Supplement

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

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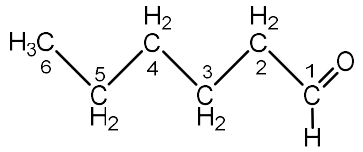
S1: Rate coefficients of H-abstractions predicted by SAR

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 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).

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

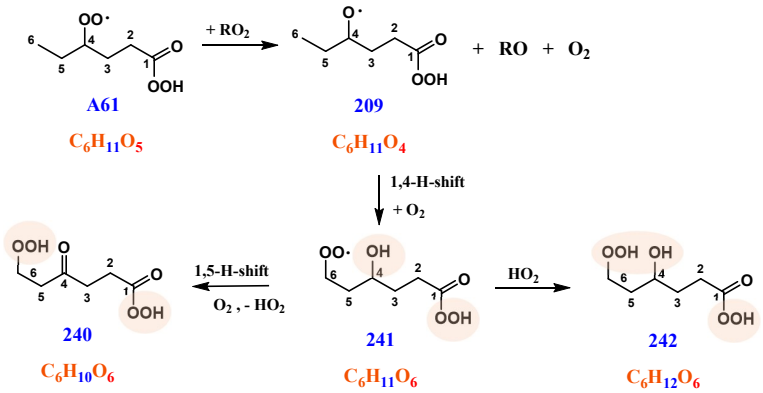


Figure S1: Formation of $C_6H_{10\text{-}12}O_6$ products likely involve A61 ($C_6H_{11}O_5$) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture.

$C_6H_{10}O_5$

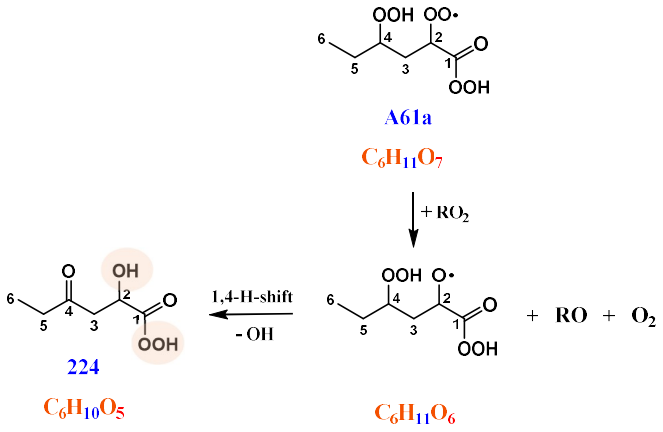
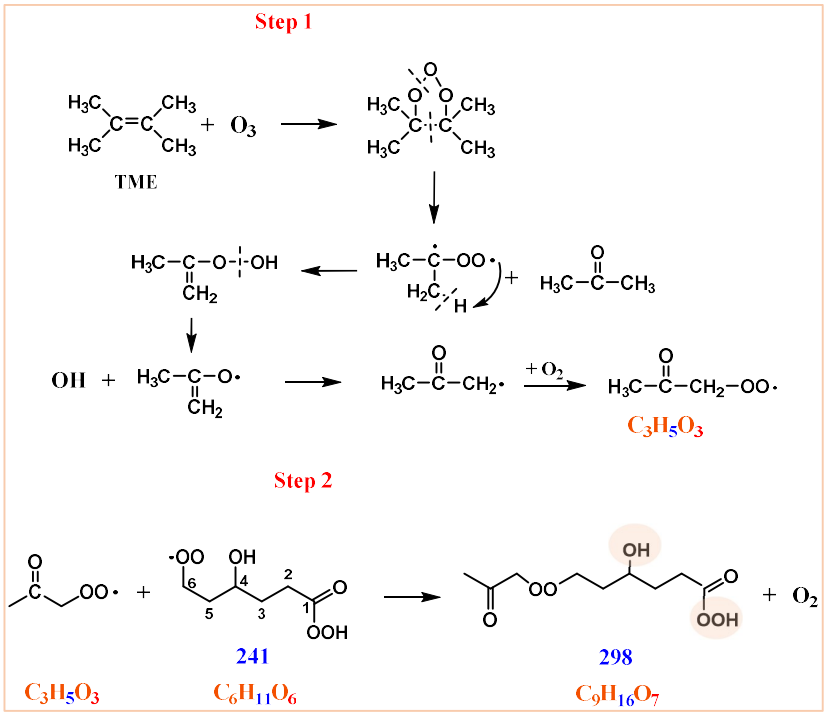


Figure S2: Formation of $C_6H_{10}O_5$ product likely involves A61a ($C_6H_{11}O_7$) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture.

38 **$C_9H_{16}O_7$**



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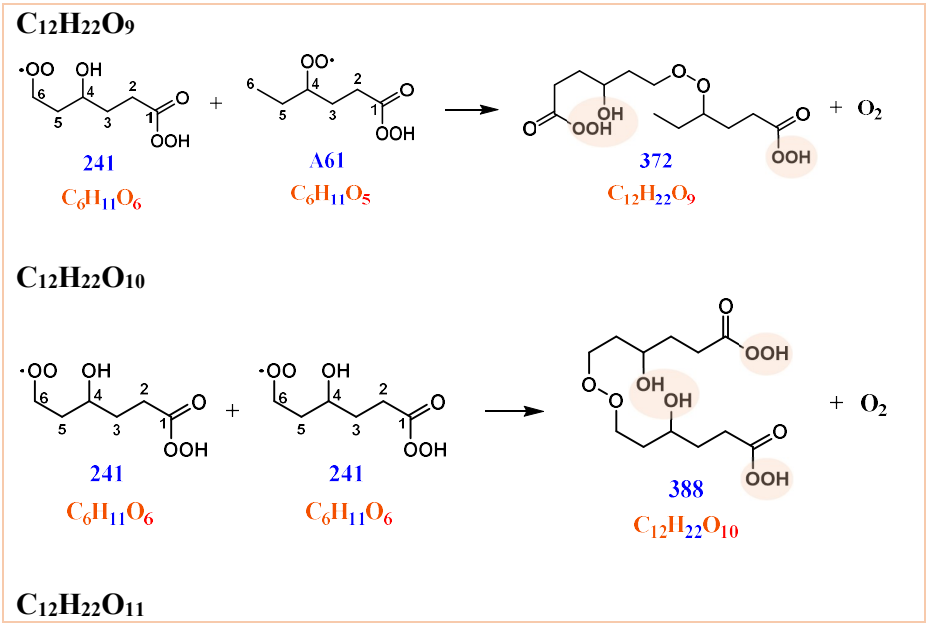
40 Figure S3: Production of oxidant OH in tetramethylethylene (TME) ozonolysis. The keto
41 peroxy radical $C_3H_5O_3$ is a biproduct and reacts with hexanal derived peroxy radicals yielding
42 closed shell products with nine C atoms; a pathway producing $C_9H_{16}O_7$ peroxide accretion
43 product is shown as an example.

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



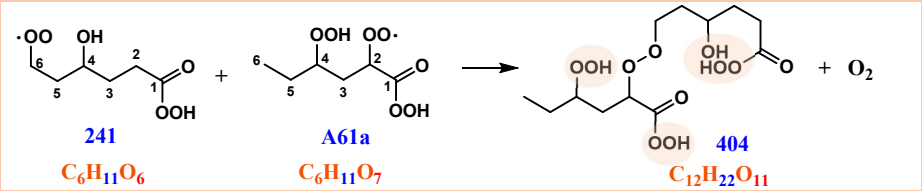


Figure S4: HOM accretion products ($C_{12}H_{22}O_{9\text{-}11}$) are formed by self and cross RO_2 + RO_2 reactions.

S3: Kinetic modelling of HOM formation

Kinetic modelling using calculated rate constants is carried out using Kinetiscope Program[3,4] 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.[5] 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}).[6] 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.[7,8]

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 x10^{-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 x10^{-15} cm^3 $molecule^{-1}$ s^{-1})
13. F_pr + O_2 => F
14. A + RO_2 => Sink_a (Alkyl peroxy bimolecular rate k=3.2x10^{-11} cm^3 $molecule^{-1}$ s^{-1})
15. A + NO => Sink_aa (Bimolecular rate k=9.2x10^{-12} cm^3 $molecule^{-1}$ s^{-1})
16. A => A61_pr (1,6-H-shift rate k=1.69x10^{-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 S2. 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 S5). 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.

Supplementary Table S2: 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 S2 (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.

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 4.0×10^3 molecules cm^{-3} as early as 1.7 s reaction time. At 10 s, the D52 intermediate and D52n HOM concentrations reach at 4.3×10^3 and 8.7×10^3 molecules cm^{-3} respectively.

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. 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.

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. 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.

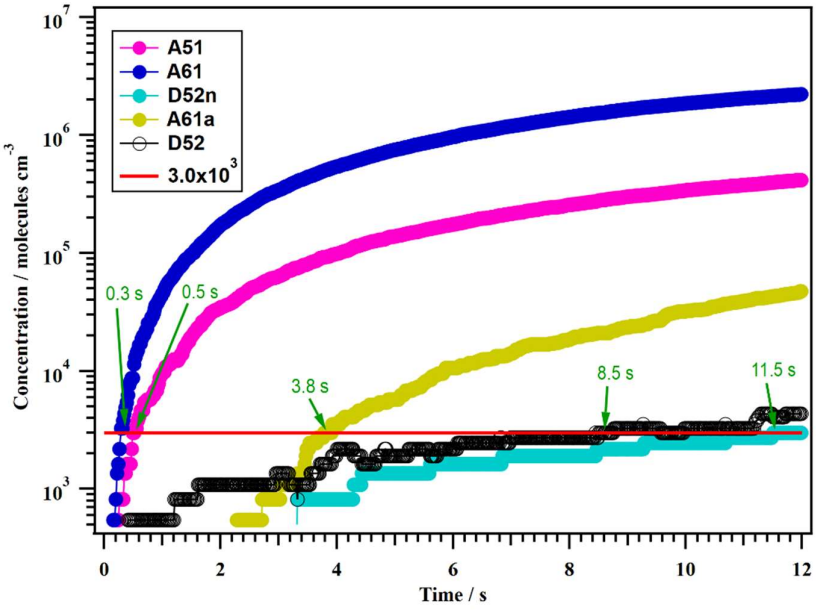


Figure S5: Time profile of hexanal oxidation products showing the appearance of different species with five to seven O atoms. Reactant concentrations: hexanal=1ppb (2.46×10^{10} molecules cm^{-3}), OH=1.0×10^7 molecules cm^{-3}, NO=0.1 ppb (2.46×10^9 molecules cm^{-3}), and RO_2=1.0×10^8 molecules cm^{-3}. 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.

S4: 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 S6 and Table S3). 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.

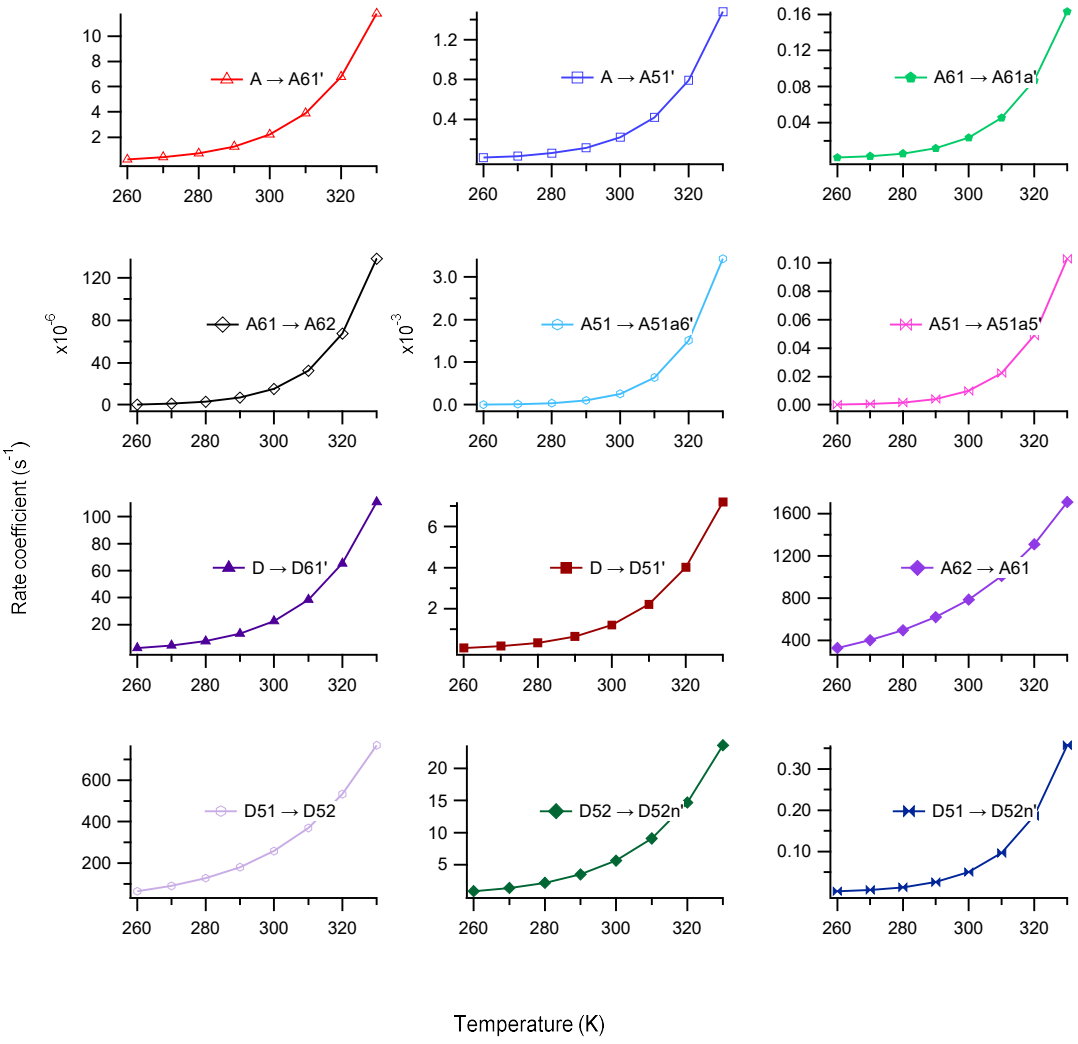


Figure S6: Positive temperature dependency of H-shift rate coefficients shown for the transition of different intermediates (e.g., A→A61′, A61→A62, etc.) along the path to HOM.

Supplementary Table S3: 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'	$2.34x10^{-1}$	$4.10X10^{-1}$	$7.20X10^{-1}$	1.26	2.22	3.89	6.79	$1.18X10^{1}$
A→A51'	$1.67x10^{-2}$	$3.19X10^{-2}$	$6.09X10^{-2}$	$1.16X10^{-1}$	$2.21X10^{-1}$	$4.20X10^{-1}$	$7.92X10^{-1}$	1.48
A61→A61a'	$1.29x10^{-3}$	$2.76X10^{-3}$	$5.75X10^{-3}$	$1.17X10^{-2}$	$2.32X10^{-2}$	$4.53X10^{-2}$	$8.68X10^{-2}$	$1.63X10^{-1}$
A61→A62	$5.82X10^{-7}$	$1.38X10^{-6}$	$3.17X10^{-6}$	$7.07X10^{-6}$	$1.53X10^{-5}$	$3.25X10^{-5}$	$6.75X10^{-5}$	$1.38X10^{-4}$

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'	$3.60X10^{-3}$	$6.93X10^{-3}$	$1.34X10^{-2}$	$2.59X10^{-2}$	$5.00X10^{-2}$	$9.66X10^{-2}$	$1.86X10^{-1}$	$3.57X10^{-1}$

S5: 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"/>
```

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237       <bond atomRefs2="a2 a1" order="1"/>
238       <bond atomRefs2="a19 a20" order="1"/>
239       <bond atomRefs2="a19 a10" order="1"/>
240       <bond atomRefs2="a11 a10" order="1"/>
241       <bond atomRefs2="a3 a1" order="2"/>
242       <bond atomRefs2="a5 a4" order="1"/>
243       <bond atomRefs2="a1 a4" order="1"/>
244       <bond atomRefs2="a15 a17" order="1"/>
245       <bond atomRefs2="a15 a12" order="1"/>
246       <bond atomRefs2="a10 a12" order="1"/>
247       <bond atomRefs2="a10 a7" order="1"/>
248       <bond atomRefs2="a4 a7" order="1"/>
249       <bond atomRefs2="a4 a6" order="1"/>
250       <bond atomRefs2="a12 a13" order="1"/>
251       <bond atomRefs2="a12 a14" order="1"/>
252       <bond atomRefs2="a7 a8" order="1"/>
253       <bond atomRefs2="a7 a9" order="1"/>
254     </bondArray>
255         <propertyList>
256           <property dictRef="me:ZPE">
257             <scalar units="kcal/mol">0.0</scalar>
258           </property>
259           <property dictRef="me:rotConsts">
260             <array units="cm-1">0.082 0.033 0.027</array>
261           </property>
262           <property dictRef="me:symmetryNumber">
263             <scalar>1</scalar>
264           </property>
265           <property dictRef="me:vibFreqs">
266             <array units="cm-1">
```

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485.44 593.66 667.65 725.42 780.58 821.11 871.50 939.58 949.90 995.34 1055.29 1068.61
1125.72 1137.97 1163.79 1220.81 1245.96 1270.27 1322.76 1332.17 1383.56 1397.28
1411.41 1420.92 1426.98 1429.49 1453.80 1471.02 1486.75 1506.65 1511.84 1838.30
2914.42 3046.12 3053.62 3061.54 3074.92 3084.32 3098.48 3112.41 3126.28 3131.10
3136.97
          </array>
        </property>
        <property dictRef="me:MW">
          <scalar>131.15</scalar>
        </property>
        <property dictRef="me:epsilon">
          <scalar>343.0</scalar>
        </property>
        <property dictRef="me:sigma">
          <scalar>6.25</scalar>
        </property>
        <property dictRef="me:spinMultiplicity">
          <scalar>2</scalar>
        </property>
      </propertyList>
      <me:energyTransferModel xsi:type="me:ExponentialDown">
        <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
      </me:energyTransferModel>
    </molecule>

    <molecule id="D_1-6-aldHshift-TS">
      <atomArray>
  <atom id="a1" elementType="C" hydrogenCount="0" x3="2.171388" y3="0.048934" z3="-
0.247665"/>
  <atom id="a2" elementType="O" hydrogenCount="0" x3="3.287959" y3="0.088910" z3="-
0.627350"/>
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<atom id="a3" elementType="C" hydrogenCount="2" x3="1.255292" y3="-1.160226"
z3="-0.175406"/>
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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>
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```
336     <bondArray>
337      <bond atomRefs2="a13 a11" order="1"/>
338      <bond atomRefs2="a4 a3" order="1"/>
339      <bond atomRefs2="a16 a14" order="1"/>
340      <bond atomRefs2="a17 a14" order="1"/>
341      <bond atomRefs2="a2 a1" order="2"/>
342      <bond atomRefs2="a14 a11" order="1"/>
343      <bond atomRefs2="a14 a15" order="1"/>
344      <bond atomRefs2="a11 a12" order="1"/>
345      <bond atomRefs2="a11 a9" order="1"/>
346      <bond atomRefs2="a1 a3" order="1"/>
347      <bond atomRefs2="a3 a5" order="1"/>
348      <bond atomRefs2="a3 a6" order="1"/>
349      <bond atomRefs2="a18 a19" order="1"/>
350      <bond atomRefs2="a18 a9" order="1"/>
351      <bond atomRefs2="a20 a19" order="1"/>
352      <bond atomRefs2="a9 a6" order="1"/>
353      <bond atomRefs2="a9 a10" order="1"/>
354      <bond atomRefs2="a6 a8" order="1"/>
355      <bond atomRefs2="a6 a7" order="1"/>
356     </bondArray>
357         <propertyList>
358           <property dictRef="me:ZPE">
359             <scalar units="kcal/mol">18.67</scalar>
360           </property>
361           <property dictRef="me:rotConsts">
362             <array units="cm-1">
363               0.104 0.031 0.028
364             </array>
365           </property>
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```
366         <property dictRef="me:symmetryNumber">
367           <scalar>1</scalar>
368         </property>
369         <property dictRef="me:vibFreqs">
370           <array units="cm-1">
371             47.77 97.38 129.80 207.11 228.21 263.19 292.95 338.32 386.36 390.63 452.66
372 510.86 597.23 609.74 766.99 827.35 848.41 874.73 951.05 978.22 1017.83 1061.22 1080.44
373 1088.88 1097.35 1155.81 1183.00 1228.56 1256.97 1305.59 1332.93 1349.51 1371.85
374 1396.76 1419.91 1425.35 1447.49 1485.23 1500.47 1503.50 1513.27 1607.94 1925.47
375 3039.22 3050.59 3054.34 3065.86 3077.43 3092.19 3118.14 3120.90 3124.09 3144.45
376           </array>
377         </property>
378         <property dictRef="me:MW">
379           <scalar>131.15</scalar>
380         </property>
381         <property dictRef="me:imFreqs">
382           <scalar units="cm-1">1805.75</scalar>
383         </property>
384         <property dictRef="me:spinMultiplicity">
385           <scalar>2</scalar>
386         </property>
387       </propertyList>
388       <me:DOSCMethod xsi:type="ClassicalRotors"/>
389     </molecule>
390
391 <molecule id="D61_pr">
392       <atomArray>
393   <atom id="a1" elementType="C" hydrogenCount="0" x3="-2.591004" y3="-0.009787"
394 z3="-0.357272"/>
395   <atom id="a2" elementType="O" hydrogenCount="0" x3="-2.535322" y3="0.972415"
396 z3="0.292868"/>
397   <atom id="a3" elementType="C" hydrogenCount="2" x3="-1.765467" y3="-1.268641"
398 z3="-0.278670"/>
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<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"
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<atom id="a16" elementType="H" hydrogenCount="0" x3="4.068149" y3="0.026669"
z3="0.329198"/>
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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"/>
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<bondArray>
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435       <bond atomRefs2="a5 a3" order="1"/>
436       <bond atomRefs2="a10 a9" order="1"/>
437       <bond atomRefs2="a15 a14" order="1"/>
438       <bond atomRefs2="a18 a9" order="1"/>
439       <bond atomRefs2="a18 a19" order="1"/>
440       <bond atomRefs2="a17 a14" order="1"/>
441       <bond atomRefs2="a1 a3" order="1"/>
442       <bond atomRefs2="a1 a2" order="2"/>
443       <bond atomRefs2="a3 a4" order="1"/>
444       <bond atomRefs2="a3 a6" order="1"/>
445       <bond atomRefs2="a9 a6" order="1"/>
446       <bond atomRefs2="a9 a11" order="1"/>
447       <bond atomRefs2="a14 a16" order="1"/>
448       <bond atomRefs2="a14 a11" order="1"/>
449       <bond atomRefs2="a19 a20" order="1"/>
450       <bond atomRefs2="a6 a7" order="1"/>
451       <bond atomRefs2="a6 a8" order="1"/>
452       <bond atomRefs2="a11 a12" order="1"/>
453       <bond atomRefs2="a11 a13" order="1"/>
454     </bondArray>
455         <propertyList>
456           <property dictRef="me:ZPE">
457             <scalar units="kcal/mol">2.87</scalar>
458           </property>
459           <property dictRef="me:rotConsts">
460             <array units="cm-1">
461               0.102 0.035 0.029
462             </array>
463           </property>
464           <property dictRef="me:symmetryNumber">
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        </property>
        <property dictRef="me:vibFreqs">
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482.85 522.10 582.51 647.59 764.50 795.32 840.28 874.94 936.86 960.32 1016.85 1024.01
1064.20 1097.54 1138.90 1150.35 1226.58 1243.76 1306.59 1316.70 1348.76 1377.98
1397.48 1409.89 1425.80 1444.43 1457.39 1479.98 1490.94 1503.94 1511.67 1941.48
3035.93 3050.65 3054.16 3059.27 3069.35 3099.99 3106.20 3116.03 3122.78 3142.14
3723.51
          </array>
        </property>
        <property dictRef="me:MW">
          <scalar>131.15</scalar>
        </property>
        <property dictRef="me:epsilon">
          <scalar>343.0</scalar>
        </property>
        <property dictRef="me:sigma">
          <scalar>6.25</scalar>
        </property>
        <property dictRef="me:spinMultiplicity">
          <scalar>2</scalar>
        </property>
      </propertyList>
      <me:energyTransferModel xsi:type="me:ExponentialDown">
        <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
      </me:energyTransferModel>
    </molecule>

<molecule id="C6H11O5-A62">
      <atomArray>
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z3="-1.556808"/>
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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"
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<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"
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<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"/>
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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>
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  <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>
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      <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>
```

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<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"/>
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633   <atom id="a18" elementType="O" hydrogenCount="1" x3="-0.251036" y3="1.824014"
634  z3="-0.523727"/>
635   <atom id="a19" elementType="H" hydrogenCount="0" x3="-2.130636" y3="0.798245"
636  z3="1.581944"/>
637   <atom id="a20" elementType="H" hydrogenCount="0" x3="-1.146920" y3="1.271563"
638  z3="0.037928"/>
639  </atomArray>
640  <bondArray>
641   <bond atomRefs2="a14 a13" order="1"/>
642   <bond atomRefs2="a9 a8" order="1"/>
643   <bond atomRefs2="a3 a1" order="2"/>
644   <bond atomRefs2="a16 a13" order="1"/>
645   <bond atomRefs2="a13 a15" order="1"/>
646   <bond atomRefs2="a13 a10" order="1"/>
647   <bond atomRefs2="a18 a20" order="1"/>
648   <bond atomRefs2="a18 a17" order="1"/>
649   <bond atomRefs2="a2 a1" order="1"/>
650   <bond atomRefs2="a1 a4" order="1"/>
651   <bond atomRefs2="a8 a17" order="1"/>
652   <bond atomRefs2="a8 a10" order="1"/>
653   <bond atomRefs2="a8 a5" order="1"/>
654   <bond atomRefs2="a10 a11" order="1"/>
655   <bond atomRefs2="a10 a12" order="1"/>
656   <bond atomRefs2="a4 a5" order="1"/>
657   <bond atomRefs2="a4 a19" order="1"/>
658   <bond atomRefs2="a6 a5" order="1"/>
659   <bond atomRefs2="a5 a7" order="1"/>
660  </bondArray>
661     <propertyList>
662       <property dictRef="me:ZPE">
663         <scalar units="kcal/mol">21.09</scalar>
```

```
664         </property>
665         <property dictRef="me:rotConsts">
666           <array units="cm-1">
667             0.090 0.032 0.029
668           </array>
669         </property>
670         <property dictRef="me:symmetryNumber">
671           <scalar>1</scalar>
672         </property>
673         <property dictRef="me:vibFreqs">
674           <array units="cm-1">
675             58.88 101.46 102.90 173.21 209.10 240.96 270.76 307.56 381.97 444.39 502.42
676 521.99 643.83 676.41 769.49 782.12 879.16 900.15 953.23 970.22 1005.16 1048.14 1082.02
677 1114.17 1117.14 1129.50 1161.18 1174.34 1236.98 1288.13 1317.10 1350.06 1366.73
678 1393.98 1415.39 1425.05 1425.95 1463.56 1486.74 1504.89 1512.57 1556.93 1764.84
679 2943.00 3054.68 3055.75 3063.63 3071.97 3097.64 3127.11 3129.13 3139.53 3157.90
680           </array>
681         </property>
682         <property dictRef="me:MW">
683           <scalar>131.15</scalar>
684         </property>
685                   <property dictRef="me:imFreqs">
686           <scalar units="cm-1">1935.56</scalar>
687         </property>
688         <property dictRef="me:spinMultiplicity">
689           <scalar>2</scalar>
690         </property>
691       </propertyList>
692       <me:DOSCMethod xsi:type="ClassicalRotors"/>
693     </molecule>
694
695           <molecule id="D51_pr">
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696         <atomArray>
697     <atom id="a1" elementType="C" hydrogenCount="1" x3="2.424466" y3="-0.404465"
698   z3="-0.601898"/>
699     <atom id="a2" elementType="H" hydrogenCount="0" x3="3.032948" y3="-0.770016"
700   z3="-1.443473"/>
701     <atom id="a3" elementType="O" hydrogenCount="0" x3="2.723837" y3="0.648707" z3="-
702   0.043837"/>
703     <atom id="a4" elementType="C" hydrogenCount="1" x3="1.300936" y3="-1.202309"
704   z3="-0.232773"/>
705     <atom id="a5" elementType="H" hydrogenCount="0" x3="1.058882" y3="-2.042782"
706   z3="-0.871849"/>
707     <atom id="a6" elementType="C" hydrogenCount="2" x3="0.477540" y3="-0.948298"
708   z3="0.971107"/>
709     <atom id="a7" elementType="H" hydrogenCount="0" x3="1.047613" y3="-0.370167"
710   z3="1.698014"/>
711     <atom id="a8" elementType="H" hydrogenCount="0" x3="0.226104" y3="-1.912137"
712   z3="1.420528"/>
713     <atom id="a9" elementType="C" hydrogenCount="1" x3="-0.863829" y3="-0.204765"
714   z3="0.741736"/>
715     <atom id="a10" elementType="H" hydrogenCount="0" x3="-1.452279" y3="-0.327984"
716   z3="1.655178"/>
717     <atom id="a11" elementType="C" hydrogenCount="2" x3="-1.662375" y3="-0.725877"
718   z3="-0.444346"/>
719     <atom id="a12" elementType="H" hydrogenCount="0" x3="-1.750810" y3="-1.810396"
720   z3="-0.336367"/>
721     <atom id="a13" elementType="H" hydrogenCount="0" x3="-1.096320" y3="-0.541996"
722   z3="-1.358230"/>
723     <atom id="a14" elementType="C" hydrogenCount="3" x3="-3.041888" y3="-0.092880"
724   z3="-0.551505"/>
725     <atom id="a15" elementType="H" hydrogenCount="0" x3="-3.633506" y3="-0.282963"
726   z3="0.345800"/>
727     <atom id="a16" elementType="H" hydrogenCount="0" x3="-3.587949" y3="-0.494979"
728   z3="-1.404139"/>
729     <atom id="a17" elementType="H" hydrogenCount="0" x3="-2.960558" y3="0.985542"
730   z3="-0.676653"/>
731     <atom id="a18" elementType="O" hydrogenCount="0" x3="-0.689331" y3="1.200034"
732   z3="0.724140"/>
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 <atom id="a19" elementType="O" hydrogenCount="1" x3="0.012856" y3="1.579026"
z3="-0.453707"/>
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z3="-0.135504"/>
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  <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">
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764           <array units="cm-1">
765             0.094 0.035 0.031
766           </array>
767         </property>
768         <property dictRef="me:symmetryNumber">
769           <scalar>1</scalar>
770         </property>
771         <property dictRef="me:vibFreqs">
772           <array units="cm-1">
773             56.02 81.32 120.30 168.43 177.90 201.16 256.70 263.21 301.84 348.54 406.83
774 518.23 589.73 614.76 706.07 722.14 777.39 811.74 908.59 943.33 981.47 1003.45 1017.61
775 1025.87 1083.52 1123.74 1156.18 1176.74 1264.20 1269.39 1316.43 1342.24 1385.29
776 1405.96 1415.93 1424.32 1455.33 1467.30 1485.70 1486.75 1503.83 1510.97 1634.96
777 2987.94 3047.56 3049.89 3051.31 3064.22 3100.07 3119.44 3123.22 3141.40 3189.68
778 3705.66
779           </array>
780         </property>
781         <property dictRef="me:MW">
782           <scalar>131.15</scalar>
783         </property>
784         <property dictRef="me:epsilon">
785           <scalar>343.0</scalar>
786         </property>
787         <property dictRef="me:sigma">
788           <scalar>6.25</scalar>
789         </property>
790         <property dictRef="me:spinMultiplicity">
791           <scalar>2</scalar>
792         </property>
793       </propertyList>
794       <me:energyTransferModel xsi:type="me:ExponentialDown">
795         <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
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    </molecule>

        <molecule id="C6H11O5-D51">
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  <atom id="a1" elementType="C" hydrogenCount="1" x3="-1.679583" y3="1.016706"
z3="-0.232156"/>
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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"/>
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<atom id="a16" elementType="H" hydrogenCount="0" x3="4.398358" y3="-1.021967"
z3="-0.071457"/>
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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"/>
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<bond atomRefs2="a2 a1" order="1"/>
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<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">
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    </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">
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  <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>
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          <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>
```

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927         </property>
928         <property dictRef="me:MW">
929           <scalar>32</scalar>
930         </property>
931         <property dictRef="me:spinMultiplicity">
932           <scalar>3</scalar>
933         </property>
934       </propertyList>
935       <me:DOSCMethod xsi:type="ClassicalRotors"/>
936     </molecule>
937
938     <molecule id="N2">
939       <propertyList>
940         <property dictRef="me:epsilon">
941           <scalar>48.0</scalar>
942         </property>
943         <property dictRef="me:sigma">
944           <scalar>3.9</scalar>
945         </property>
946         <property dictRef="me:MW">
947           <scalar units="amu">28.0</scalar>
948         </property>
949       </propertyList>
950     </molecule>
951   </moleculeList>
952
953   <reactionList>
954     <reaction id="R1">
955       <reactant>
956         <molecule ref="C6H11O3-D"  role="modelled" />
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      </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>
```

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      <product>
        <molecule ref="C6H11O5-A62" me:type="sink"/>
      </product>
      <me:MCRCMethod name="SimpleBimolecularSink" />
      <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
      <me:excessReactantConc>5.0E18</me:excessReactantConc>
    </reaction>
        <reaction id="R4">
      <reactant>
        <molecule ref="D51_pr" me:type="modelled"/>
      </reactant>
      <reactant>
        <molecule ref="O2" me:type="excessReactant"/>
      </reactant>
      <product>
        <molecule ref="C6H11O5-D51" me:type="sink"/>
      </product>
      <me:MCRCMethod name="SimpleBimolecularSink" />
      <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
      <me:excessReactantConc>5.0E18</me:excessReactantConc>
    </reaction>
  </reactionList>

  <!-- Data taken from Seakins et al, J. Phys. Chem. Vol. 97, p. 4450 (1993). -->
  <me:conditions>
    <me:bathGas>N2</me:bathGas>
    <me:PTs>
      <me:PTpair units="Torr" P="760.00" T="298.15" precision="qd" />
    </me:PTs>
  </me:conditions>
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    <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

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