	k_{SAR} (10^{-12} cm^3 $molecule^{-1}$ s^{-1})
C1 (ald H; –C(=O)H)	20.8	1.23 X= –CH_2–	–	25.58
C2 (α H; –CH_2–)	0.77	0.75 X= –C(=O)H	1.23 Y = –CH_2–	0.71
C3 (β H; –CH_2–)	0.77	1.23 X= –CH_2–	1.23 Y= –CH_2–	1.16
C4 (γ H; –CH_2–)	0.77	1.23 X= –CH_2–	1.23 Y = –CH_2–	1.16
C5 (δ H; –CH_2–)	0.77	1.23 X= –CH_2–	1.00 Y = –CH_3	0.95
C6 (prim H; –CH_3)	0.13	1.23 X= –CH_2–	–	0.16

[a] values taken from ref. 1 (Jenkin et al. 2018), [b] taken from ref. 2 (Ziemann et al. 2012)

S2: Bimolecular TST expressions for H-abstraction reactions – a comparison

The rate coefficients (k) of the H-abstraction reactions of hexanal by OH, are calculated in three different ways. A simpler approach which is based on the reaction free energy barrier ($\Delta G^{\neq}$) is given in Eq. (1).

$$k = \frac{k_B T}{h * c^{\circ}} exp\left(-\frac{G_{TS} - G_R}{k_B T}\right) \quad (1)$$

The constants, k_B, and h are Boltzmann's constant and Planck's constant, respectively. Absolute temperature, T, is set to 298.15 K. c° is the total concentration of molecules in

standard condition, 2.46×10^{19} molecules cm^{-3}. G_{TS} and G_R are the Gibbs free energies (at 298.15 K and 1 atm) of the TS and the reactant, respectively.

The equation that accounts for multiple conformers of TS and hexanal, based on multiconformer transition-state theory (MC-TST),[3] is shown in Eq. (2).

$$k = \sigma \kappa \frac{k_B T}{h * c^{\circ}} \frac{\sum_i^{all\ TS\ conf.} \exp\left(-\frac{\Delta E_i}{k_B T}\right) Q_{TS,i}}{Q_{OH} \sum_j^{all\ R\ conf.} \exp\left(-\frac{\Delta E_j}{k_B T}\right) Q_{Hex,j}} exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (2)$$

where, σ is the symmetry factor,[4] and κ is quantum mechanical tunneling.[5] ΔE_i is the zero-point-corrected energy of the i^{th} TS conformer relative to the lowest-energy transition state conformer, and $Q_{TS,i}$ is the partition function of the i^{th} transition state conformer. Similarly, ΔE_j and $Q_{Hex,j}$ are the corresponding values for hexanal conformer j. Q_{OH} is the partition function of the lowest energy OH conformer. $E_a = E_{TS}$-E_R is the zero-point corrected barrier height corresponding to the lowest energy TS and reactant conformers. In the case of only lowest-energy reactant and TS conformers, Eq. (2) is reduced to Eq. (3) as below. The approach is called lowest-conformer TST (LC-TST). The rate coefficients calculated using all the approaches are given in Supplementary Table S2.

$$k = \sigma \kappa \frac{k_B T}{h * c^{\circ}} \frac{Q_{TS}}{Q_{OH}\, Q_{Hex}} exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (3)$$

Supplementary Table S2. Overall reaction and TS energies in kcal/mol of the different OH H-abstraction reactions of hexanal along with calculated rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}).

H-abstraction channels	$\Delta G^{\neq}$	*k* (simple)	E_a	κ	*k (LC-TST)*	*k* (MC-TST)
C1 (aldehydic H)[‡]	6.75	2.86×10^{-12}	-0.58	1.0	2.84×10^{-12}	8.57×10^{-13}
C2 (α H)	9.52	2.67×10^{-14}	2.0	1.2	6.36×10^{-14}	5.01×10^{-14}
C3 (β H)	9.18	4.73×10^{-14}	1.5	1.05	9.99×10^{-14}	4.50×10^{-14}
C4 (γ H)	8.79	9.14×10^{-14}	0.1	1.47	2.69×10^{-13}	9.22×10^{-14}
C5 (δ H)	10.28	7.39×10^{-15}	1.6	1.04	1.53×10^{-14}	5.78×10^{-15}
C6 (primary H)	10.29	7.27×10^{-15}	2.7	1.29	2.80×10^{-14}	1.39×10^{-14}

[‡] aldehydic H-abstraction barrier calculated at RHF-RCCSD(T)-F12a/VDZ-F12// MN15/def2-tzvp level of theory. $k_{overall\ (simple)} = 3.03 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $k_{overall\ (LC\text{-}TST)} = 3.32 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Table S2 clearly shows that the overall H-abstraction rate coefficient is dominated by the aldehydic H-abstraction channel (C1). Using both approaches, the simple bimolecular TST and LC-TST, the overall rate coefficients are similar with values of 3.03×10^{-12} and 3.32×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively, whereas the overall MC-TST rate coefficient is lower because of the aldehydic H-abstraction getting lowered by a factor of around 3. The lower aldehydic H-abstraction rate coefficient in the MC-TST approach is due to the contribution of only three TS

conformers against 18 hexanal conformers in the partition function term of the Eq. (2). The other H-abstraction rate coefficients (C2–C6 channels) show a little increase in both LC-TST and MC-TST approaches compared to the simple bimolecular TST approach except a little decrease in δ H-abstraction (C5 channel) in the MC-TST approach. The γ H-abstraction rate coefficient (C4 channel) in the LC-TST approach according to Eq. (3) shows an increase by a factor of 2 compared to the simple expression in Eq. (1). The tunneling factor (κ) in all the H-abstraction cases is close to 1, and therefore, it does not seem to have a significant effect in the rate coefficients. On the other hand, the symmetry factor (σ) shows a significant influence in the rate coefficients except for the aldehydic H-abstraction. Although the relatively more sophisticated bimolecular TST approach (i.e., LC-TST) do not seem to affect the aldehydic H-abstraction rate coefficient of hexanal, both LC-TST and MC-TST do have an effect on the non-aldehydic H-abstractions as well as the branching ratios.

S3: Hindered rotor treatment on H-shift rate coefficients

We perform hindered rotor calculations on Gaussian to identify the hindered rotors, the corresponding periodicities and barriers, and the corrected partition functions. In the subsequent MESMER simulation, we use the HinderedRotorQM1D method with the Gaussian derived periodicities and barriers. The harmonic frequencies corresponding to the hindered rotors are removed. Hindered rotor coefficients of all the lowest energy conformers (in an excel file) and one MESMER example file are available in the Zenodo data archive (https://doi.org/10.5281/zenodo.8212748). We also incorporate the corrected partition functions in the MC-TST rate coefficients calculated using Eq. (1) of the main manuscript. All the rate coefficients, before and after hindered rotor treatment, are presented in Supplementary Table S3. While executing the hindered rotor calculations, in one or more conformers, one-to-one correspondence between vibrational and internal rotation modes are not achieved. Accordingly, hindered rotor treatment is not applied to MESMER rate coefficients for the reactions, A61→A61a', D→D51', and D52→D52n', as Gaussian hindered rotor calculations failed for their lowest energy TSs. For the reactions, D→D61', and D51→D52n', hindered rotor calculations are not achieved for their corresponding products. In the MESMER input file, for the reactions with a failed product hindered rotor calculation, we use the product information without hindered rotor potential as this is tested to have a minimal effect in the rate coefficient (e.g., a factor of 1.1 overestimation tested for A→A61' reaction).

Supplementary Table S3. Calculated rate coefficients for H-migration in peroxy radicals before and after hindered rotor treatment. The migrating H-atoms are marked in red.

Reactant	Product	Substitution pattern		Span[a]	$k_{MC\text{-}TST}$ (s^{-1})	$k_{MC\text{-}TST}$ (s^{-1}) hindered rotor	k_{MESMER} (s^{-1})	k_{MESMER} (s^{-1}) hindered rotor
		H-atom	–OO					
A	A61′	–CH_2–	–C(=O)OO	1,6	1.69×10^{-1}	6.65×10^{-2}[c]	2.0	5.30×10^{-1}
A	A51′	–CH_2–	–C(=O)OO	1,5	3.49×10^{-2}	4.48×10^{-2}[c]	1.97×10^{-1}	8.70×10^{-2}
A61	A61a′	–CH_2–	>CHOO	1,5	3.90×10^{-3}	1.95×10^{-3}[d]	2.05×10^{-2}	–
A61	A62	–C(=O)OOH	>CHOO	1,8[‡]	3.72×10^{-6}	3.12×10^{-7}	1.33×10^{-5}	7.32×10^{-6}

A62	A62a6′	–CH(OOH)–	–C(=O)OO	1,6	2.08	1.03×10^{-1}	–	–
A51	A51a6′	$–CH_3$	>CHOO	1,6	2.77×10^{-5}	1.47×10^{-5}[c]	2.19×10^{-4}	1.32×10^{-4}
A51	A51a5′	$–CH_2–$	>CHOO	1,5	7.81×10^{-4}	3.15×10^{-4}[c]	8.57×10^{-3}	6.12×10^{-3}
D	D61′	–C(=O)H	>CHOO	1,6	8.63×10^{-1}	4.25×10^{-2}[c]	4.04	3.58[b]
D	D51′	$–CH_2–$	>CHOO	1,5	3.91×10^{-2}	2.06×10^{-3}[e]	2.15×10^{-1}	–
A62	A61	–CH(OOH)–	–C(=O)OO	1,8[‡]	6.92×10^{2}	2.58×10^{1}	7.53×10^{2}	2.89×10^{2}
D51	D52	–CH(OOH)–	>CHOO	1,7[‡]	8.96×10^{1}	7.03×10^{1}	2.41×10^{2}	4.00×10^{2}
D52	D52n′	–C(=O)H	>CHOO	1,6	1.38×10^{-1}	1.45×10^{-2}[f]	5.15	–
D51	D52n′	–C(=O)H	>CHOO	1,4	2.67×10^{-2}	9.75×10^{-2}[g]	4.43×10^{-2}	8.50×10^{-2}[b]

[a] H-shift span, [‡]H-scrambling reactions, [b] hindered rotor calculation failed for the product conformer, [c] hindered rotor calculation failed for 1 reactant conformer, [d] hindered rotor calculations failed for 4 TS conformers, [e] hindered rotor calculations failed for 1 reactant and 1 TS conformer, [f] hindered rotor calculations failed for 5 reactant and 2 TS conformers, [g] hindered rotor calculation failed for 1 TS conformer.

Table S3 shows that the hindered rotor treatment either decreases or increases the MESMER rate coefficients within a factor of 2 except for the reaction of A→A61' which decreases by a factor of 3.8. In the MC-TST rate coefficients where hindered rotor calculation failed in one or more conformers, we use the original partition functions for those conformers instead. The resultant MC-TST rate coefficients with hindered rotor treatment either decrease or increase by a factor of around 2 to 3 except for the reaction of D52→A52n' where hindered rotor calculations failed for five reactant and two TS conformers and decrease the MC-TST rate by a factor of 9.5.

S4: Background spectra in mass spectrometry

In order to ensure that the hexanal + OH oxidation products shown in Figure 6 of the main manuscript are either distinct or significantly bigger than any background signals, we record all the possible background spectra separately. Supplementary Figure S1 clearly shows that the key oxidation products $C_6H_{11}O_{5\text{-}7}$, their corresponding closed-shell products $C_6H_{10,12}O_{5\text{-}7}$ as well as the accretion products $C_{12}H_{22}O_{9\text{-}11}$ are distinct from any background signals originating from TME + O_3, hexanal, hexanal + O_3, and hexanal + TME experiments except the mass of 226 that matches with $C_6H_{12}O_5$ at unit mass resolution. However, the reported hexanal OH oxidation spectra in the main manuscript (Figure 6) are all relevant background subtracted indicating that the product signal $C_6H_{12}O_5$ (m/z 226) is significant in 3.1 s and 12 s reaction time experiments.

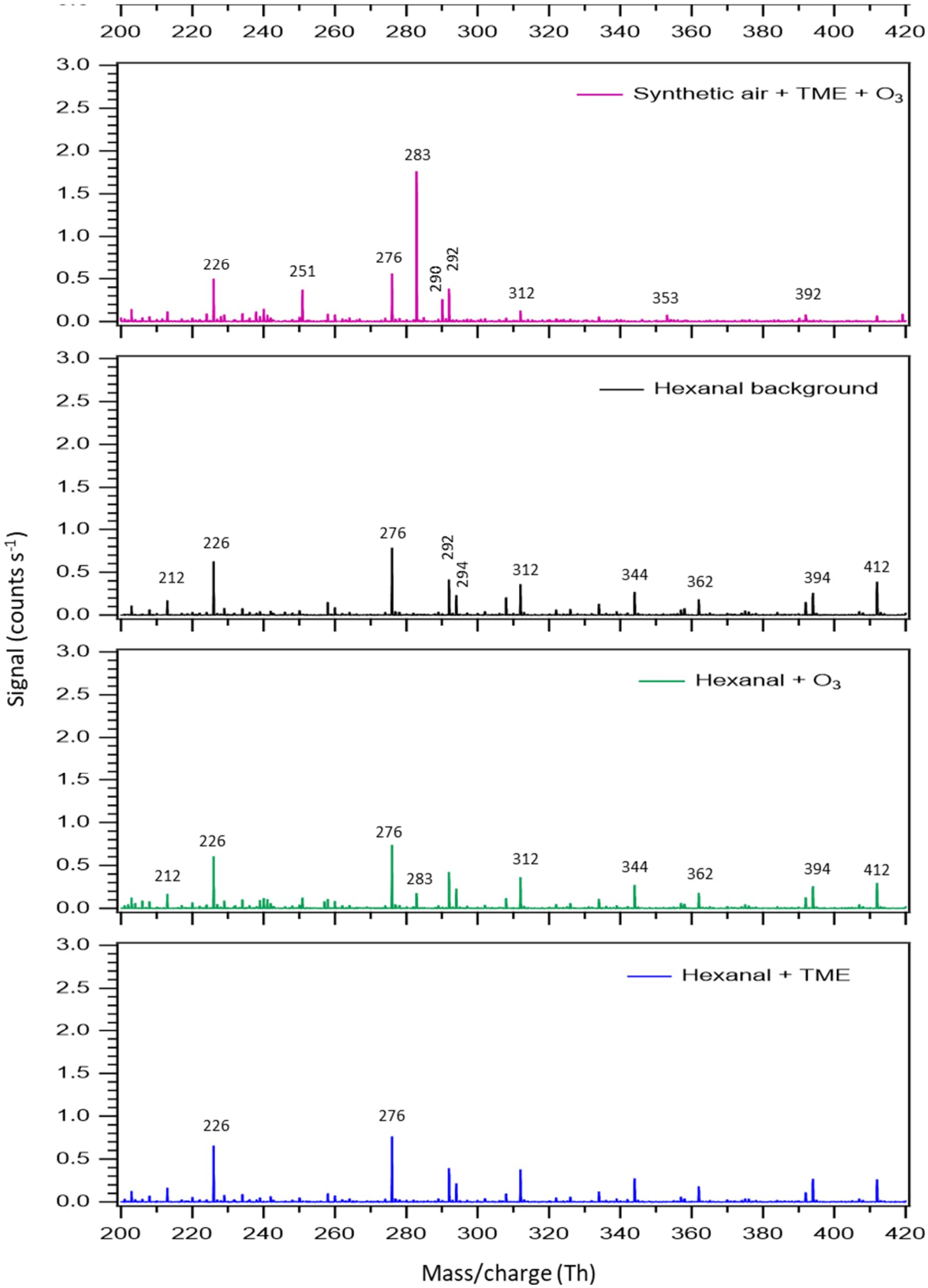


Figure S1: All background spectra (TME + O_3, hexanal, hexanal + O_3, and hexanal + TME) recorded during hexanal OH oxidation experiments. The reaction of TME + O_3 is the source of the oxidant OH.

S5: Bimolecular reaction products

This section describes potential reaction mechanisms leading to identified products which involve one bimolecular RO_2 + RO_2 reaction step. The labile hydrogen containing groups are marked in light-brown shapes. The structures associated with the proposed mechanisms are in agreement with the hydrogen to deuterium (H to D) exchange experiments (see Figure 6 in the main manuscript).

$C_6H_{10\text{-}12}O_6$

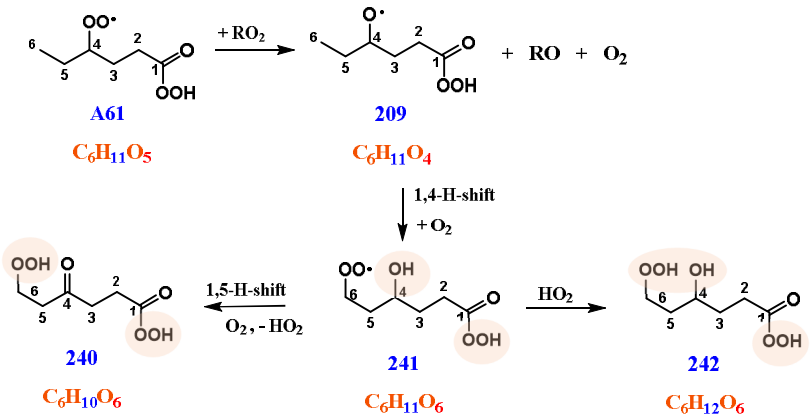
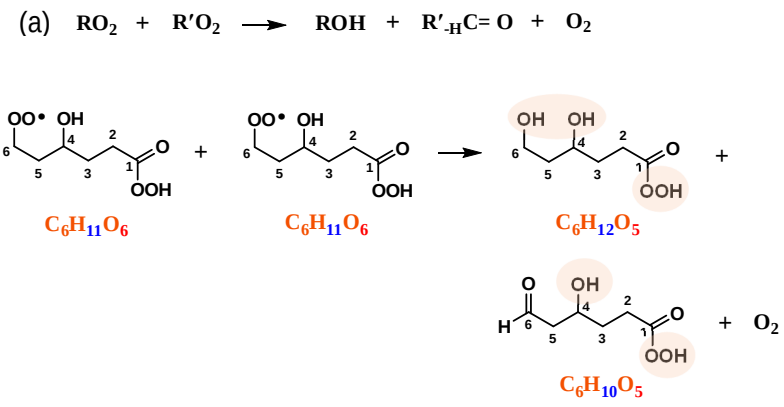


Figure S2: Formation of $C_6H_{10\text{-}12}O_6$ products likely involve A61 ($C_6H_{11}O_5$) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture.

$C_6H_{10}O_5$



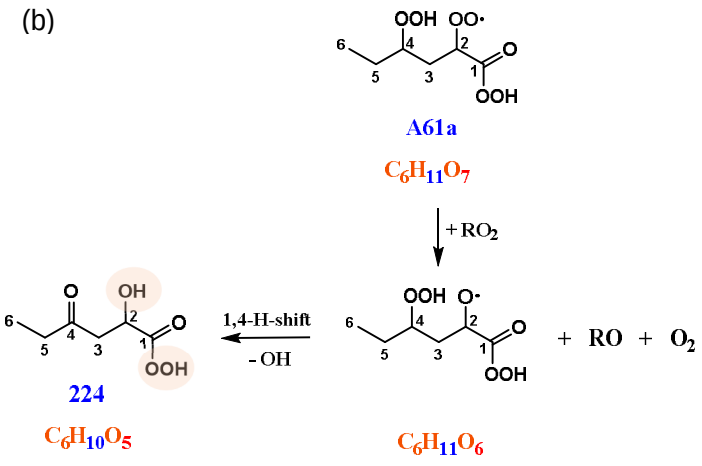


Figure S3: The Russell mechanism producing closed-shell products, an alcohol and a carbonyl compound directly from a single RO_2 + RO_2 reaction (a). Formation of $C_6H_{10}O_5$ product likely involves A61a ($C_6H_{11}O_7$) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture (b).

$C_9H_{16}O_7$

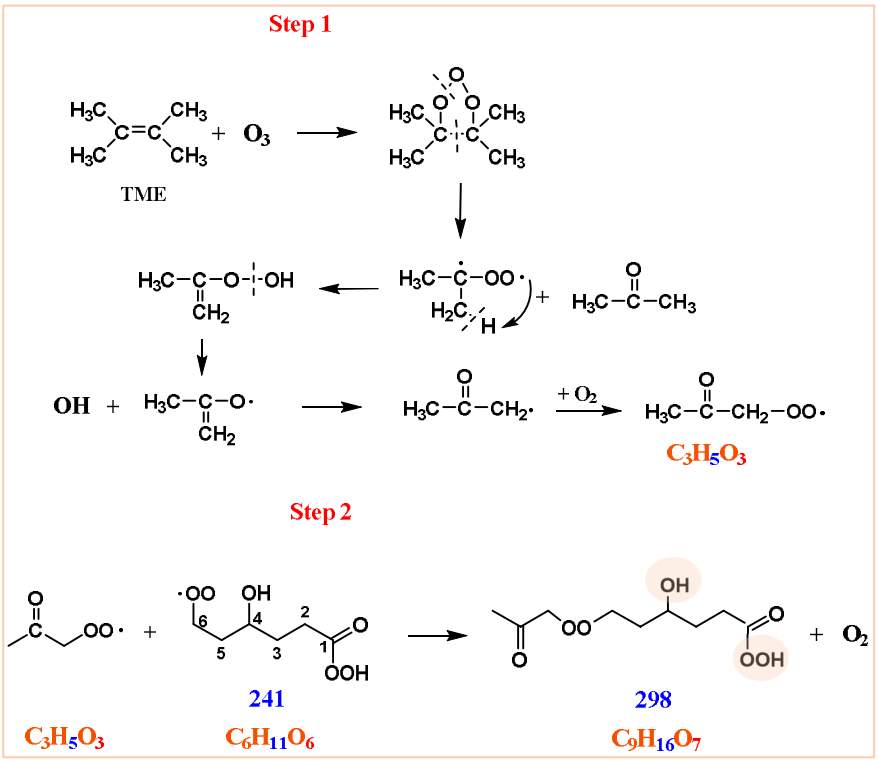


Figure S4: Production of oxidant OH in tetramethylethylene (TME) ozonolysis. The keto peroxy radical $C_3H_5O_3$ is a biproduct and reacts with hexanal derived peroxy radicals yielding closed shell products with nine C atoms; a pathway producing $C_9H_{16}O_7$ peroxide accretion product is shown as an example.

HOM accretion products ($C_{12}H_{22}O_{9\text{-}11}$)

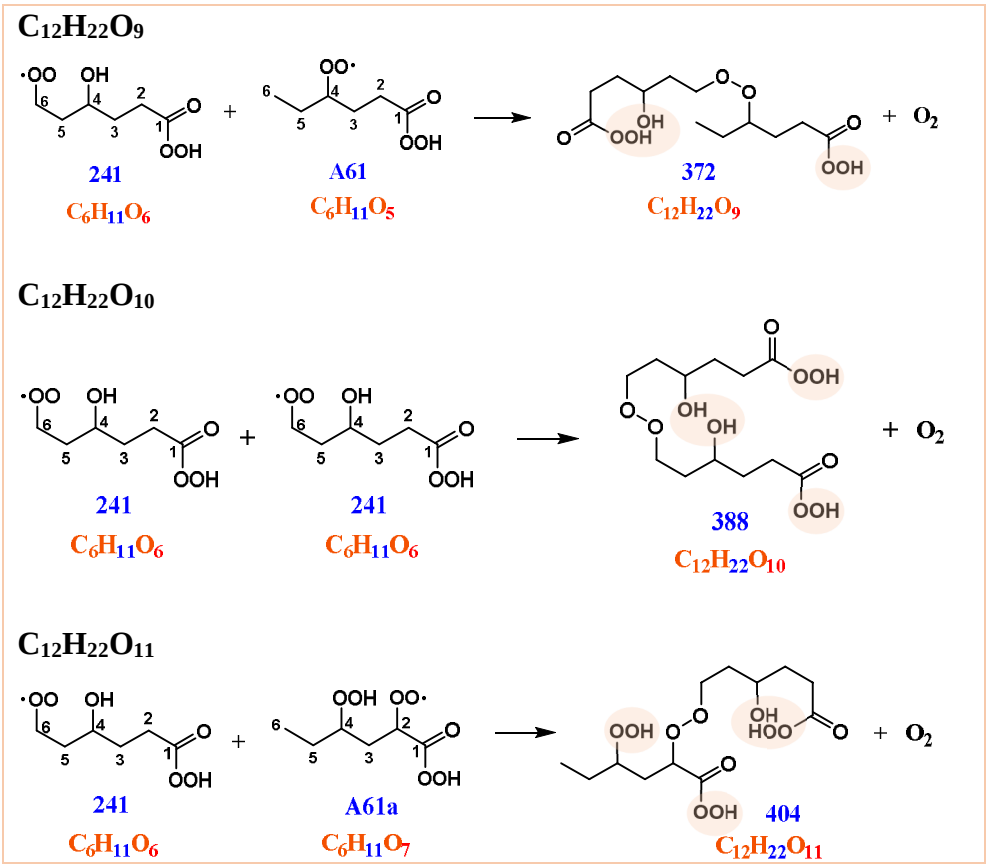


Figure S5: HOM accretion products ($C_{12}H_{22}O_{9\text{-}11}$) are formed by self and cross RO_2 + RO_2 reactions.

S6: Hexanal OH oxidation reaction in presence of CO

An additional set of hexanal + OH oxidation experiments are conducted with a variable CO concentration ranging from 4–324 ppm. The inclusion of CO in OH-initiated oxidation reaction is an additional source of HO_2 ($CO + OH \xrightarrow{O2} CO_2 + HO_2$) in the reactor. We adopt this technique to artificially increase the HO_2 concentration and achieve a control on RO_2 + HO_2 reactions leading to the formation of closed-shell $C_6H_{12}O_x$ (i.e., ROOH) products in our flow reactor. The resultant spectra with high-resolution peak fitting are shown in the Supplementary Figure S6. It is certain that the inclusion of CO in the reaction mixture introduce more complexity and can lead to an overall decrease in the product signals and can produce additional signals.

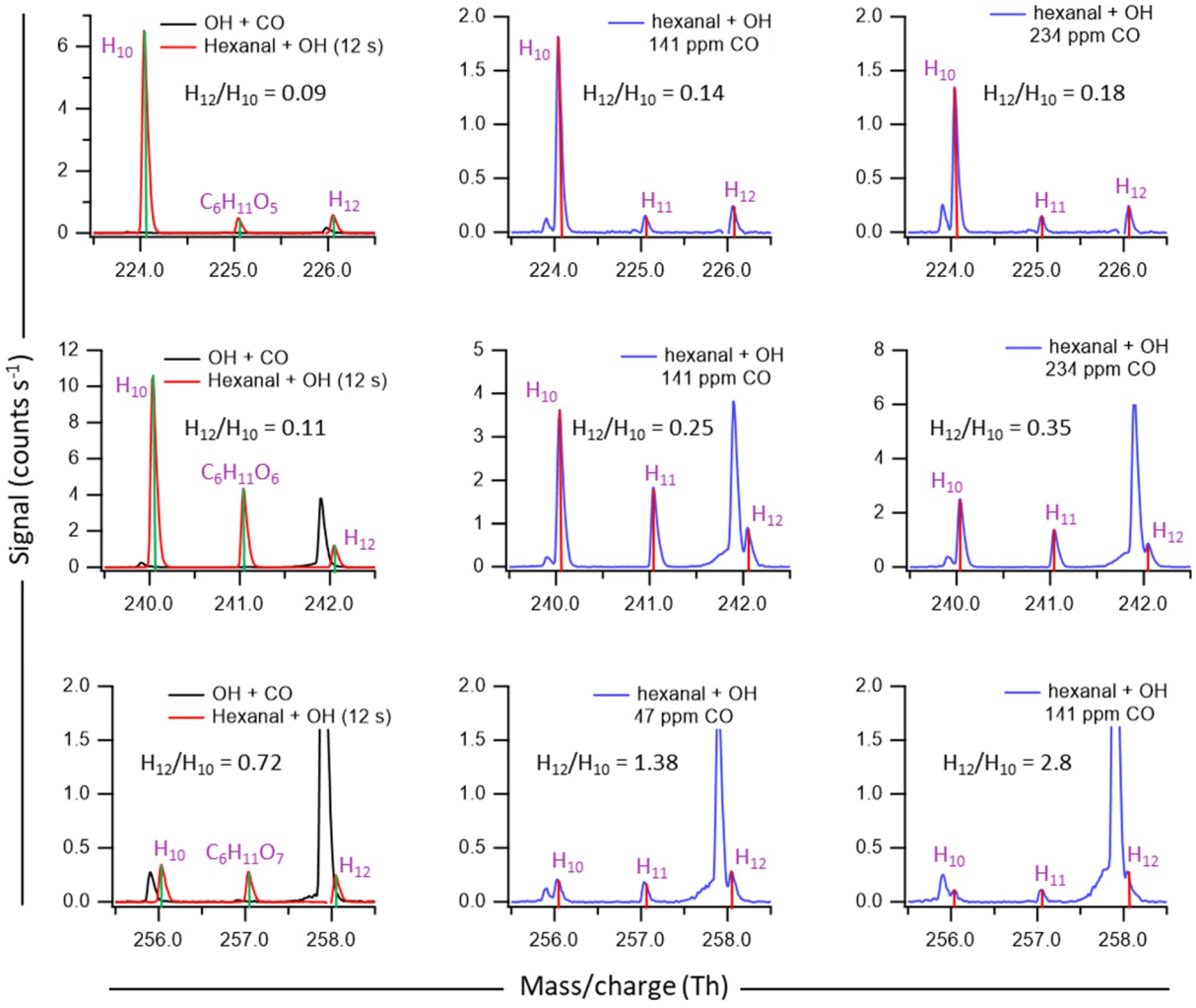


Figure S6: Mass spectra showing the key oxidation products ($C_6H_{10\text{-}12}O_{5\text{-}7}$) with high-resolution peak fitting in hexanal OH oxidation reaction in presence of variable concentrations of CO. TME ozonolysis (TME + O_3) is the source of oxidant OH. The left-most panel of the figure presents the spectra under conditions without hexanal (CO + OH) and without CO (hexanal + OH) added to the flow reactor.

While injecting CO, we conduct experiments with and without hexanal to be able to track any additional signals originating from OH oxidation where CO cylinder can be a source. Apparently, Figure S6 shows that significant background signals originating from CO + OH reaction, where TME ozonolysis is the source of OH, are present just left to our product peaks of interest (i.e., closed-shell products $C_6H_{10,12}O_{5\text{-}7}$ of hexanal OH oxidation). Despite of the presence of these background signals, high-resolution peak fitting of our mass spectrometry data allowed us to clearly resolve the closed-shell hexanal OH oxidation products and observe the ratio of $C_6H_{12}O_x$ to $C_6H_{10}O_x$ (i.e., H_{12}/H_{10}) product peaks in presence of variable CO concentrations. We see that with the increase of CO concentration, the H_{12}/H_{10} ratio is increased which supports that the RO_2 + HO_2 reaction can be likely source of closed-shell $C_6H_{12}O_x$ products.

S7: Kinetic modelling of HOM formation

Kinetic modelling using calculated rate constants is carried out using Kinetiscope Program[6,7] to estimate the time-scale of HOM formation. We include all oxidation initiation channels C1-C6 and the subsequent steps of the studied C1 and C4 channels in the simulation.

In our simulation, we also include bimolecular RO_2 + RO_2 and RO_2 + NO reactions with variable concentrations to see the potential of autoxidation processes in HOM formation under atmospheric conditions. Initial concentration of hexanal is set to 1 ppb (2.46×10^{10} molecules cm^{-3}), an average concentration in urban environment.[8] In higher aldehydes, the length of the carbon chain favors HOM formation tendency via autoxidation. Total concentration of aldehydes (hexanal-decanal) in Monti Cimini forest in Italy was measured to be 8.8 ppb (2.16×10^{11} molecules cm^{-3}).[9] We test this concentration as the higher limit of hexanal concentration to see the influence. A generic concentration of oxidant [OH]=1.0×10^7 molecules cm^{-3} is used. A variable concentration of NO (0.01 – 40 ppb, i.e., 2.46×10^8 – 9.84×10^{11} molecules cm^{-3}) is used to mimic the very clean to very high NO_x conditions. A generic value of [RO_2]=1.0×10^7 molecules cm^{-3} is used for VOC limited condition (high NO_x) and a higher value of [RO_2]=1.5×10^9 molecules cm^{-3} is used for NO_x limited condition. For pseudo-unimolecular O_2 addition reaction, we use a rate coefficient of 1×10^7 s^{-1}. Bimolecular rate coefficients for RO_2 + RO_2 and RO_2 + NO reactions are set to the generic values of 3.2×10^{-11} and 9.0×10^{-12} cm^3 $molecules^{-1}$ s^{-1} respectively.[10,11]

One example of the reaction steps is as follows. In this work, we do not study the further reactions of bimolecular (i.e., RO_2 + RO_2, RO_2 + NO, etc.) reaction products. Therefore, in the simulation, we term the bimolecular products as sinks (e.g., Sink_a in reaction step 14, Sink_b in reaction step 18, and so on).

1. Hexanal + OH => A_pr (aldehydic H-abstraction rate k=2.14×10^{-12} cm^3 $molecule^{-1}$ s^{-1})
2. A_pr + O_2 => A (pseudo unimolecular rate k=1×10^7 s^{-1})
3. A_pr => C_5H_{11} + CO (β-scission rate k=2.27×10^3 s^{-1})
4. Hexanal + OH => B_pr (α-H-abstraction rate k=2.66×10^{-14} cm^3 $molecule^{-1}$ s^{-1})
5. B_pr + O_2 => B
6. Hexanal + OH => C_pr (β-H-abstraction rate k=4.76×10^{-14} cm^3 $molecule^{-1}$ s^{-1})
7. C_pr + O_2 => C
8. Hexanal + OH => D_pr (γ-H-abstraction rate k=9.16×10^{-14} cm^3 $molecule^{-1}$ s^{-1})
9. D_pr + O_2 => D
10. Hexanal + OH => E_pr (δ-H-abstraction rate k=7.35×10^{-15} cm^3 $molecule^{-1}$ s^{-1})
11. E_pr + O_2 => E
12. Hexanal + OH => F_pr (primary H-abstraction rate k=7.27×10^{-15} cm^3 $molecule^{-1}$ s^{-1})
13. F_pr + O_2 => F
14. A + RO_2 => Sink_a (Alkyl peroxy bimolecular rate k=3.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1})
15. A + NO => Sink_aa (Bimolecular rate k=9.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1})
16. A => A61_pr (1,6-H-shift rate k=1.69×10^{-1} s^{-1})
17. A61_pr + O_2 => A61
18. A61 + RO_2 => Sink_b
19. A61 + NO => Sink_bb

20. A61 => A61a_pr (1,5-H-shift rate k=3.9x10^{-3} s^{-1})
21. A61a_pr + O_2 => A61a
22. A61 => A62 (H-scrambling rate k=3.27x10^{-6} s^{-1})
23. A62 => A62a6_pr (1,6-H-shift rate k=2.08 s^{-1})
24. A => A51_pr (1,5-H-shift rate k=3.49x10^{-2} s^{-1})
25. A51_pr + O_2 => A51
26. A51 + RO_2 => Sink_c
27. A51 + NO => Sink_cc
28. A51 => A51a5_pr (1,5-H-shift rate k=7.81x10^{-4} s^{-1})
29. A51a5_pr + O_2 => A51a5
30. A51 => A51a6_pr (1,6-H-shift rate k=2.77x10^{-5} s^{-1})
31. A51a6_pr + O_2 => A51a6
32. D + RO_2 => Sink_d
33. D + NO => Sink_dd
34. D => D61_pr (1,6-H-shift rate k=8.63x10^{-1} s^{-1})
35. D61_pr + O_2 => A62
36. A62 => A61 (H-scrambling rate k=6.92x10^{2} s^{-1})
37. D => D51_pr (1,5-H-shift rate k=3.91x10^{-2} s^{-1})
38. D51_pr + O_2 => D51
39. D51 => D52 (H-scrambling rate k=8.96x10^{1} s^{-1})
40. D52 + RO_2 => Sink_e
41. D52 + NO => Sink_ee
42. D52 => D52n_pr (1,6-H-shift rate k=1.38x10^{-1} s^{-1})
43. D52n_pr + O_2 => D52
44. D51 => D52n_pr (1,4-H-shift rate k=2.67x10^{-2} s^{-1})

The detailed results are given in Supplementary Table S4. For a cleaner environment (1 ppb=2.46 x 10^{10} molecules cm^{-3} hexanal, 0.1 ppb=2.46 x 10^{9} molecules cm^{-3} NO, and 1.0 x 10^{8} molecules cm^{-3} RO_2), referring to a product concentration of 3.0 x 10^{3} molecules cm^{-3}, simulation results show that the O_5 intermediates A61 and A51 from C1 channel appear at 0.3 s and 0.5 s respectively, while D52 from C4 channels appeared at 8.5 s of reaction time (see Supplementary Figure S7). The fastest O_7 HOM (A61a at 3.8 s) is associated with the C1 oxidation channel. On the other hand, the O_7 HOM (D52n) associated with C4 channel appear at 11.5 s of reaction time. After 10 s of reaction time, the O_5 intermediates A61 and A51 comes with the concentrations of 1.9 x 10^{6} and 3.4 x 10^{5} molecules cm^{-3} respectively while the concentration of D52 increases only slightly to 3.3 x 10^{3} molecules cm^{-3}. Among the O_7 HOM, A61a shows the highest concentration (3.2 x 10^{4} molecules cm^{-3}) where the concentration of D52n is 2.4 x 10^{3} molecules cm^{-3} at the end of the 10 s simulation reaction time (see light blue bars of Supplementary Figure S8a).

At this RO_2 and NO level, when we increase the hexanal concentration to 8.8 ppb, the O_5-intermediate and the O_7 HOM concentrations increase by a factor of 3 to 4 with the occurrence of A61a HOM concentration of 4.0 x 10^{3} molecules cm^{-3} as early as 1.7 s reaction time. At 10 s, the D52 intermediate and D52n HOM concentrations reach at 4.3 x 10^{3} and 8.7 x 10^{3} molecules cm^{-3} respectively (see blue bars of Supplementary Figure S8a).

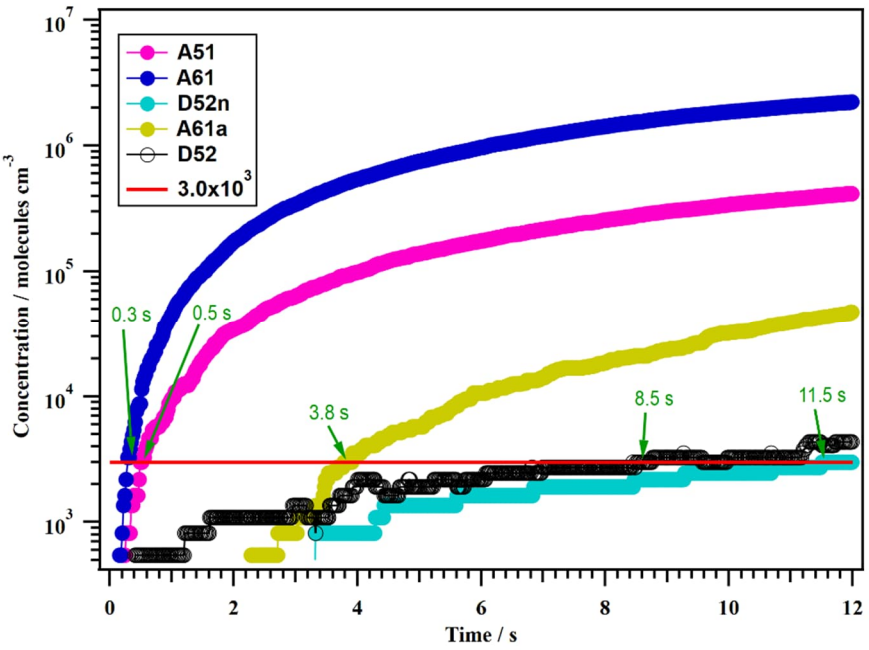


Figure S7: Time profile of hexanal oxidation products showing the appearance of different species with five to seven O atoms. Reactant concentrations: hexanal=1ppb (2.46×10^{10} molecules cm^{-3}), OH=1.0×10^7 molecules cm^{-3}, NO=0.1 ppb (2.46×10^9 molecules cm^{-3}), and RO_2=1.0×10^8 molecules cm^{-3}. The red straight line indicating an arbitrary reference concentration of 3.0×10^3 molecules cm^{-3} intersects the product curves at different reaction times (RTs). Among the intermediates with five O atoms, A61 reaches the reference concentration very fast at 0.3 s while A51 and D52 reaches at 0.5 and 8.5 s respectively. Among the species with seven O atoms, A61a the concentration level at 3.8 s while D52n at 11.5 s.

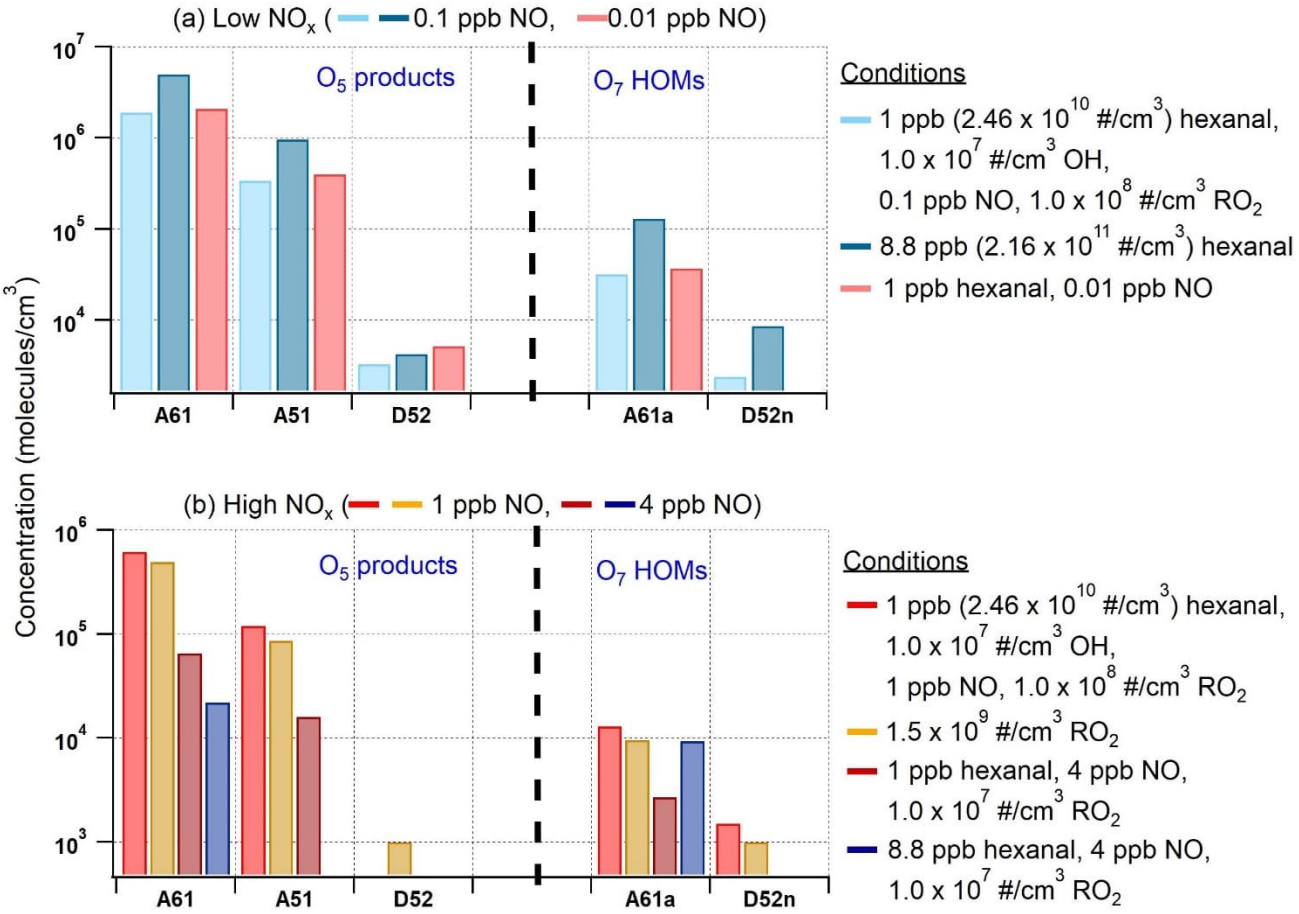


Figure S8: Kinetic simulation results showing the distribution of major autoxidation products in OH initiated hexanal oxidation reactions with variable precursor concentrations. The concentrations presented in the bar plots are extracted after 10 s of simulation time.

When the NO concentration is set to a one order of magnitude lower value (0.01 ppb), the product concentrations are increased only by a factor of up to 1.6. Increasing the NO concentration to 1 ppb, keeping the hexanal concentration at 1 ppb, and RO_2 concentration at 1.0×10^8 molecules cm^{-3}, we can still see the appearance of significant O_7 HOM concentrations resulting 1.3×10^4 and 1.5×10^3 molecules cm^{-3} for A61a and D52n respectively after 10 s reaction time (see red bars of Supplementary Figure S8b). Increasing the RO_2 concentration to 1.5×10^9 molecules cm^{-3} at this point, drops the O_7 HOM concentrations by a factor maximum 1.5 (see orange bars of Supplementary Figure S8b).

On the other hand, a NO concentration of 4 ppb stops the production of D52n HOM associated with C4 channel regardless of how big the hexanal concentration is while A61a HOM associated with C1 channel is still produced after 10 s of rection time (see Supplementary Figure S8b). When we set the NO concentration to the highest (40 ppb), it completely stops the formation of any O_5 intermediate and O_7 HOM after 10 s reaction time.

Supplementary Table S4: Kinetic modelling results of selected oxidation products corresponding to variable reactant concentrations of atmospheric relevance.

Reactant concentrations (#/cm3)				Product concentrations (#/cm3)				
				O_5-intermediate			O_7-HOM	
Hexanal	*OH*	*NO*	*RO2*	*A61*	*A51*	*D52*	*A61a*	*D52n*
2.46E+10 (1 ppb)	1.0E+7	2.46E+8 (.01 ppb)	1.0E+7	2.1E+6 [a](10 s)	4.0E+5 (10 s)	5.2E+3 (10 s)	3.7E+4 (10 s)	1.7E+3 (10 s)
				4.2E+6 (20 s)	8.3E+5 (20 s)	3.2E+3 (20 s)	1.6E+5 (20 s)	1.0E+4 (20 s)
			1.5E+9	1.6E+6 (10 s)	2.8E+5 (10 s)	1.8E+3 (10 s)	2.7E+4 (10 s)	2.4E+3 (10 s)
				2.3E+6 (20 s)	4.5E+5 (20 s)	1.3E+3 (20 s)	1.1E+5 (20 s)	5.2E+3 (20 s)
2.16E+11 (8.8 ppb)	1.0E+7	2.46E+8 (.01 ppb)	1.0E+7	6.2E+6 (10 s)	1.1E+6 (10 s)	8.7E+3 (10 s)	1.2E+5 (10 s)	1.1E+4 (10 s)
				7.1E+6 (20 s)	1.4E+6 (20 s)	0 (20 s)	3.98E+5 (20 s)	1.9E+4 (20 s)
			1.5E+9	4.1E+6 (10 s)	7.9E+5 (10 s)	0 (10 s)	1.2E+5 (10 s)	1.3E+4 (10 s)
				3.1E+6 (20 s)	6.1E+5 (20 s)	0 (20 s)	2.7E+5 (20 s)	1.3E+4 (20 s)
2.46E+10 (1 ppb)	1.0E+7	2.46E+9 (0.1 ppb)	1.0E+8	3.0E+3 [b](0.3 s)	3.0+3 (0.5 s)	3.0E+3 (8.5 s)	3.0E+3 (3.8 s)	3.0E+3 (11.5 s)
				1.9E+6 (10 s)	3.4E+5 (10 s)	3.3E+3 (10 s)	3.2E+4 (10 s)	2.4E+3 (10 s)
				3.2E+6 (20 s)	6.1E+5 (20 s)	2.2E+3 (20 s)	1.4E+5 (20 s)	6.8E+3 (20 s)
2.16E+11 (8.8 ppb)	1.0E+7	2.46E+9 (0.1 ppb)	1.0E+8	5.0E+6 (10 s)	9.7E+5 (10 s)	4.3E+3 (10 s)	1.3E+5 (10 s)	8.7E+3 (10 s)
				4.7E+6 (20 s)	9.4E+5 (20 s)	0 (20 s)	3.1E+5 (20 s)	1.3E+4 (20 s)
2.46E+10 (1 ppb)	1.0E+7	2.46E+10 (1 ppb)	1.0E+7	6.3E+5 (10 s)	1.2E+5 (10 s)	4.9E+2 (10 s)	1.2E+4 (10 s)	1.4E+3 (10 s)
				4.6E+5 (20 s)	9.7E+4 (20 s)	1.4E+3 (20 s)	3.5E+4 (20 s)	3.4E+3 (20 s)
			1.0E+8	6.2E+5 (10 s)	1.2E+5 (10 s)	4.9E+2 (10 s)	1.3E+4 (10 s)	1.5E+3 (10 s)
				4.5E+5 (20 s)	9.5E+4 (20 s)	1.9E+3 (20 s)	3.8E+4 (20 s)	3.5E+3 (20 s)
			1.5E+9	4.95E+5 (10 s)	8.7E+4 (10 s)	1.0E+3 (10 s)	9.6E+3 (10 s)	1.0E+3 (10 s)
				3.4E+5 (20 s)	6.7E+4 (20 s)	5.1E+2 (20 s)	3.0E+4 (20 s)	2.0E+3 (20 s)

[a] below the product concentrations in the parenthesis are the reaction times. [b] the reaction times colored in red indicate how fast the corresponding products appeared, in the simulation.

Supplementary Table S4 (continued)

Reactant concentrations (#/cm3)				Product concentrations (#/cm3)				
				O_5-intermediate			O_7-HOM	
Hexanal	*OH*	*NO*	*RO2*	*A61*	*A51*	*D52*	*A61a*	*D52n*
2.16E+11 (8.8 ppb)	1.0E+7	2.46E+10 (1 ppb)	1.0E+7	1.1E+6 [a](10 s)	2.2E+5 (10 s)	0 (10 s)	5.5E+4 (10 s)	2.4E+3 (10 s)
				1.6E+5 (20 s)	3.8E+4 (20 s)	0 (20 s)	7.5E+4 (20 s)	2.4E+3 (20 s)
			1.0E+8	1.0E+6 (10 s)	2.3E+5 (10 s)	0 (10 s)	3.6E+4 (10 s)	2.4E+3 (10 s)
				1.4E+5 (20 s)	3.4E+4 (20 s)	0 (20 s)	5.5E+4 (20 s)	2.4E+3 (20 s)
			1.5E+9	7.3E+5 (10 s)	1.6E+5 (10 s)	0 (10 s)	4.8E+4 (10 s)	2.4E+3 (10 s)
				7.0E+4 (20 s)	7.3E+3 (20 s)	0 (20 s)	5.3E+4 (20 s)	2.4E+3 (20 s)
2.46E+10 (1 ppb)	1.0E+7	9.84E+10 (4 ppb)	1.0E+7	6.5E+4 (10 s)	1.6E+4 (10 s)	0 (10 s)	2.7E+3 (10 s)	0 (10 s)
				3.4E+4 (20 s)	9.8E+3 (20 s)	1.2E+3 (20 s)	6.1E+3 (20 s)	0 (20 s)
2.16E+11 (8.8 ppb)	1.0E+7	9.84E+10 (4 ppb)	1.0E+7	2.2E+4 (10 s)	0 (10 s)	0 (10 s)	9.4E+3 (10 s)	0 (10 s)
				0 (20 s)	0 (20 s)	0 (20 s)	9.4E+3 (20 s)	0 (20 s)
2.46E+10 (1 ppb)	1.0E+7	9.84E+11 (40 ppb)	1.0E+7	0 (10 s)	0 (10 s)	0 (10 s)	0 (10 s)	0 (10 s)
				0 (20 s)	0 (20 s)	0 (20 s)	0 (20 s)	0 (20 s)
2.16E+11 (8.8 ppb)	1.0E+7	9.84E+11 (40 ppb)	1.0E+7	0 (10 s)	0 (10 s)	0 (10 s)	0 (10 s)	0 (10 s)
				0 (20 s)	0 (20 s)	0 (20 s)	0 (20 s)	0 (20 s)

[a] below the product concentrations in the parenthesis are the reaction times.

S8: Temperature dependency of H-shift rate coefficients

In general, the H-shift reaction which are key to autoxidation are highly dependent on temperature. To test this, we apply a temperature range of 260-330 K in the MESMER simulation. Given that all our H-shift reactions have positive barriers, we observe a positive temperature dependency in these reactions (see Supplementary Figure S9 and Table S5). The results show that at 310 K, the H-shift rate coefficients are increased by factors of 1.3-3 relative to the rate coefficients at 298.15 K. At 330 K, the factors increase to 2.3-8 for different H-shift reactions. The second H-shift reactions which by a subsequent O_2 addition reaction lead to O_7 HOM A61a′ and D52n′ (via C1 and C4 channels respectively) get faster by factors of 2.2 and 1.8 respectively at 310 K in terms of their rate coefficients. The factors for these H-shift reactions increase to 8 and 4.6 respectively at a temperature of 330 K.

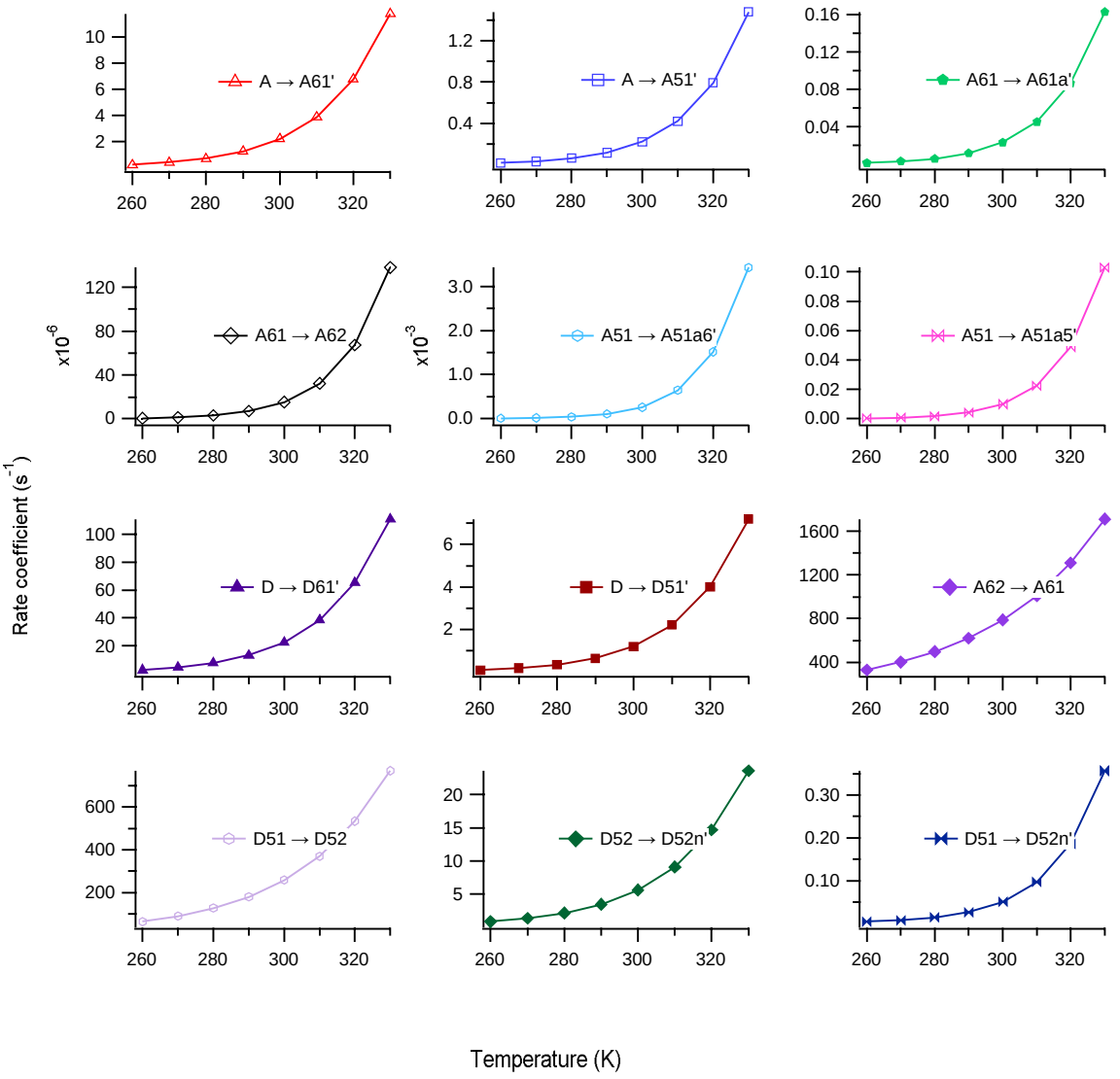


Figure S9: Positive temperature dependency of H-shift rate coefficients shown for the transition of different intermediates (e.g., A→A61′, A61→A62, etc.) along the path to HOM.

Supplementary Table S5: MESMER rate coefficients of H-shift reactions at different simulation temperatures.

Transition	Rate coefficients (s-1) at different temperatures							
	260 K	270 K	280 K	290 K	300 K	310 K	320 K	330 K
A→A61'	2.34×10^{-1}	4.10×10^{-1}	7.20×10^{-1}	1.26	2.22	3.89	6.79	1.18×10^{1}
A→A51'	1.67×10^{-2}	3.19×10^{-2}	6.09×10^{-2}	1.16×10^{-1}	2.21×10^{-1}	4.20×10^{-1}	7.92×10^{-1}	1.48
A61→A61a'	1.29×10^{-3}	2.76×10^{-3}	5.75×10^{-3}	1.17×10^{-2}	2.32×10^{-2}	4.53×10^{-2}	8.68×10^{-2}	1.63×10^{-1}
A61→A62	5.82×10^{-7}	1.38×10^{-6}	3.17×10^{-6}	7.07×10^{-6}	1.53×10^{-5}	3.25×10^{-5}	6.75×10^{-5}	1.38×10^{-4}

A51→A51a6'	$4.21X10^{-6}$	$1.29X10^{-5}$	$3.70X10^{-5}$	$1.01X10^{-4}$	$2.59X10^{-4}$	$6.39X10^{-4}$	$1.51X10^{-3}$	$3.43X10^{-3}$
A51→A51a5'	$2.65X10^{-4}$	$7.01X10^{-4}$	$1.77X10^{-3}$	$4.29X10^{-3}$	$9.99X10^{-3}$	$2.25X10^{-2}$	$4.89X10^{-2}$	$1.03X10^{-1}$
D→D61'	2.62	4.50	7.70	$1.32X10^{1}$	$2.26X10^{1}$	$3.85X10^{1}$	$6.54X10^{1}$	$1.11X10^{2}$
D→D51'	$9.15X10^{-2}$	$1.79X10^{-1}$	$3.44X10^{-1}$	$6.49X10^{-1}$	1.21	2.21	4.01	7.19
A62→A61	$3.30X10^{2}$	$4.03X10^{2}$	$4.97X10^{2}$	$6.22X10^{2}$	$7.88X10^{2}$	$1.01X10^{3}$	$1.31X10^{3}$	$1.71X10^{3}$
D51→D52	$6.44X10^{1}$	$9.02X10^{1}$	$1.27X10^{2}$	$1.81X10^{2}$	$2.58X10^{2}$	$3.70X10^{2}$	$5.33X10^{2}$	$7.69X10^{2}$
D52→D52n'	$8.56X10^{-1}$	1.36	2.18	3.49	5.63	9.08	$1.47X10^{1}$	$2.36X10^{1}$
D51→D52n'	$3.60X10^{-3}$	$6.93X10^{-3}$	$1.34X10^{-2}$	$2.59X10^{-2}$	$5.00X10^{-2}$	$9.66X10^{-2}$	$1.86X10^{-1}$	$3.57X10^{-1}$

S9: MESMER input for branching of D towards A62 and D51

(Unimolecular H-shift reactions followed by pseudo-unimolecular O_2 addition reactions)

The example MESMER input contains all the geometries, vibrational frequencies, and corrected relative energies of the studied species.

```
<?xml version="1.0" encoding="utf-8"?>
<?xml-stylesheet type='text/xsl' href='../../mesmer1.xsl'?>
<me:mesmer xmlns="http://www.xml-cml.org/schema"
xmlns:me="http://www.chem.leeds.ac.uk/mesmer"
        xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance">
  <me:title>Unimolecular reactions of D</me:title>
  <moleculeList>
    <molecule id="C6H11O3-D" spinMultiplicity="2">
      <atomArray>
  <atom id="a1" elementType="C" hydrogenCount="1" x3="-2.707588" y3="-0.240514"
z3="-0.364066"/>
  <atom id="a2" elementType="H" hydrogenCount="0" x3="-3.608384" y3="0.161997"
z3="-0.867971"/>
  <atom id="a3" elementType="O" hydrogenCount="0" x3="-2.470574" y3="-1.418154"
z3="-0.398732"/>
  <atom id="a4" elementType="C" hydrogenCount="2" x3="-1.868059" y3="0.786144"
z3="0.343080"/>
```

```
<atom id="a5" elementType="H" hydrogenCount="0" x3="-1.645911" y3="1.582943"
z3="-0.372793"/>
<atom id="a6" elementType="H" hydrogenCount="0" x3="-2.518628" y3="1.252841"
z3="1.089656"/>
<atom id="a7" elementType="C" hydrogenCount="2" x3="-0.604756" y3="0.243308"
z3="0.993245"/>
<atom id="a8" elementType="H" hydrogenCount="0" x3="-0.854162" y3="-0.627181"
z3="1.600523"/>
<atom id="a9" elementType="H" hydrogenCount="0" x3="-0.180523" y3="0.997016"
z3="1.656558"/>
<atom id="a10" elementType="C" hydrogenCount="1" x3="0.468040" y3="-0.184789"
z3="0.005911"/>
<atom id="a11" elementType="H" hydrogenCount="0" x3="0.061558" y3="-0.884551"
z3="-0.724064"/>
<atom id="a12" elementType="C" hydrogenCount="2" x3="1.699549" y3="-0.768724"
z3="0.672808"/>
<atom id="a13" elementType="H" hydrogenCount="0" x3="1.360710" y3="-1.600315"
z3="1.293524"/>
<atom id="a14" elementType="H" hydrogenCount="0" x3="2.116167" y3="-0.018070"
z3="1.346698"/>
<atom id="a15" elementType="C" hydrogenCount="3" x3="2.757726" y3="-1.250688"
z3="-0.310247"/>
<atom id="a16" elementType="H" hydrogenCount="0" x3="2.352979" y3="-2.009694"
z3="-0.981292"/>
<atom id="a17" elementType="H" hydrogenCount="0" x3="3.602403" y3="-1.688787"
z3="0.219709"/>
<atom id="a18" elementType="H" hydrogenCount="0" x3="3.134094" y3="-0.429746"
z3="-0.919232"/>
<atom id="a19" elementType="O" hydrogenCount="0" x3="0.840050" y3="0.948129"
z3="-0.849279"/>
<atom id="a20" elementType="O" hydrogenCount="0" x3="1.344302" y3="1.939415"
z3="-0.175202"/>
</atomArray>
<bondArray>
<bond atomRefs2="a16 a15" order="1"/>
<bond atomRefs2="a18 a15" order="1"/>
```

```
<bond atomRefs2="a2 a1" order="1"/>
<bond atomRefs2="a19 a20" order="1"/>
<bond atomRefs2="a19 a10" order="1"/>
<bond atomRefs2="a11 a10" order="1"/>
<bond atomRefs2="a3 a1" order="2"/>
<bond atomRefs2="a5 a4" order="1"/>
<bond atomRefs2="a1 a4" order="1"/>
<bond atomRefs2="a15 a17" order="1"/>
<bond atomRefs2="a15 a12" order="1"/>
<bond atomRefs2="a10 a12" order="1"/>
<bond atomRefs2="a10 a7" order="1"/>
<bond atomRefs2="a4 a7" order="1"/>
<bond atomRefs2="a4 a6" order="1"/>
<bond atomRefs2="a12 a13" order="1"/>
<bond atomRefs2="a12 a14" order="1"/>
<bond atomRefs2="a7 a8" order="1"/>
<bond atomRefs2="a7 a9" order="1"/>
</bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0.0</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.082 0.033 0.027</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">
```

```
392             440.60 73.15 93.23 134.47 138.80 200.70 220.01 245.83 310.61 320.21 398.72
393     485.44 593.66 667.65 725.42 780.58 821.11 871.50 939.58 949.90 995.34 1055.29 1068.61
394     1125.72 1137.97 1163.79 1220.81 1245.96 1270.27 1322.76 1332.17 1383.56 1397.28
395     1411.41 1420.92 1426.98 1429.49 1453.80 1471.02 1486.75 1506.65 1511.84 1838.30
396     2914.42 3046.12 3053.62 3061.54 3074.92 3084.32 3098.48 3112.41 3126.28 3131.10
397     3136.97
398           </array>
399         </property>
400         <property dictRef="me:MW">
401           <scalar>131.15</scalar>
402         </property>
403         <property dictRef="me:epsilon">
404           <scalar>343.0</scalar>
405         </property>
406         <property dictRef="me:sigma">
407           <scalar>6.25</scalar>
408         </property>
409         <property dictRef="me:spinMultiplicity">
410           <scalar>2</scalar>
411         </property>
412       </propertyList>
413       <me:energyTransferModel xsi:type="me:ExponentialDown">
414         <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
415       </me:energyTransferModel>
416     </molecule>
417
418     <molecule id="D_1-6-aldHshift-TS">
419       <atomArray>
420   <atom id="a1" elementType="C" hydrogenCount="0" x3="2.171388" y3="0.048934" z3="-
421   0.247665"/>
422   <atom id="a2" elementType="O" hydrogenCount="0" x3="3.287959" y3="0.088910" z3="-
423   0.627350"/>
```

```
<atom id="a3" elementType="C" hydrogenCount="2" x3="1.255292" y3="-1.160226"
z3="-0.175406"/>
<atom id="a4" elementType="H" hydrogenCount="0" x3="0.783889" y3="-1.241738"
z3="-1.157544"/>
<atom id="a5" elementType="H" hydrogenCount="0" x3="1.884981" y3="-2.039904"
z3="-0.040988"/>
<atom id="a6" elementType="C" hydrogenCount="2" x3="0.214830" y3="-1.022117"
z3="0.936377"/>
<atom id="a7" elementType="H" hydrogenCount="0" x3="0.708013" y3="-0.665626"
z3="1.840369"/>
<atom id="a8" elementType="H" hydrogenCount="0" x3="-0.192406" y3="-2.005209"
z3="1.173172"/>
<atom id="a9" elementType="C" hydrogenCount="1" x3="-0.947718" y3="-0.084169"
z3="0.587824"/>
<atom id="a10" elementType="H" hydrogenCount="0" x3="-1.398134" y3="0.286239"
z3="1.513740"/>
<atom id="a11" elementType="C" hydrogenCount="2" x3="-2.017656" y3="-0.741095"
z3="-0.271303"/>
<atom id="a12" elementType="H" hydrogenCount="0" x3="-2.365067" y3="-1.627128"
z3="0.263552"/>
<atom id="a13" elementType="H" hydrogenCount="0" x3="-1.565969" y3="-1.092450"
z3="-1.202612"/>
<atom id="a14" elementType="C" hydrogenCount="3" x3="-3.197340" y3="0.172959"
z3="-0.577401"/>
<atom id="a15" elementType="H" hydrogenCount="0" x3="-3.661687" y3="0.527370"
z3="0.344152"/>
<atom id="a16" elementType="H" hydrogenCount="0" x3="-3.955731" y3="-0.356938"
z3="-1.152644"/>
<atom id="a17" elementType="H" hydrogenCount="0" x3="-2.882706" y3="1.044036"
z3="-1.148722"/>
<atom id="a18" elementType="O" hydrogenCount="0" x3="-0.491500" y3="1.041580"
z3="-0.166657"/>
<atom id="a19" elementType="O" hydrogenCount="1" x3="0.485120" y3="1.720209"
z3="0.528334"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="1.519405" y3="1.080043"
z3="0.178357"/>
</atomArray>
```

```
461     <bondArray>
462      <bond atomRefs2="a13 a11" order="1"/>
463      <bond atomRefs2="a4 a3" order="1"/>
464      <bond atomRefs2="a16 a14" order="1"/>
465      <bond atomRefs2="a17 a14" order="1"/>
466      <bond atomRefs2="a2 a1" order="2"/>
467      <bond atomRefs2="a14 a11" order="1"/>
468      <bond atomRefs2="a14 a15" order="1"/>
469      <bond atomRefs2="a11 a12" order="1"/>
470      <bond atomRefs2="a11 a9" order="1"/>
471      <bond atomRefs2="a1 a3" order="1"/>
472      <bond atomRefs2="a3 a5" order="1"/>
473      <bond atomRefs2="a3 a6" order="1"/>
474      <bond atomRefs2="a18 a19" order="1"/>
475      <bond atomRefs2="a18 a9" order="1"/>
476      <bond atomRefs2="a20 a19" order="1"/>
477      <bond atomRefs2="a9 a6" order="1"/>
478      <bond atomRefs2="a9 a10" order="1"/>
479      <bond atomRefs2="a6 a8" order="1"/>
480      <bond atomRefs2="a6 a7" order="1"/>
481     </bondArray>
482        <propertyList>
483          <property dictRef="me:ZPE">
484            <scalar units="kcal/mol">18.67</scalar>
485          </property>
486          <property dictRef="me:rotConsts">
487            <array units="cm-1">
488              0.104 0.031 0.028
489            </array>
490          </property>
```

```
491         <property dictRef="me:symmetryNumber">
492           <scalar>1</scalar>
493         </property>
494         <property dictRef="me:vibFreqs">
495           <array units="cm-1">
496             47.77 97.38 129.80 207.11 228.21 263.19 292.95 338.32 386.36 390.63 452.66
497 510.86 597.23 609.74 766.99 827.35 848.41 874.73 951.05 978.22 1017.83 1061.22 1080.44
498 1088.88 1097.35 1155.81 1183.00 1228.56 1256.97 1305.59 1332.93 1349.51 1371.85
499 1396.76 1419.91 1425.35 1447.49 1485.23 1500.47 1503.50 1513.27 1607.94 1925.47
500 3039.22 3050.59 3054.34 3065.86 3077.43 3092.19 3118.14 3120.90 3124.09 3144.45
501           </array>
502         </property>
503         <property dictRef="me:MW">
504           <scalar>131.15</scalar>
505         </property>
506         <property dictRef="me:imFreqs">
507           <scalar units="cm-1">1805.75</scalar>
508         </property>
509         <property dictRef="me:spinMultiplicity">
510           <scalar>2</scalar>
511         </property>
512       </propertyList>
513       <me:DOSCMethod xsi:type="ClassicalRotors"/>
514     </molecule>
515
516 <molecule id="D61_pr">
517       <atomArray>
518   <atom id="a1" elementType="C" hydrogenCount="0" x3="-2.591004" y3="-0.009787"
519 z3="-0.357272"/>
520   <atom id="a2" elementType="O" hydrogenCount="0" x3="-2.535322" y3="0.972415"
521 z3="0.292868"/>
522   <atom id="a3" elementType="C" hydrogenCount="2" x3="-1.765467" y3="-1.268641"
523 z3="-0.278670"/>
```

```
<atom id="a4" elementType="H" hydrogenCount="0" x3="-2.448039" y3="-1.998674"
z3="0.165560"/>
<atom id="a5" elementType="H" hydrogenCount="0" x3="-1.591793" y3="-1.610412"
z3="-1.299722"/>
<atom id="a6" elementType="C" hydrogenCount="2" x3="-0.465352" y3="-1.171123"
z3="0.520995"/>
<atom id="a7" elementType="H" hydrogenCount="0" x3="-0.157903" y3="-2.179492"
z3="0.802600"/>
<atom id="a8" elementType="H" hydrogenCount="0" x3="-0.633886" y3="-0.622273"
z3="1.448795"/>
<atom id="a9" elementType="C" hydrogenCount="1" x3="0.679564" y3="-0.528312"
z3="-0.255168"/>
<atom id="a10" elementType="H" hydrogenCount="0" x3="0.818642" y3="-1.070521"
z3="-1.197097"/>
<atom id="a11" elementType="C" hydrogenCount="2" x3="1.989311" y3="-0.538171"
z3="0.521288"/>
<atom id="a12" elementType="H" hydrogenCount="0" x3="2.217204" y3="-1.577451"
z3="0.770015"/>
<atom id="a13" elementType="H" hydrogenCount="0" x3="1.842062" y3="-0.011980"
z3="1.465088"/>
<atom id="a14" elementType="C" hydrogenCount="3" x3="3.146410" y3="0.081218"
z3="-0.249032"/>
<atom id="a15" elementType="H" hydrogenCount="0" x3="3.312520" y3="-0.437604"
z3="-1.194910"/>
<atom id="a16" elementType="H" hydrogenCount="0" x3="4.068149" y3="0.026669"
z3="0.329198"/>
<atom id="a17" elementType="H" hydrogenCount="0" x3="2.945867" y3="1.127456"
z3="-0.472606"/>
<atom id="a18" elementType="O" hydrogenCount="0" x3="0.335468" y3="0.765424"
z3="-0.740110"/>
<atom id="a19" elementType="O" hydrogenCount="1" x3="0.247042" y3="1.667694"
z3="0.357754"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="-0.711102" y3="1.718909"
z3="0.486140"/>
</atomArray>
<bondArray>
```

```
560       <bond atomRefs2="a5 a3" order="1"/>
561       <bond atomRefs2="a10 a9" order="1"/>
562       <bond atomRefs2="a15 a14" order="1"/>
563       <bond atomRefs2="a18 a9" order="1"/>
564       <bond atomRefs2="a18 a19" order="1"/>
565       <bond atomRefs2="a17 a14" order="1"/>
566       <bond atomRefs2="a1 a3" order="1"/>
567       <bond atomRefs2="a1 a2" order="2"/>
568       <bond atomRefs2="a3 a4" order="1"/>
569       <bond atomRefs2="a3 a6" order="1"/>
570       <bond atomRefs2="a9 a6" order="1"/>
571       <bond atomRefs2="a9 a11" order="1"/>
572       <bond atomRefs2="a14 a16" order="1"/>
573       <bond atomRefs2="a14 a11" order="1"/>
574       <bond atomRefs2="a19 a20" order="1"/>
575       <bond atomRefs2="a6 a7" order="1"/>
576       <bond atomRefs2="a6 a8" order="1"/>
577       <bond atomRefs2="a11 a12" order="1"/>
578       <bond atomRefs2="a11 a13" order="1"/>
579     </bondArray>
580         <propertyList>
581           <property dictRef="me:ZPE">
582             <scalar units="kcal/mol">2.87</scalar>
583           </property>
584           <property dictRef="me:rotConsts">
585             <array units="cm-1">
586               0.102 0.035 0.029
587             </array>
588           </property>
589           <property dictRef="me:symmetryNumber">
```

```
590           <scalar>1</scalar>
591         </property>
592         <property dictRef="me:vibFreqs">
593           <array units="cm-1">
594             67.19 82.78 121.62 150.00 182.52 189.81 207.85 265.10 304.05 321.73 401.49
595 482.85 522.10 582.51 647.59 764.50 795.32 840.28 874.94 936.86 960.32 1016.85 1024.01
596 1064.20 1097.54 1138.90 1150.35 1226.58 1243.76 1306.59 1316.70 1348.76 1377.98
597 1397.48 1409.89 1425.80 1444.43 1457.39 1479.98 1490.94 1503.94 1511.67 1941.48
598 3035.93 3050.65 3054.16 3059.27 3069.35 3099.99 3106.20 3116.03 3122.78 3142.14
599 3723.51
600           </array>
601         </property>
602         <property dictRef="me:MW">
603           <scalar>131.15</scalar>
604         </property>
605         <property dictRef="me:epsilon">
606           <scalar>343.0</scalar>
607         </property>
608         <property dictRef="me:sigma">
609           <scalar>6.25</scalar>
610         </property>
611         <property dictRef="me:spinMultiplicity">
612           <scalar>2</scalar>
613         </property>
614       </propertyList>
615       <me:energyTransferModel xsi:type="me:ExponentialDown">
616         <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
617       </me:energyTransferModel>
618     </molecule>
619
620 <molecule id="C6H11O5-A62">
621       <atomArray>
```

```
<atom id="a1" elementType="H" hydrogenCount="0" x3="-3.299530" y3="-0.442021"
z3="-1.556808"/>
<atom id="a2" elementType="C" hydrogenCount="3" x3="-3.373600" y3="-1.102928"
z3="-0.695105"/>
<atom id="a3" elementType="H" hydrogenCount="0" x3="-4.133145" y3="-0.698268"
z3="-0.024688"/>
<atom id="a4" elementType="H" hydrogenCount="0" x3="-3.716512" y3="-2.077519"
z3="-1.040749"/>
<atom id="a5" elementType="C" hydrogenCount="2" x3="-2.030843" y3="-1.220494"
z3="0.014110"/>
<atom id="a6" elementType="H" hydrogenCount="0" x3="-1.300866" y3="-1.674410"
z3="-0.659900"/>
<atom id="a7" elementType="H" hydrogenCount="0" x3="-2.118514" y3="-1.884179"
z3="0.876947"/>
<atom id="a8" elementType="C" hydrogenCount="1" x3="-1.497534" y3="0.120203"
z3="0.504450"/>
<atom id="a9" elementType="H" hydrogenCount="0" x3="-2.301087" y3="0.661709"
z3="1.012412"/>
<atom id="a10" elementType="C" hydrogenCount="2" x3="-0.316526" y3="0.009499"
z3="1.471109"/>
<atom id="a11" elementType="H" hydrogenCount="0" x3="-0.643120" y3="-0.579497"
z3="2.328861"/>
<atom id="a12" elementType="H" hydrogenCount="0" x3="-0.070561" y3="1.001090"
z3="1.850716"/>
<atom id="a13" elementType="C" hydrogenCount="2" x3="0.929836" y3="-0.644360"
z3="0.882652"/>
<atom id="a14" elementType="H" hydrogenCount="0" x3="0.697788" y3="-1.521864"
z3="0.282847"/>
<atom id="a15" elementType="H" hydrogenCount="0" x3="1.585464" y3="-1.012316"
z3="1.675832"/>
<atom id="a16" elementType="C" hydrogenCount="0" x3="1.764972" y3="0.290348"
z3="0.067524"/>
<atom id="a17" elementType="O" hydrogenCount="0" x3="1.705666" y3="1.473157"
z3="-0.019954"/>
<atom id="a18" elementType="O" hydrogenCount="0" x3="-1.156013" y3="0.839719"
z3="-0.671506"/>
```

```
<atom id="a19" elementType="O" hydrogenCount="1" x3="-1.021099" y3="2.215035"
z3="-0.342899"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="-0.060584" y3="2.294490"
z3="-0.244798"/>
<atom id="a21" elementType="O" hydrogenCount="0" x3="2.830727" y3="-0.291473"
z3="-0.675756"/>
<atom id="a22" elementType="O" hydrogenCount="0" x3="2.953572" y3="-1.584040"
z3="-0.536024"/>
</atomArray>
<bondArray>
<bond atomRefs2="a1 a2" order="1"/>
<bond atomRefs2="a4 a2" order="1"/>
<bond atomRefs2="a2 a3" order="1"/>
<bond atomRefs2="a2 a5" order="1"/>
<bond atomRefs2="a21 a22" order="1"/>
<bond atomRefs2="a21 a16" order="1"/>
<bond atomRefs2="a18 a19" order="1"/>
<bond atomRefs2="a18 a8" order="1"/>
<bond atomRefs2="a6 a5" order="1"/>
<bond atomRefs2="a19 a20" order="1"/>
<bond atomRefs2="a17 a16" order="2"/>
<bond atomRefs2="a5 a8" order="1"/>
<bond atomRefs2="a5 a7" order="1"/>
<bond atomRefs2="a16 a13" order="1"/>
<bond atomRefs2="a14 a13" order="1"/>
<bond atomRefs2="a8 a9" order="1"/>
<bond atomRefs2="a8 a10" order="1"/>
<bond atomRefs2="a13 a10" order="1"/>
<bond atomRefs2="a13 a15" order="1"/>
<bond atomRefs2="a10 a12" order="1"/>
<bond atomRefs2="a10 a11" order="1"/>
</bondArray>
```

```
      <propertyList>
        <property dictRef="me:ZPE">
          <scalar units="kcal/mol">-30.87</scalar>
        </property>
        <property dictRef="me:rotConsts">
          <array units="cm-1">
            0.055 0.022 0.019
          </array>
        </property>
        <property dictRef="me:symmetryNumber">
          <scalar>1</scalar>
        </property>
        <property dictRef="me:vibFreqs">
          <array units="cm-1">
            34.92 52.51 80.17 119.38 160.41 162.94 197.91 214.93 236.09 284.59 323.91 340.88
414.11 496.53 511.37 517.24 569.86 599.10 643.02 765.57 770.38 870.19 903.98 938.47
986.09 1011.86 1039.09 1063.16 1076.55 1090.81 1143.06 1190.91 1232.95 1247.85
1267.81 1312.73 1337.83 1375.52 1392.80 1405.25 1423.88 1424.48 1452.48 1465.56
1485.75 1494.79 1505.18 1513.85 1897.98 3042.61 3052.68 3054.11 3070.71 3080.88
3091.96 3119.83 3124.56 3138.43 3143.35 3708.15
          </array>
        </property>
        <property dictRef="me:MW">
          <scalar>163.15</scalar>
        </property>
        <property dictRef="me:spinMultiplicity">
          <scalar>2</scalar>
        </property>
      </propertyList>
      <me:DOSCMethod xsi:type="ClassicalRotors"/>
    </molecule>
```

```
<molecule id="D_1-5Hshift_RR-TS">
    <atomArray>
  <atom id="a1" elementType="C" hydrogenCount="1" x3="-2.629360" y3="-0.283299"
z3="-0.224138"/>
  <atom id="a2" elementType="H" hydrogenCount="0" x3="-3.605403" y3="0.232118"
z3="-0.279199"/>
  <atom id="a3" elementType="O" hydrogenCount="0" x3="-2.379290" y3="-1.206994"
z3="-0.964757"/>
  <atom id="a4" elementType="C" hydrogenCount="1" x3="-1.679910" y3="0.255775"
z3="0.756364"/>
  <atom id="a5" elementType="C" hydrogenCount="2" x3="-0.426800" y3="-0.518010"
z3="1.029928"/>
  <atom id="a6" elementType="H" hydrogenCount="0" x3="-0.612316" y3="-1.586320"
z3="0.903206"/>
  <atom id="a7" elementType="H" hydrogenCount="0" x3="-0.072637" y3="-0.335185"
z3="2.043298"/>
  <atom id="a8" elementType="C" hydrogenCount="1" x3="0.710774" y3="-0.147623"
z3="0.043884"/>
  <atom id="a9" elementType="H" hydrogenCount="0" x3="0.415466" y3="-0.440234"
z3="-0.966317"/>
  <atom id="a10" elementType="C" hydrogenCount="2" x3="2.048733" y3="-0.743659"
z3="0.428315"/>
  <atom id="a11" elementType="H" hydrogenCount="0" x3="1.899804" y3="-1.816392"
z3="0.563595"/>
  <atom id="a12" elementType="H" hydrogenCount="0" x3="2.342624" y3="-0.342239"
z3="1.401001"/>
  <atom id="a13" elementType="C" hydrogenCount="3" x3="3.139806" y3="-0.491322"
z3="-0.604064"/>
  <atom id="a14" elementType="H" hydrogenCount="0" x3="2.865342" y3="-0.913407"
z3="-1.571581"/>
  <atom id="a15" elementType="H" hydrogenCount="0" x3="4.078143" y3="-0.948501"
z3="-0.292792"/>
  <atom id="a16" elementType="H" hydrogenCount="0" x3="3.311413" y3="0.575487"
z3="-0.739574"/>
  <atom id="a17" elementType="O" hydrogenCount="0" x3="0.839784" y3="1.267191"
z3="0.080579"/>
```

```
<atom id="a18" elementType="O" hydrogenCount="1" x3="-0.251036" y3="1.824014"
z3="-0.523727"/>
<atom id="a19" elementType="H" hydrogenCount="0" x3="-2.130636" y3="0.798245"
z3="1.581944"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="-1.146920" y3="1.271563"
z3="0.037928"/>
</atomArray>
<bondArray>
<bond atomRefs2="a14 a13" order="1"/>
<bond atomRefs2="a9 a8" order="1"/>
<bond atomRefs2="a3 a1" order="2"/>
<bond atomRefs2="a16 a13" order="1"/>
<bond atomRefs2="a13 a15" order="1"/>
<bond atomRefs2="a13 a10" order="1"/>
<bond atomRefs2="a18 a20" order="1"/>
<bond atomRefs2="a18 a17" order="1"/>
<bond atomRefs2="a2 a1" order="1"/>
<bond atomRefs2="a1 a4" order="1"/>
<bond atomRefs2="a8 a17" order="1"/>
<bond atomRefs2="a8 a10" order="1"/>
<bond atomRefs2="a8 a5" order="1"/>
<bond atomRefs2="a10 a11" order="1"/>
<bond atomRefs2="a10 a12" order="1"/>
<bond atomRefs2="a4 a5" order="1"/>
<bond atomRefs2="a4 a19" order="1"/>
<bond atomRefs2="a6 a5" order="1"/>
<bond atomRefs2="a5 a7" order="1"/>
</bondArray>
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kcal/mol">21.09</scalar>
```

```
789          </property>
790          <property dictRef="me:rotConsts">
791            <array units="cm-1">
792              0.090 0.032 0.029
793            </array>
794          </property>
795          <property dictRef="me:symmetryNumber">
796            <scalar>1</scalar>
797          </property>
798          <property dictRef="me:vibFreqs">
799            <array units="cm-1">
800              58.88 101.46 102.90 173.21 209.10 240.96 270.76 307.56 381.97 444.39 502.42
801    521.99 643.83 676.41 769.49 782.12 879.16 900.15 953.23 970.22 1005.16 1048.14 1082.02
802    1114.17 1117.14 1129.50 1161.18 1174.34 1236.98 1288.13 1317.10 1350.06 1366.73
803    1393.98 1415.39 1425.05 1425.95 1463.56 1486.74 1504.89 1512.57 1556.93 1764.84
804    2943.00 3054.68 3055.75 3063.63 3071.97 3097.64 3127.11 3129.13 3139.53 3157.90
805            </array>
806          </property>
807          <property dictRef="me:MW">
808            <scalar>131.15</scalar>
809          </property>
810                    <property dictRef="me:imFreqs">
811            <scalar units="cm-1">1935.56</scalar>
812          </property>
813          <property dictRef="me:spinMultiplicity">
814            <scalar>2</scalar>
815          </property>
816        </propertyList>
817        <me:DOSCMethod xsi:type="ClassicalRotors"/>
818      </molecule>
819
820            <molecule id="D51_pr">
```

```
821         <atomArray>
822       <atom id="a1" elementType="C" hydrogenCount="1" x3="2.424466" y3="-0.404465"
823     z3="-0.601898"/>
824       <atom id="a2" elementType="H" hydrogenCount="0" x3="3.032948" y3="-0.770016"
825     z3="-1.443473"/>
826       <atom id="a3" elementType="O" hydrogenCount="0" x3="2.723837" y3="0.648707" z3="-
827     0.043837"/>
828       <atom id="a4" elementType="C" hydrogenCount="1" x3="1.300936" y3="-1.202309"
829     z3="-0.232773"/>
830       <atom id="a5" elementType="H" hydrogenCount="0" x3="1.058882" y3="-2.042782"
831     z3="-0.871849"/>
832       <atom id="a6" elementType="C" hydrogenCount="2" x3="0.477540" y3="-0.948298"
833     z3="0.971107"/>
834       <atom id="a7" elementType="H" hydrogenCount="0" x3="1.047613" y3="-0.370167"
835     z3="1.698014"/>
836       <atom id="a8" elementType="H" hydrogenCount="0" x3="0.226104" y3="-1.912137"
837     z3="1.420528"/>
838       <atom id="a9" elementType="C" hydrogenCount="1" x3="-0.863829" y3="-0.204765"
839     z3="0.741736"/>
840       <atom id="a10" elementType="H" hydrogenCount="0" x3="-1.452279" y3="-0.327984"
841     z3="1.655178"/>
842       <atom id="a11" elementType="C" hydrogenCount="2" x3="-1.662375" y3="-0.725877"
843     z3="-0.444346"/>
844       <atom id="a12" elementType="H" hydrogenCount="0" x3="-1.750810" y3="-1.810396"
845     z3="-0.336367"/>
846       <atom id="a13" elementType="H" hydrogenCount="0" x3="-1.096320" y3="-0.541996"
847     z3="-1.358230"/>
848       <atom id="a14" elementType="C" hydrogenCount="3" x3="-3.041888" y3="-0.092880"
849     z3="-0.551505"/>
850       <atom id="a15" elementType="H" hydrogenCount="0" x3="-3.633506" y3="-0.282963"
851     z3="0.345800"/>
852       <atom id="a16" elementType="H" hydrogenCount="0" x3="-3.587949" y3="-0.494979"
853     z3="-1.404139"/>
854       <atom id="a17" elementType="H" hydrogenCount="0" x3="-2.960558" y3="0.985542"
855     z3="-0.676653"/>
856       <atom id="a18" elementType="O" hydrogenCount="0" x3="-0.689331" y3="1.200034"
857     z3="0.724140"/>
```

```
<atom id="a19" elementType="O" hydrogenCount="1" x3="0.012856" y3="1.579026"
z3="-0.453707"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="0.927872" y3="1.617310"
z3="-0.135504"/>
</atomArray>
<bondArray>
<bond atomRefs2="a2 a1" order="1"/>
<bond atomRefs2="a16 a14" order="1"/>
<bond atomRefs2="a13 a11" order="1"/>
<bond atomRefs2="a5 a4" order="1"/>
<bond atomRefs2="a17 a14" order="1"/>
<bond atomRefs2="a1 a4" order="1"/>
<bond atomRefs2="a1 a3" order="2"/>
<bond atomRefs2="a14 a11" order="1"/>
<bond atomRefs2="a14 a15" order="1"/>
<bond atomRefs2="a19 a20" order="1"/>
<bond atomRefs2="a19 a18" order="1"/>
<bond atomRefs2="a11 a12" order="1"/>
<bond atomRefs2="a11 a9" order="1"/>
<bond atomRefs2="a4 a6" order="1"/>
<bond atomRefs2="a18 a9" order="1"/>
<bond atomRefs2="a9 a6" order="1"/>
<bond atomRefs2="a9 a10" order="1"/>
<bond atomRefs2="a6 a8" order="1"/>
<bond atomRefs2="a6 a7" order="1"/>
</bondArray>
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kcal/mol">6.16</scalar>
</property>
<property dictRef="me:rotConsts">
```

```
889           <array units="cm-1">
890             0.094 0.035 0.031
891           </array>
892         </property>
893         <property dictRef="me:symmetryNumber">
894           <scalar>1</scalar>
895         </property>
896         <property dictRef="me:vibFreqs">
897           <array units="cm-1">
898             56.02 81.32 120.30 168.43 177.90 201.16 256.70 263.21 301.84 348.54 406.83
899 518.23 589.73 614.76 706.07 722.14 777.39 811.74 908.59 943.33 981.47 1003.45 1017.61
900 1025.87 1083.52 1123.74 1156.18 1176.74 1264.20 1269.39 1316.43 1342.24 1385.29
901 1405.96 1415.93 1424.32 1455.33 1467.30 1485.70 1486.75 1503.83 1510.97 1634.96
902 2987.94 3047.56 3049.89 3051.31 3064.22 3100.07 3119.44 3123.22 3141.40 3189.68
903 3705.66
904           </array>
905         </property>
906         <property dictRef="me:MW">
907           <scalar>131.15</scalar>
908         </property>
909         <property dictRef="me:epsilon">
910           <scalar>343.0</scalar>
911         </property>
912         <property dictRef="me:sigma">
913           <scalar>6.25</scalar>
914         </property>
915         <property dictRef="me:spinMultiplicity">
916           <scalar>2</scalar>
917         </property>
918       </propertyList>
919       <me:energyTransferModel xsi:type="me:ExponentialDown">
920         <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
```

```
        </me:energyTransferModel>
      </molecule>

            <molecule id="C6H11O5-D51">
        <atomArray>
  <atom id="a1" elementType="C" hydrogenCount="1" x3="-1.679583" y3="1.016706"
z3="-0.232156"/>
  <atom id="a2" elementType="H" hydrogenCount="0" x3="-2.025198" y3="0.878997"
z3="-1.269083"/>
  <atom id="a3" elementType="O" hydrogenCount="0" x3="-1.484024" y3="2.104712"
z3="0.242018"/>
  <atom id="a4" elementType="C" hydrogenCount="1" x3="-1.509098" y3="-0.252399"
z3="0.588005"/>
  <atom id="a5" elementType="H" hydrogenCount="0" x3="-2.231053" y3="-0.213646"
z3="1.405441"/>
  <atom id="a6" elementType="C" hydrogenCount="2" x3="-0.099885" y3="-0.442493"
z3="1.120948"/>
  <atom id="a7" elementType="H" hydrogenCount="0" x3="-0.067627" y3="-1.353504"
z3="1.718606"/>
  <atom id="a8" elementType="H" hydrogenCount="0" x3="0.118056" y3="0.391478"
z3="1.789051"/>
  <atom id="a9" elementType="C" hydrogenCount="1" x3="0.957465" y3="-0.511050"
z3="0.022390"/>
  <atom id="a10" elementType="H" hydrogenCount="0" x3="0.707955" y3="-1.313333"
z3="-0.677086"/>
  <atom id="a11" elementType="C" hydrogenCount="2" x3="2.354760" y3="-0.744185"
z3="0.575827"/>
  <atom id="a12" elementType="H" hydrogenCount="0" x3="2.328387" y3="-1.675630"
z3="1.146132"/>
  <atom id="a13" elementType="H" hydrogenCount="0" x3="2.592796" y3="0.052586"
z3="1.281407"/>
  <atom id="a14" elementType="C" hydrogenCount="3" x3="3.420180" y3="-0.824068"
z3="-0.507815"/>
  <atom id="a15" elementType="H" hydrogenCount="0" x3="3.200881" y3="-1.623803"
z3="-1.217151"/>
```

```
<atom id="a16" elementType="H" hydrogenCount="0" x3="4.398358" y3="-1.021967"
z3="-0.071457"/>
<atom id="a17" elementType="H" hydrogenCount="0" x3="3.478549" y3="0.110166"
z3="-1.063457"/>
<atom id="a18" elementType="O" hydrogenCount="0" x3="0.877714" y3="0.629090"
z3="-0.832288"/>
<atom id="a19" elementType="O" hydrogenCount="1" x3="1.318906" y3="1.780465"
z3="-0.125327"/>
<atom id="a20" elementType="H" hydrogenCount="0" x3="0.481012" y3="2.233918"
z3="0.058295"/>
<atom id="a21" elementType="O" hydrogenCount="0" x3="-1.840896" y3="-1.402382"
z3="-0.219239"/>
<atom id="a22" elementType="O" hydrogenCount="0" x3="-3.077343" y3="-1.351927"
z3="-0.628151"/>
</atomArray>
<bondArray>
<bond atomRefs2="a2 a1" order="1"/>
<bond atomRefs2="a15 a14" order="1"/>
<bond atomRefs2="a17 a14" order="1"/>
<bond atomRefs2="a18 a19" order="1"/>
<bond atomRefs2="a18 a9" order="1"/>
<bond atomRefs2="a10 a9" order="1"/>
<bond atomRefs2="a22 a21" order="1"/>
<bond atomRefs2="a14 a16" order="1"/>
<bond atomRefs2="a14 a11" order="1"/>
<bond atomRefs2="a1 a3" order="2"/>
<bond atomRefs2="a1 a4" order="1"/>
<bond atomRefs2="a21 a4" order="1"/>
<bond atomRefs2="a19 a20" order="1"/>
<bond atomRefs2="a9 a11" order="1"/>
<bond atomRefs2="a9 a6" order="1"/>
<bond atomRefs2="a11 a12" order="1"/>
<bond atomRefs2="a11 a13" order="1"/>
```

```
    <bond atomRefs2="a4 a6" order="1"/>
    <bond atomRefs2="a4 a5" order="1"/>
    <bond atomRefs2="a6 a7" order="1"/>
    <bond atomRefs2="a6 a8" order="1"/>
   </bondArray>
      <propertyList>
       <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-13.59</scalar>
       </property>
       <property dictRef="me:rotConsts">
        <array units="cm-1">
         0.056 0.025 0.020
        </array>
       </property>
       <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
       </property>
       <property dictRef="me:vibFreqs">
        <array units="cm-1">
         62.55 71.80 97.45 117.72 149.76 183.99 206.03 213.77 228.86 286.52 298.07 332.45
357.21 422.38 480.16 503.17 577.88 597.43 655.76 786.83 826.75 870.19 910.67 954.64
986.44 1016.35 1029.14 1045.27 1098.16 1123.53 1148.46 1185.06 1250.26 1263.50
1290.83 1316.87 1325.16 1334.00 1380.94 1398.91 1412.29 1416.35 1427.34 1471.53
1473.98 1488.40 1504.96 1511.77 1820.68 2996.38 3053.21 3058.27 3068.30 3079.98
3091.84 3103.17 3125.57 3130.21 3142.82 3689.10
        </array>
       </property>
       <property dictRef="me:MW">
        <scalar>163.15</scalar>
       </property>
       <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
```

```
      </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>

<molecule id="O2">
    <atomArray>
  <atom id="a1" elementType="O" hydrogenCount="0" x3="0.000000" y3="0.000000"
z3="0.597994"/>
  <atom id="a2" elementType="O" hydrogenCount="0" x3="0.000000" y3="0.000000" z3="-
0.597994"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a2 a1" order="2"/>
 </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0.00</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">
          1.473
        </array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">
          1703.81
        </array>
```

```
1052          </property>
1053          <property dictRef="me:MW">
1054            <scalar>32</scalar>
1055          </property>
1056          <property dictRef="me:spinMultiplicity">
1057            <scalar>3</scalar>
1058          </property>
1059        </propertyList>
1060        <me:DOSCMethod xsi:type="ClassicalRotors"/>
1061      </molecule>
1062
1063      <molecule id="N2">
1064        <propertyList>
1065          <property dictRef="me:epsilon">
1066            <scalar>48.0</scalar>
1067          </property>
1068          <property dictRef="me:sigma">
1069            <scalar>3.9</scalar>
1070          </property>
1071          <property dictRef="me:MW">
1072            <scalar units="amu">28.0</scalar>
1073          </property>
1074        </propertyList>
1075      </molecule>
1076    </moleculeList>
1077
1078    <reactionList>
1079      <reaction id="R1">
1080        <reactant>
1081          <molecule ref="C6H11O3-D"  role="modelled" />
```

```
      </reactant>
      <product>
        <molecule ref="D61_pr"  role="modelled" />
      </product>
            <me:transitionState>
        <molecule ref="D_1-6-aldHshift-TS" role="transitionState" />
      </me:transitionState>
            <me:tunneling name="Eckart" />
      <me:MCRCMethod name="RRKM"/>
    </reaction>
          <reaction id="R2">
      <reactant>
        <molecule ref="C6H11O3-D"  role="modelled" />
      </reactant>
      <product>
        <molecule ref="D51_pr"  role="modelled" />
      </product>
            <me:transitionState>
        <molecule ref="D_1-5Hshift_RR-TS" role="transitionState" />
      </me:transitionState>
            <me:tunneling name="Eckart" />
      <me:MCRCMethod name="RRKM"/>
    </reaction>
    <reaction id="R3">
      <reactant>
        <molecule ref="D61_pr" me:type="modelled"/>
      </reactant>
      <reactant>
        <molecule ref="O2" me:type="excessReactant"/>
      </reactant>
```

```
1112          <product>
1113            <molecule ref="C6H11O5-A62" me:type="sink"/>
1114          </product>
1115          <me:MCRCMethod name="SimpleBimolecularSink" />
1116          <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
1117          <me:excessReactantConc>5.0E18</me:excessReactantConc>
1118        </reaction>
1119              <reaction id="R4">
1120          <reactant>
1121            <molecule ref="D51_pr" me:type="modelled"/>
1122          </reactant>
1123          <reactant>
1124            <molecule ref="O2" me:type="excessReactant"/>
1125          </reactant>
1126          <product>
1127            <molecule ref="C6H11O5-D51" me:type="sink"/>
1128          </product>
1129          <me:MCRCMethod name="SimpleBimolecularSink" />
1130          <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
1131          <me:excessReactantConc>5.0E18</me:excessReactantConc>
1132        </reaction>
1133      </reactionList>
1134
1135      <!-- Data taken from Seakins et al, J. Phys. Chem. Vol. 97, p. 4450 (1993). -->
1136      <me:conditions>
1137        <me:bathGas>N2</me:bathGas>
1138        <me:PTs>
1139          <me:PTpair units="Torr" P="760.00" T="298.15" precision="qd" />
1140        </me:PTs>
1141      </me:conditions>
```

```
    <me:modelParameters>
      <me:grainSize units="cm-1">100</me:grainSize>
      <me:energyAboveTheTopHill>30</me:energyAboveTheTopHill>
    </me:modelParameters>

    <me:control>
      <me:ForceMacroDetailedBalance/>
      <me:testDOS />
      <me:printSpeciesProfile />
      <me:testMicroRates />
      <me:testRateConstants />
      <me:printGrainDOS />
      <me:printTunnellingCoefficients />
      <me:printGrainkfE />
      <me:printGrainkbE />
      <me:eigenvalues>3</me:eigenvalues>
    </me:control>
  </me:mesmer>
```

References

[1] Jenkin, M. E.; Valorso, R.; Aumont, B.; Rickard, A. R.; Wallington, T. J. Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction. *Atmos. Chem. Phys.* **2018**, 18, 9297-9328.

[2] Ziemann, P. J.; Atkinson, R. Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chem. Soc. Rev.* **2012**, 41, 6582-6605.

[3] Møller, K. H.; Otkjær, R. V.; Hyttinen, N.; Kurte´n, T.; Kjaergaard, H. G. Cost-effective implementation of multiconformer transition state theory for peroxy radical hydrogen shift reactions. *The Journal of Physical Chemistry A* **2016**, 120, 10072–10087.

[4] Castañeda, R.; Iuga, C.; Álvarez-Idaboy, J. R.; Vivier-Bunge, A. Rate constants and branching ratios in the oxidation of aliphatic aldehydes by OH radicals under atmospheric conditions. *Journal of the Mexican Chemical Society* **2012**, 56, 316–324.

[5] Henriksen, N. E.; Hansen, F. Y. Theories of molecular reaction dynamics: the microscopic foundation of chemical kinetics, *Oxford University Press* **2018**.

[6] Bunker, D. L.; Garrett, B.; Kliendienst, T.; Long III, G. S. Discrete simulation methods in combustion kinetics. *Combustion and Flame* **1974**, 23, 373-379.

[7] Gillespie, D. T. A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *J. Comput. Phys.* **1976**, 22, 403-434.

[8] Williams, I. D.; Revitt, D. M.; Hamilton, R. S. A comparison of carbonyl compound concentrations at urban roadside and indoor sites. *The Science of the Total Environment* **1996**, 189/190, 475-483.

[9] Ciccioli, P.; Brancaleoni, E.; Frattoni, M.; Cecinato, A.; Brachetti, A. Ubiquitous occurrence of semi-volatile carbonyl compounds in tropospheric samples and their possible sources. *Atmospheric Environment* **1993**, Vol. 27A, No. 12, pp. 1891–1901.

[10] Berndt, T.; Scholz, W.; Mentler, B.; Fischer, L.; Herrmann, H.; Kulmala, M.; Hansel, A. Accretion Product Formation from Self- and Cross-Reactions of RO_2 Radicals in the Atmosphere. *Angew. Chem. Int. Ed.* **2018**, 57, 3820-3824.

[11] Jenkin, M. E.; Valorso, R.; Aumont, B.; Rickard, A. R. Estimation of Rate Coefficients and Branching Ratios for Reactions of Organic Peroxy Radicals for use in Automated Mechanism Construction. *Atmos. Chem. Phys. Diss.* **2019**, https://doi.org/10.5194/acp-2019-44.