

1    **Supplement**

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

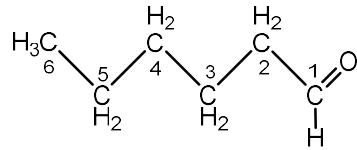
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10    **S1: Rate coefficients of H-abstractions predicted by SAR**

11    To place the calculated H-abstraction rate coefficients of hexanal + OH reaction in perspective,  
12    we compare them to a structure-activity relationship (SAR) data reported in the literature.<sup>[1,2]</sup>  
13    The SAR rate coefficients are calculated by using the formula,  $k_{\text{SAR}} = k_{\text{abs}} \times F(X) \times F(Y)$  and the  
14    resulting values are shown in Supplementary Table S1. Here,  $k_{\text{abs}}$  indicates the rate coefficient  
15    associated with the group ( $-\text{C}(=\text{O})\text{H}$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ) from which the H atom is being  
16    abstracted, where,  $F(X)$  and  $F(Y)$  are the substituent group factors. For aldehydic H-abstraction  
17    on C1, the substituent group factor  $F(X)$  corresponds to a  $-\text{CH}_2-$  group. Accordingly, for non-  
18    aldehydic H-abstraction from the secondary carbon C2, the substituent group factors  $F(X)$  and  
19     $F(Y)$  correspond to  $-\text{C}(=\text{O})\text{H}$  and  $-\text{CH}_2-$  groups respectively.



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

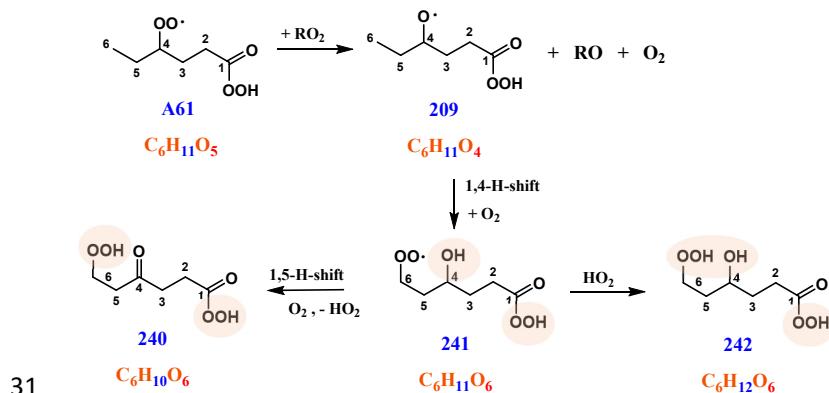
H-abstraction channels	$k_{\text{abs}}^{\text{a}}$ ( $10^{-12} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$ )	$F(X)^{\text{b}}$	$F(Y)^{\text{b}}$	$k_{\text{SAR}}$ ( $10^{-12} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$ )
C1 (ald H; $-\text{C}(=\text{O})\text{H}$ )	20.8	1.23 $X = -\text{CH}_2-$	—	25.58
C2 ( $\alpha$ H; $-\text{CH}_2-$ )	0.77	0.75 $X = -\text{C}(=\text{O})\text{H}$	1.23 $Y = -\text{CH}_2-$	0.71
C3 ( $\beta$ H; $-\text{CH}_2-$ )	0.77	1.23 $X = -\text{CH}_2-$	1.23 $Y = -\text{CH}_2-$	1.16
C4 ( $\gamma$ H; $-\text{CH}_2-$ )	0.77	1.23 $X = -\text{CH}_2-$	1.23 $Y = -\text{CH}_2-$	1.16
C5 ( $\delta$ H; $-\text{CH}_2-$ )	0.77	1.23 $X = -\text{CH}_2-$	1.00 $Y = -\text{CH}_3$	0.95
C6 (prim H; $-\text{CH}_3$ )	0.13	1.23 $X = -\text{CH}_2-$	—	0.16

23 <sup>a</sup> values taken from ref. 1 (Jenkin et al. 2018), <sup>b</sup> taken from ref. 2 (Ziemann et al. 2012)

## 24 S2: Bimolecular reaction products

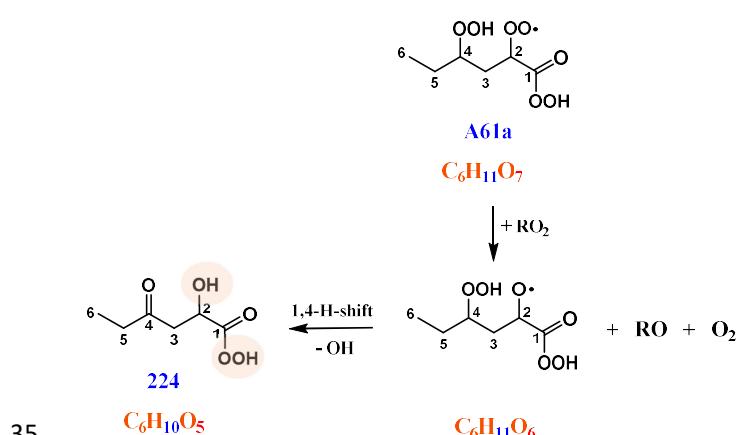
25 This section describes potential reaction mechanisms leading to identified products which  
26 involve one bimolecular RO<sub>2</sub> + RO<sub>2</sub> reaction step. The labile hydrogen containing groups are  
27 marked in light-brown shapes. The structures associated with the proposed mechanisms are in  
28 agreement with the hydrogen to deuterium (H to D) exchange experiments (see Figure 6 in the  
29 main manuscript).

### 30 C<sub>6</sub>H<sub>10-12</sub>O<sub>6</sub>



31 Figure S1: Formation of C<sub>6</sub>H<sub>10-12</sub>O<sub>6</sub> products likely involve A61 (C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture.

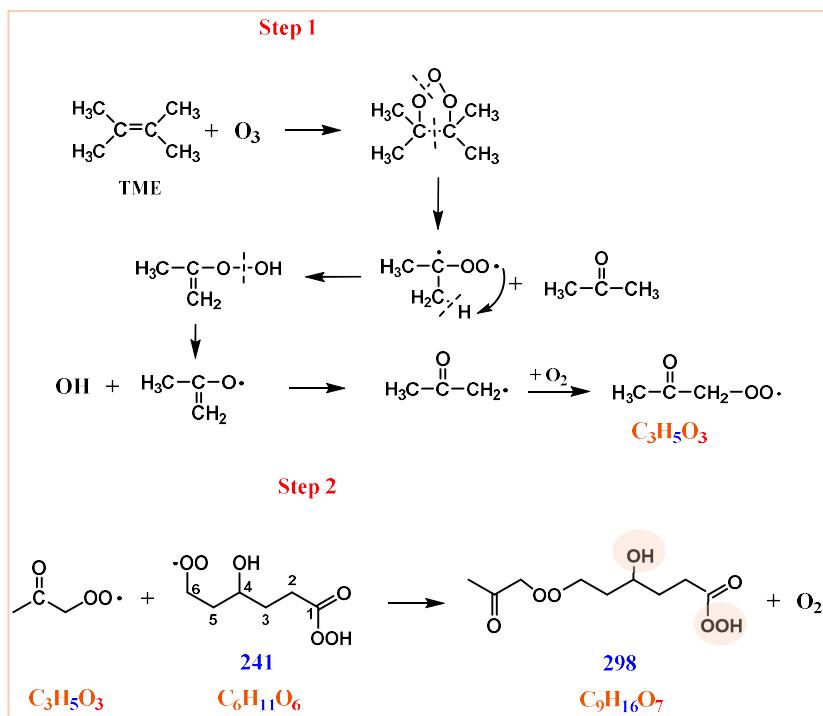
### 34 C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>



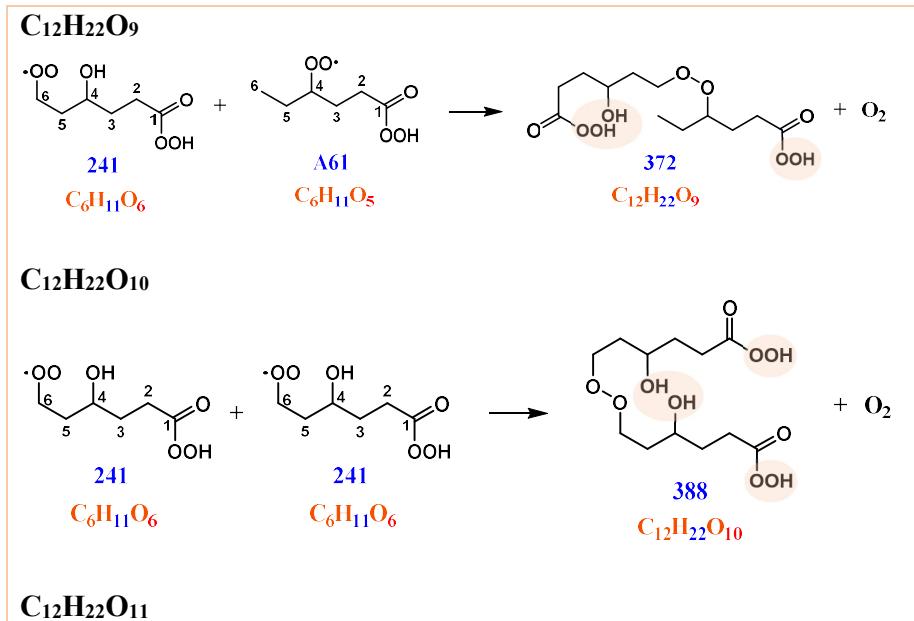
35 Figure S2: Formation of C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> product likely involves A61a (C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>) peroxy radical undergoing bimolecular reactions with other peroxy radicals in the gas mixture.

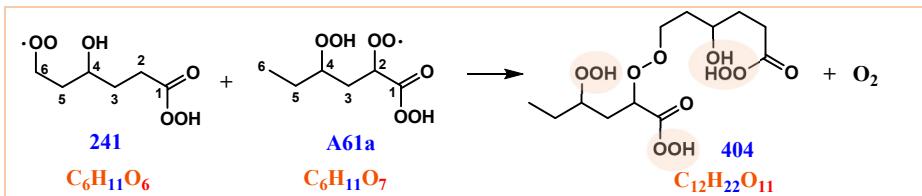
38 **C<sub>9</sub>H<sub>16</sub>O<sub>7</sub>**

39



40 Figure S3: Production of oxidant OH in tetramethylethylene (TME) ozonolysis. The keto  
 41 peroxy radical C<sub>3</sub>H<sub>5</sub>O<sub>3</sub> is a biproduct and reacts with hexanal derived peroxy radicals yielding  
 42 closed shell products with nine C atoms; a pathway producing C<sub>9</sub>H<sub>16</sub>O<sub>7</sub> peroxide accretion  
 43 product is shown as an example.

44 **HOM accretion products (C<sub>12</sub>H<sub>22</sub>O<sub>9-11</sub>)**



45 Figure S4: HOM accretion products ( $\text{C}_{12}\text{H}_{22}\text{O}_{9-11}$ ) are formed by self and cross  $\text{RO}_2 + \text{RO}_2$   
46 reactions.

47

### 48 S3: Kinetic modelling of HOM formation

49 Kinetic modelling using calculated rate constants is carried out using Kinetiscope Program<sup>[3,4]</sup>  
50 to estimate the time-scale of HOM formation. We include all oxidation initiation channels C1-  
51 C6 and the subsequent steps of the studied C1 and C4 channels in the simulation.

52 In our simulation, we also include bimolecular  $\text{RO}_2 + \text{RO}_2$  and  $\text{RO}_2 + \text{NO}$  reactions with  
53 variable concentrations to see the potential of autoxidation processes in HOM formation under  
54 atmospheric conditions. Initial concentration of hexanal is set to 1 ppb ( $2.46 \times 10^{10}$  molecules  
55  $\text{cm}^{-3}$ ), an average concentration in urban environment.<sup>[5]</sup> In higher aldehydes, the length of the  
56 carbon chain favors HOM formation tendency via autoxidation. Total concentration of  
57 aldehydes (hexanal-decanal) in Monti Cimini forest in Italy was measured to be 8.8 ppb ( $2.16 \times 10^{11}$  molecules  $\text{cm}^{-3}$ ).<sup>[6]</sup> We test this concentration as the higher limit of hexanal concentration  
58 to see the influence. A generic concentration of oxidant  $[\text{OH}] = 1.0 \times 10^7$  molecules  $\text{cm}^{-3}$  is used.  
59 A variable concentration of NO (0.01 – 40 ppb, i.e.,  $2.46 \times 10^8$  –  $9.84 \times 10^{11}$  molecules  $\text{cm}^{-3}$ ) is  
60 used to mimic the very clean to very high  $\text{NO}_x$  conditions. A generic value of  $[\text{RO}_2] = 1.0 \times 10^7$   
61 molecules  $\text{cm}^{-3}$  is used for VOC limited condition (high  $\text{NO}_x$ ) and a higher value of  $[\text{RO}_2] = 1.5 \times 10^9$  molecules  $\text{cm}^{-3}$  is used for  $\text{NO}_x$  limited condition. For pseudo-unimolecular  $\text{O}_2$  addition  
62 reaction, we use a rate coefficient of  $1 \times 10^7 \text{ s}^{-1}$ . Bimolecular rate coefficients for  $\text{RO}_2 + \text{RO}_2$   
63 and  $\text{RO}_2 + \text{NO}$  reactions are set to the generic values of  $3.2 \times 10^{-11}$  and  $9.0 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$   
64 respectively.<sup>[7,8]</sup>

65 One example of the reaction steps is as follows. In this work, we do not study the further  
66 reactions of bimolecular (i.e.,  $\text{RO}_2 + \text{RO}_2$ ,  $\text{RO}_2 + \text{NO}$ , etc.) reaction products. Therefore, in the  
67 simulation, we term the bimolecular products as sinks (e.g., Sink\_a in reaction step 14, Sink\_b  
68 in reaction step 18, and so on).

- 69 1. Hexanal + OH  $\Rightarrow$  A\_pr (aldehydic H-abstraction rate  $k = 2.14 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
- 70 2. A\_pr + O<sub>2</sub>  $\Rightarrow$  A (pseudo unimolecular rate  $k = 1 \times 10^7 \text{ s}^{-1}$ )
- 71 3. A\_pr  $\Rightarrow$  C<sub>5</sub>H<sub>11</sub> + CO ( $\beta$ -scission rate  $k = 2.27 \times 10^3 \text{ s}^{-1}$ )
- 72 4. Hexanal + OH  $\Rightarrow$  B\_pr ( $\alpha$ -H-abstraction rate  $k = 2.66 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
- 73 5. B\_pr + O<sub>2</sub>  $\Rightarrow$  B
- 74 6. Hexanal + OH  $\Rightarrow$  C\_pr ( $\beta$ -H-abstraction rate  $k = 4.76 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
- 75 7. C\_pr + O<sub>2</sub>  $\Rightarrow$  C
- 76 8. Hexanal + OH  $\Rightarrow$  D\_pr ( $\gamma$ -H-abstraction rate  $k = 9.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
- 77 9. D\_pr + O<sub>2</sub>  $\Rightarrow$  D

81        10. Hexanal + OH => E\_pr ( $\delta$ -H-abstraction rate  $k=7.35 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
 82        11. E\_pr + O<sub>2</sub> => E  
 83        12. Hexanal + OH => F\_pr (primary H-abstraction rate  $k=7.27 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
 84        13. F\_pr + O<sub>2</sub> => F  
 85        14. A + RO<sub>2</sub> => Sink\_a (Alkyl peroxy bimolecular rate  $k=3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
 86        15. A + NO => Sink\_aa (Bimolecular rate  $k=9.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
 87        16. A => A61\_pr (1,6-H-shift rate  $k=1.69 \times 10^{-1} \text{ s}^{-1}$ )  
 88        17. A61\_pr + O<sub>2</sub> => A61  
 89        18. A61 + RO<sub>2</sub> => Sink\_b  
 90        19. A61 + NO => Sink\_bb  
 91        20. A61 => A61a\_pr (1,5-H-shift rate  $k=3.9 \times 10^{-3} \text{ s}^{-1}$ )  
 92        21. A61a\_pr + O<sub>2</sub> => A61a  
 93        22. A61 => A62 (H-scrambling rate  $k=3.27 \times 10^{-6} \text{ s}^{-1}$ )  
 94        23. A62 => A62a6\_pr (1,6-H-shift rate  $k=2.08 \text{ s}^{-1}$ )  
 95        24. A => A51\_pr (1,5-H-shift rate  $k=3.49 \times 10^{-2} \text{ s}^{-1}$ )  
 96        25. A51\_pr + O<sub>2</sub> => A51  
 97        26. A51 + RO<sub>2</sub> => Sink\_c  
 98        27. A51 + NO => Sink\_cc  
 99        28. A51 => A51a5\_pr (1,5-H-shift rate  $k=7.81 \times 10^{-4} \text{ s}^{-1}$ )  
 100      29. A51a5\_pr + O<sub>2</sub> => A51a5  
 101      30. A51 => A51a6\_pr (1,6-H-shift rate  $k=2.77 \times 10^{-5} \text{ s}^{-1}$ )  
 102      31. A51a6\_pr + O<sub>2</sub> => A51a6  
 103      32. D + RO<sub>2</sub> => Sink\_d  
 104      33. D + NO => Sink\_dd  
 105      34. D => D61\_pr (1,6-H-shift rate  $k=8.63 \times 10^{-1} \text{ s}^{-1}$ )  
 106      35. D61\_pr + O<sub>2</sub> => A62  
 107      36. A62 => A61 (H-scrambling rate  $k=6.92 \times 10^2 \text{ s}^{-1}$ )  
 108      37. D => D51\_pr (1,5-H-shift rate  $k=3.91 \times 10^{-2} \text{ s}^{-1}$ )  
 109      38. D51\_pr + O<sub>2</sub> => D51  
 110      39. D51 => D52 (H-scrambling rate  $k=8.96 \times 10^1 \text{ s}^{-1}$ )  
 111      40. D52 + RO<sub>2</sub> => Sink\_e  
 112      41. D52 + NO => Sink\_ee  
 113      42. D52 => D52n\_pr (1,6-H-shift rate  $k=1.38 \times 10^{-1} \text{ s}^{-1}$ )  
 114      43. D52n\_pr + O<sub>2</sub> => D52  
 115      44. D51 => D52n\_pr (1,4-H-shift rate  $k=2.67 \times 10^{-2} \text{ s}^{-1}$ )

116      The detailed results are given in Supplementary Table S2. For a cleaner environment (1  
 117      ppb=2.46  $\times 10^{10}$  molecules  $\text{cm}^{-3}$  hexanal, 0.1 ppb=2.46  $\times 10^9$  molecules  $\text{cm}^{-3}$  NO, and 1.0  $\times 10^8$   
 118      molecules  $\text{cm}^{-3}$  RO<sub>2</sub>), referring to a product concentration of  $3.0 \times 10^3$  molecules  $\text{cm}^{-3}$ ,  
 119      simulation results show that the O<sub>5</sub> intermediates A61 and A51 from C1 channel appear at 0.3  
 120      s and 0.5 s respectively, while D52 from C4 channels appeared at 8.5 s of reaction time (see  
 121      Supplementary Figure S5). The fastest O<sub>7</sub> HOM (A61a at 3.8 s) is associated with the C1  
 122      oxidation channel. On the other hand, the O<sub>7</sub> HOM (D52n) associated with C4 channel appear  
 123      at 11.5 s of reaction time. After 10 s of reaction time, the O<sub>5</sub> intermediates A61 and A51 comes  
 124      with the concentrations of  $1.9 \times 10^6$  and  $3.4 \times 10^5$  molecules  $\text{cm}^{-3}$  respectively while the  
 125      concentration of D52 increases only slightly to  $3.3 \times 10^3$  molecules  $\text{cm}^{-3}$ . Among the O<sub>7</sub> HOM,

126 A61a shows the highest concentration ( $3.2 \times 10^4$  molecules  $\text{cm}^{-3}$ ) where the concentration of  
 127 D52n is  $2.4 \times 10^3$  molecules  $\text{cm}^{-3}$  at the end of the 10 s simulation reaction time.

128 Supplementary Table S2: Kinetic modelling results of selected oxidation products  
 129 corresponding to variable reactant concentrations of atmospheric relevance.

Reactant concentrations (#/cm3)				Product concentrations (#/cm3)				
<i>Hexanal</i>	<i>OH</i>	<i>NO</i>	<i>RO2</i>	O <sub>5</sub> -intermediate		O <sub>7</sub> -HOM		
				<i>A61</i>	<i>A51</i>	<i>D52</i>	<i>A61a</i>	<i>D52n</i>
2.46E+10 (1 ppb)	1.0E+7	2.46E+8 (.01 ppb)	1.0E+7	2.1E+6 <sup>a</sup> (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)
			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)
2.16E+11 (8.8 ppb)	1.0E+7	2.46E+8 (.01 ppb)	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)
			1.0E+8	3.0E+3 <sup>b</sup> (0.3 s)	3.0E+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)
			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)
2.46E+10 (1 ppb)	1.0E+7	2.46E+10 (1 ppb)	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)

<sup>a</sup> below the product concentrations in the parenthesis are the reaction times. <sup>b</sup> the reaction times colored in red indicate how fast the corresponding products appeared, in the simulation.

130  
131

132 Supplementary Table S2 (continued)

Reactant concentrations (#/cm3)				Product concentrations (#/cm3)				
<i>Hexanal</i>	<i>OH</i>	<i>NO</i>	<i>RO<sub>2</sub></i>	O <sub>5</sub> -intermediate			O <sub>7</sub> -HOM	
				<i>A61</i>	<i>A51</i>	<i>D52</i>	<i>A61a</i>	<i>D52n</i>
2.16E+11 (8.8 ppb)	1.0E+7	2.46E+10 (1 ppb)	1.0E+7	1.1E+6 <sup>a</sup> (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)
				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)
			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)
2.46E+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)
			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)

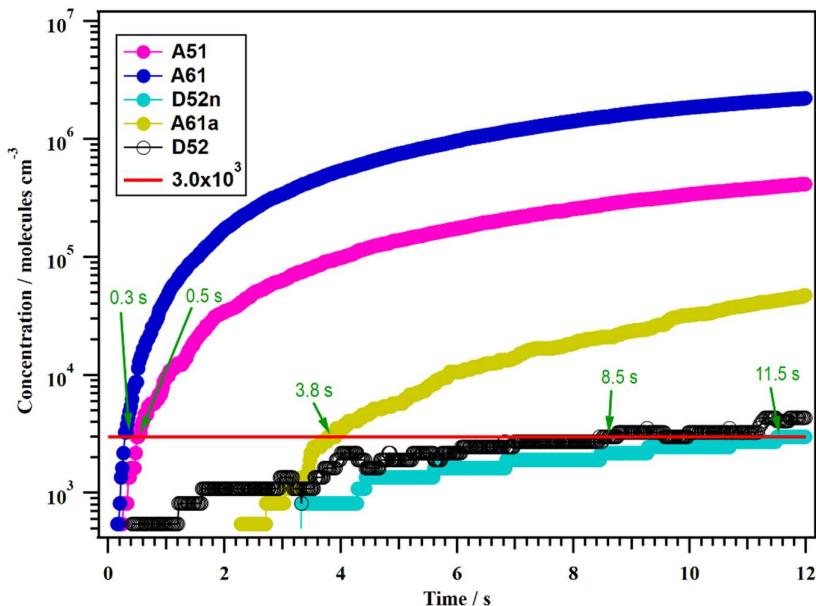
133 <sup>a</sup> below the product concentrations in the parenthesis are the reaction times.

134 At this RO<sub>2</sub> and NO level, when we increase the hexanal concentration to 8.8 ppb, the O<sub>5</sub>-  
 135 intermediate and the O<sub>7</sub> HOM concentrations increase by a factor of 3 to 4 with the occurrence  
 136 of A61a HOM concentration of  $4.0 \times 10^3$  molecules cm<sup>-3</sup> as early as 1.7 s reaction time. At 10  
 137 s, the D52 intermediate and D52n HOM concentrations reach at  $4.3 \times 10^3$  and  $8.7 \times 10^3$   
 138 molecules cm<sup>-3</sup> respectively.

139 When the NO concentration is set to a one order of magnitude lower value (0.01 ppb), the  
 140 product concentrations are increased only by a factor of up to 1.6. Increasing the NO  
 141 concentration to 1 ppb, keeping the hexanal concentration at 1 ppb, and RO<sub>2</sub> concentration at  
 142  $1.0 \times 10^8$  molecules cm<sup>-3</sup>, we can still see the appearance of significant O<sub>7</sub> HOM concentrations  
 143 resulting  $1.3 \times 10^4$  and  $1.5 \times 10^3$  molecules cm<sup>-3</sup> for A61a and D52n respectively after 10 s  
 144 reaction time. Increasing the RO<sub>2</sub> concentration to  $1.5 \times 10^9$  molecules cm<sup>-3</sup> at this point, drops  
 145 the O<sub>7</sub> HOM concentrations by a factor maximum 1.5.

146 On the other hand, a NO concentration of 4 ppb stops the production of D52n HOM associated  
 147 with C4 channel regardless of how big the hexanal concentration is while A61a HOM

148 associated with C1 channel is still produced after 10 s of rection time. When we set the NO  
149 concentration to the highest (40 ppb), it completely stops the formation of any O<sub>5</sub> intermediate  
150 and O<sub>7</sub> HOM after 10 s reaction time.

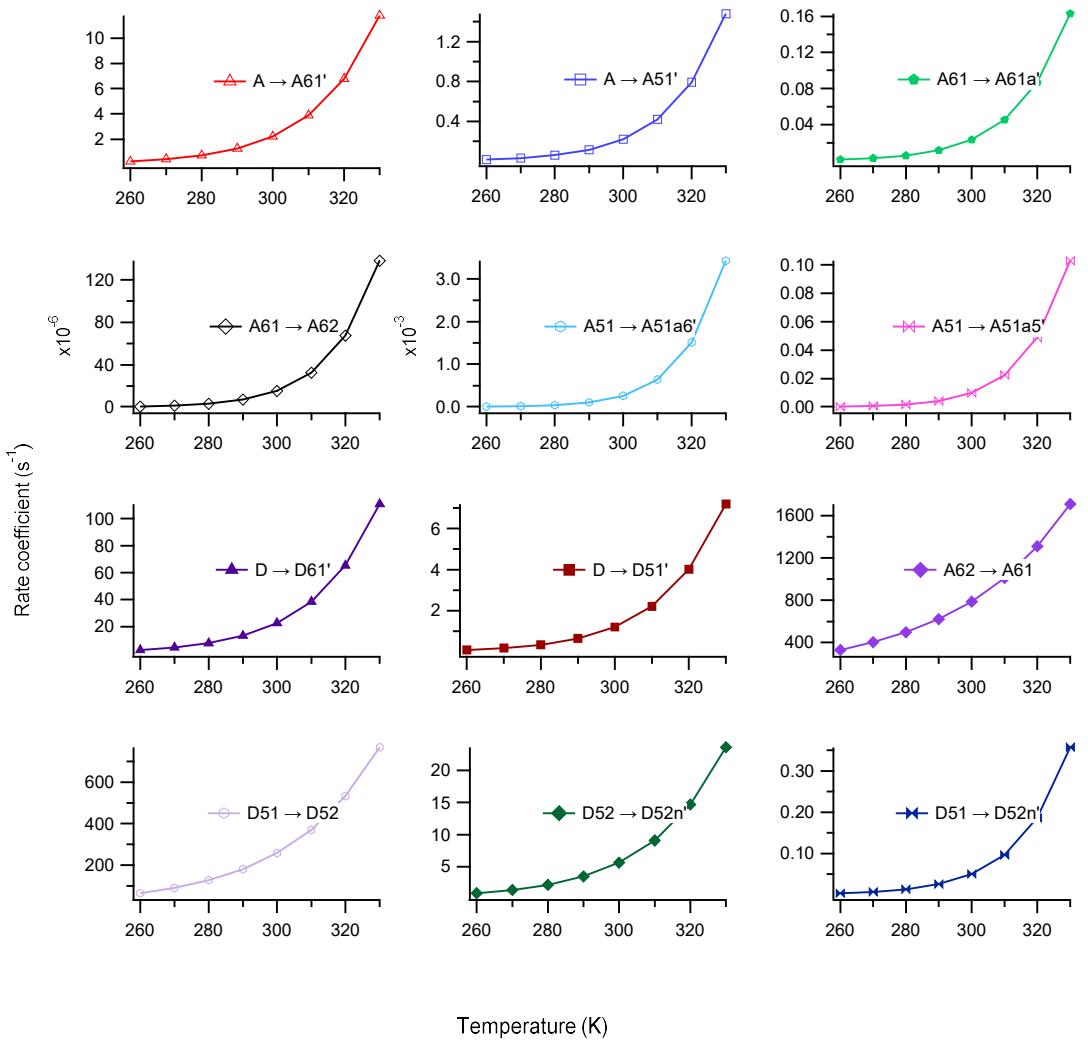


151  
152 Figure S5: Time profile of hexanal oxidation products showing the appearance of different  
153 species with five to seven O atoms. Reactant concentrations: hexanal=1ppb ( $2.46 \times 10^{10}$   
154 molecules cm<sup>-3</sup>), OH=1.0 × 10<sup>7</sup> molecules cm<sup>-3</sup>, NO=0.1 ppb ( $2.46 \times 10^9$  molecules cm<sup>-3</sup>), and  
155 RO<sub>2</sub>=1.0 × 10<sup>8</sup> molecules cm<sup>-3</sup>. The red straight line indicating an arbitrary reference  
156 concentration of  $3.0 \times 10^3$  molecules cm<sup>-3</sup> intersects the product curves at different reaction  
157 times (RTs). Among the intermediates with five O atoms, A61 reaches the reference  
158 concentration very fast at 0.3 s while A51 and D52 reaches at 0.5 and 8.5 s respectively. Among  
159 the species with seven O atoms, A61a the concentration level at 3.8 s while D52n at 11.5 s.

160

#### 161 S4: Temperature dependency of H-shift rate coefficients

162 In general, the H-shift reaction which are key to autoxidation are highly dependent on  
163 temperature. To test this, we apply a temperature range of 260-330 K in the MESMER  
164 simulation. Given that all our H-shift reactions have positive barriers, we observe a positive  
165 temperature dependency in these reactions (see Supplementary Figure S6 and Table S3). The  
166 results show that at 310 K, the H-shift rate coefficients are increased by factors of 1.3-3 relative  
167 to the rate coefficients at 298.15 K. At 330 K, the factors increase to 2.3-8 for different H-shift  
168 reactions. The second H-shift reactions which by a subsequent O<sub>2</sub> addition reaction lead to O<sub>7</sub>  
169 HOM A61a' and D52n' (via C1 and C4 channels respectively) get faster by factors of 2.2 and  
170 1.8 respectively at 310 K in terms of their rate coefficients. The factors for these H-shift  
171 reactions increase to 8 and 4.6 respectively at a temperature of 330 K.



172

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

175

176 Supplementary Table S3: MESMER rate coefficients of H-shift reactions at different  
 177 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
$A \rightarrow A61'$	$2.34 \times 10^{-1}$	$4.10 \times 10^{-1}$	$7.20 \times 10^{-1}$	1.26	2.22	3.89	6.79	$1.18 \times 10^1$
$A \rightarrow A51'$	$1.67 \times 10^{-2}$	$3.19 \times 10^{-2}$	$6.09 \times 10^{-2}$	$1.16 \times 10^{-1}$	$2.21 \times 10^{-1}$	$4.20 \times 10^{-1}$	$7.92 \times 10^{-1}$	1.48
$A61 \rightarrow A61a'$	$1.29 \times 10^{-3}$	$2.76 \times 10^{-3}$	$5.75 \times 10^{-3}$	$1.17 \times 10^{-2}$	$2.32 \times 10^{-2}$	$4.53 \times 10^{-2}$	$8.68 \times 10^{-2}$	$1.63 \times 10^{-1}$
$A61 \rightarrow A62$	$5.82 \times 10^{-7}$	$1.38 \times 10^{-6}$	$3.17 \times 10^{-6}$	$7.07 \times 10^{-6}$	$1.53 \times 10^{-5}$	$3.25 \times 10^{-5}$	$6.75 \times 10^{-5}$	$1.38 \times 10^{-4}$

---

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

---

178

179 **S5: MESMER input for branching of D towards A62 and D51**180 (Unimolecular H-shift reactions followed by pseudo-unimolecular O<sub>2</sub> addition reactions)181 The example MESMER input contains all the geometries, vibrational frequencies, and  
182 corrected relative energies of the studied species.

183

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472              1397.48 1409.89 1425.80 1444.43 1457.39 1479.98 1490.94 1503.94 1511.67 1941.48
473              3035.93 3050.65 3054.16 3059.27 3069.35 3099.99 3106.20 3116.03 3122.78 3142.14
474              3723.51
475          </array>
476      </property>
477      <property dictRef="me:MW">
478          <scalar>131.15</scalar>
479      </property>
480      <property dictRef="me:epsilon">
481          <scalar>343.0</scalar>
482      </property>
483      <property dictRef="me:sigma">
484          <scalar>6.25</scalar>
485      </property>
486      <property dictRef="me:spinMultiplicity">
487          <scalar>2</scalar>
488      </property>
489      </propertyList>
490      <me:energyTransferModel xsi:type="me:ExponentialDown">
491          <me:deltaEDown units="cm-1">225.0</me:deltaEDown>
492      </me:energyTransferModel>
493      </molecule>
494
495      <molecule id="C6H11O5-A62">
496          <atomArray>

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497 <atom id="a1" elementType="H" hydrogenCount="0" x3="-3.299530" y3="-0.442021"
498 z3="-1.556808"/>
499 <atom id="a2" elementType="C" hydrogenCount="3" x3="-3.373600" y3="-1.102928"
500 z3="-0.695105"/>
501 <atom id="a3" elementType="H" hydrogenCount="0" x3="-4.133145" y3="-0.698268"
502 z3="-0.024688"/>
503 <atom id="a4" elementType="H" hydrogenCount="0" x3="-3.716512" y3="-2.077519"
504 z3="-1.040749"/>
505 <atom id="a5" elementType="C" hydrogenCount="2" x3="-2.030843" y3="-1.220494"
506 z3="0.014110"/>
507 <atom id="a6" elementType="H" hydrogenCount="0" x3="-1.300866" y3="-1.674410"
508 z3="-0.659900"/>
509 <atom id="a7" elementType="H" hydrogenCount="0" x3="-2.118514" y3="-1.884179"
510 z3="0.876947"/>
511 <atom id="a8" elementType="C" hydrogenCount="1" x3="-1.497534" y3="0.120203"
512 z3="0.504450"/>
513 <atom id="a9" elementType="H" hydrogenCount="0" x3="-2.301087" y3="0.661709"
514 z3="1.012412"/>
515 <atom id="a10" elementType="C" hydrogenCount="2" x3="-0.316526" y3="0.009499"
516 z3="1.471109"/>
517 <atom id="a11" elementType="H" hydrogenCount="0" x3="-0.643120" y3="-0.579497"
518 z3="2.328861"/>
519 <atom id="a12" elementType="H" hydrogenCount="0" x3="-0.070561" y3="1.001090"
520 z3="1.850716"/>
521 <atom id="a13" elementType="C" hydrogenCount="2" x3="0.929836" y3="-0.644360"
522 z3="0.882652"/>
523 <atom id="a14" elementType="H" hydrogenCount="0" x3="0.697788" y3="-1.521864"
524 z3="0.282847"/>
525 <atom id="a15" elementType="H" hydrogenCount="0" x3="1.585464" y3="-1.012316"
526 z3="1.675832"/>
527 <atom id="a16" elementType="C" hydrogenCount="0" x3="1.764972" y3="0.290348"
528 z3="0.067524"/>
529 <atom id="a17" elementType="O" hydrogenCount="0" x3="1.705666" y3="1.473157"
530 z3="-0.019954"/>
531 <atom id="a18" elementType="O" hydrogenCount="0" x3="-1.156013" y3="0.839719"
532 z3="-0.671506"/>
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533 <atom id="a19" elementType="O" hydrogenCount="1" x3="-1.021099" y3="2.215035"  
534 z3="-0.342899"/>  
535 <atom id="a20" elementType="H" hydrogenCount="0" x3="-0.060584" y3="2.294490"  
536 z3="-0.244798"/>  
537 <atom id="a21" elementType="O" hydrogenCount="0" x3="2.830727" y3="-0.291473"  
538 z3="-0.675756"/>  
539 <atom id="a22" elementType="O" hydrogenCount="0" x3="2.953572" y3="-1.584040"  
540 z3="-0.536024"/>  
541 </atomArray>  
542 <bondArray>  
543 <bond atomRefs2="a1 a2" order="1"/>  
544 <bond atomRefs2="a4 a2" order="1"/>  
545 <bond atomRefs2="a2 a3" order="1"/>  
546 <bond atomRefs2="a2 a5" order="1"/>  
547 <bond atomRefs2="a21 a22" order="1"/>  
548 <bond atomRefs2="a21 a16" order="1"/>  
549 <bond atomRefs2="a18 a19" order="1"/>  
550 <bond atomRefs2="a18 a8" order="1"/>  
551 <bond atomRefs2="a6 a5" order="1"/>  
552 <bond atomRefs2="a19 a20" order="1"/>  
553 <bond atomRefs2="a17 a16" order="2"/>  
554 <bond atomRefs2="a5 a8" order="1"/>  
555 <bond atomRefs2="a5 a7" order="1"/>  
556 <bond atomRefs2="a16 a13" order="1"/>  
557 <bond atomRefs2="a14 a13" order="1"/>  
558 <bond atomRefs2="a8 a9" order="1"/>  
559 <bond atomRefs2="a8 a10" order="1"/>  
560 <bond atomRefs2="a13 a10" order="1"/>  
561 <bond atomRefs2="a13 a15" order="1"/>  
562 <bond atomRefs2="a10 a12" order="1"/>  
563 <bond atomRefs2="a10 a11" order="1"/>  
564 </bondArray>
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565    <propertyList>
566        <property dictRef="me:ZPE">
567            <scalar units="kcal/mol">-30.87</scalar>
568        </property>
569        <property dictRef="me:rotConsts">
570            <array units="cm-1">
571                0.055 0.022 0.019
572            </array>
573        </property>
574        <property dictRef="me:symmetryNumber">
575            <scalar>1</scalar>
576        </property>
577        <property dictRef="me:vibFreqs">
578            <array units="cm-1">
579                34.92 52.51 80.17 119.38 160.41 162.94 197.91 214.93 236.09 284.59 323.91 340.88
580                414.11 496.53 511.37 517.24 569.86 599.10 643.02 765.57 770.38 870.19 903.98 938.47
581                986.09 1011.86 1039.09 1063.16 1076.55 1090.81 1143.06 1190.91 1232.95 1247.85
582                1267.81 1312.73 1337.83 1375.52 1392.80 1405.25 1423.88 1424.48 1452.48 1465.56
583                1485.75 1494.79 1505.18 1513.85 1897.98 3042.61 3052.68 3054.11 3070.71 3080.88
584                3091.96 3119.83 3124.56 3138.43 3143.35 3708.15
585            </array>
586        </property>
587        <property dictRef="me:MW">
588            <scalar>163.15</scalar>
589        </property>
590        <property dictRef="me:spinMultiplicity">
591            <scalar>2</scalar>
592        </property>
593    </propertyList>
594    <me:DOSCMETHOD xsi:type="ClassicalRotors"/>
595 </molecule>
596
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597 <molecule id="D_1-5Hshift_RR-TS">
598   <atomArray>
599     <atom id="a1" elementType="C" hydrogenCount="1" x3="-2.629360" y3="-0.283299"
600       z3="-0.224138"/>
601     <atom id="a2" elementType="H" hydrogenCount="0" x3="-3.605403" y3="0.232118"
602       z3="-0.279199"/>
603     <atom id="a3" elementType="O" hydrogenCount="0" x3="-2.379290" y3="-1.206994"
604       z3="-0.964757"/>
605     <atom id="a4" elementType="C" hydrogenCount="1" x3="-1.679910" y3="0.255775"
606       z3="0.756364"/>
607     <atom id="a5" elementType="C" hydrogenCount="2" x3="-0.426800" y3="-0.518010"
608       z3="1.029928"/>
609     <atom id="a6" elementType="H" hydrogenCount="0" x3="-0.612316" y3="-1.586320"
610       z3="0.903206"/>
611     <atom id="a7" elementType="H" hydrogenCount="0" x3="-0.072637" y3="-0.335185"
612       z3="2.043298"/>
613     <atom id="a8" elementType="C" hydrogenCount="1" x3="0.710774" y3="-0.147623"
614       z3="0.043884"/>
615     <atom id="a9" elementType="H" hydrogenCount="0" x3="0.415466" y3="-0.440234"
616       z3="-0.966317"/>
617     <atom id="a10" elementType="C" hydrogenCount="2" x3="2.048733" y3="-0.743659"
618       z3="0.428315"/>
619     <atom id="a11" elementType="H" hydrogenCount="0" x3="1.899804" y3="-1.816392"
620       z3="0.563595"/>
621     <atom id="a12" elementType="H" hydrogenCount="0" x3="2.342624" y3="-0.342239"
622       z3="1.401001"/>
623     <atom id="a13" elementType="C" hydrogenCount="3" x3="3.139806" y3="-0.491322"
624       z3="-0.604064"/>
625     <atom id="a14" elementType="H" hydrogenCount="0" x3="2.865342" y3="-0.913407"
626       z3="-1.571581"/>
627     <atom id="a15" elementType="H" hydrogenCount="0" x3="4.078143" y3="-0.948501"
628       z3="-0.292792"/>
629     <atom id="a16" elementType="H" hydrogenCount="0" x3="3.311413" y3="0.575487"
630       z3="-0.739574"/>
631     <atom id="a17" elementType="O" hydrogenCount="0" x3="0.839784" y3="1.267191"
632       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>

```

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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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733    <atom id="a19" elementType="O" hydrogenCount="1" x3="0.012856" y3="1.579026"
734    z3="-0.453707"/>
735    <atom id="a20" elementType="H" hydrogenCount="0" x3="0.927872" y3="1.617310"
736    z3="-0.135504"/>
737  </atomArray>
738  <bondArray>
739    <bond atomRefs2="a2 a1" order="1"/>
740    <bond atomRefs2="a16 a14" order="1"/>
741    <bond atomRefs2="a13 a11" order="1"/>
742    <bond atomRefs2="a5 a4" order="1"/>
743    <bond atomRefs2="a17 a14" order="1"/>
744    <bond atomRefs2="a1 a4" order="1"/>
745    <bond atomRefs2="a1 a3" order="2"/>
746    <bond atomRefs2="a14 a11" order="1"/>
747    <bond atomRefs2="a14 a15" order="1"/>
748    <bond atomRefs2="a19 a20" order="1"/>
749    <bond atomRefs2="a19 a18" order="1"/>
750    <bond atomRefs2="a11 a12" order="1"/>
751    <bond atomRefs2="a11 a9" order="1"/>
752    <bond atomRefs2="a4 a6" order="1"/>
753    <bond atomRefs2="a18 a9" order="1"/>
754    <bond atomRefs2="a9 a6" order="1"/>
755    <bond atomRefs2="a9 a10" order="1"/>
756    <bond atomRefs2="a6 a8" order="1"/>
757    <bond atomRefs2="a6 a7" order="1"/>
758  </bondArray>
759  <propertyList>
760    <property dictRef="me:ZPE">
761      <scalar units="kcal/mol">6.16</scalar>
762    </property>
763    <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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796      </me:energyTransferModel>
797      </molecule>
798
799      <molecule id="C6H11O5-D51">
800      <atomArray>
801      <atom id="a1" elementType="C" hydrogenCount="1" x3="-1.679583" y3="1.016706"
802      z3="-0.232156"/>
803      <atom id="a2" elementType="H" hydrogenCount="0" x3="-2.025198" y3="0.878997"
804      z3="-1.269083"/>
805      <atom id="a3" elementType="O" hydrogenCount="0" x3="-1.484024" y3="2.104712"
806      z3="0.242018"/>
807      <atom id="a4" elementType="C" hydrogenCount="1" x3="-1.509098" y3="-0.252399"
808      z3="0.588005"/>
809      <atom id="a5" elementType="H" hydrogenCount="0" x3="-2.231053" y3="-0.213646"
810      z3="1.405441"/>
811      <atom id="a6" elementType="C" hydrogenCount="2" x3="-0.099885" y3="-0.442493"
812      z3="1.120948"/>
813      <atom id="a7" elementType="H" hydrogenCount="0" x3="-0.067627" y3="-1.353504"
814      z3="1.718606"/>
815      <atom id="a8" elementType="H" hydrogenCount="0" x3="0.118056" y3="0.391478"
816      z3="1.789051"/>
817      <atom id="a9" elementType="C" hydrogenCount="1" x3="0.957465" y3="-0.511050"
818      z3="0.022390"/>
819      <atom id="a10" elementType="H" hydrogenCount="0" x3="0.707955" y3="-1.313333"
820      z3="-0.677086"/>
821      <atom id="a11" elementType="C" hydrogenCount="2" x3="2.354760" y3="-0.744185"
822      z3="0.575827"/>
823      <atom id="a12" elementType="H" hydrogenCount="0" x3="2.328387" y3="-1.675630"
824      z3="1.146132"/>
825      <atom id="a13" elementType="H" hydrogenCount="0" x3="2.592796" y3="0.052586"
826      z3="1.281407"/>
827      <atom id="a14" elementType="C" hydrogenCount="3" x3="3.420180" y3="-0.824068"
828      z3="-0.507815"/>
829      <atom id="a15" elementType="H" hydrogenCount="0" x3="3.200881" y3="-1.623803"
830      z3="-1.217151"/>

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831   <atom id="a16" elementType="H" hydrogenCount="0" x3="4.398358" y3="-1.021967"
832   z3="-0.071457"/>
833   <atom id="a17" elementType="H" hydrogenCount="0" x3="3.478549" y3="0.110166"
834   z3="-1.063457"/>
835   <atom id="a18" elementType="O" hydrogenCount="0" x3="0.877714" y3="0.629090"
836   z3="-0.832288"/>
837   <atom id="a19" elementType="O" hydrogenCount="1" x3="1.318906" y3="1.780465"
838   z3="-0.125327"/>
839   <atom id="a20" elementType="H" hydrogenCount="0" x3="0.481012" y3="2.233918"
840   z3="0.058295"/>
841   <atom id="a21" elementType="O" hydrogenCount="0" x3="-1.840896" y3="-1.402382"
842   z3="-0.219239"/>
843   <atom id="a22" elementType="O" hydrogenCount="0" x3="-3.077343" y3="-1.351927"
844   z3="-0.628151"/>
845   </atomArray>
846   <bondArray>
847   <bond atomRefs2="a2 a1" order="1"/>
848   <bond atomRefs2="a15 a14" order="1"/>
849   <bond atomRefs2="a17 a14" order="1"/>
850   <bond atomRefs2="a18 a19" order="1"/>
851   <bond atomRefs2="a18 a9" order="1"/>
852   <bond atomRefs2="a10 a9" order="1"/>
853   <bond atomRefs2="a22 a21" order="1"/>
854   <bond atomRefs2="a14 a16" order="1"/>
855   <bond atomRefs2="a14 a11" order="1"/>
856   <bond atomRefs2="a1 a3" order="2"/>
857   <bond atomRefs2="a1 a4" order="1"/>
858   <bond atomRefs2="a21 a4" order="1"/>
859   <bond atomRefs2="a19 a20" order="1"/>
860   <bond atomRefs2="a9 a11" order="1"/>
861   <bond atomRefs2="a9 a6" order="1"/>
862   <bond atomRefs2="a11 a12" order="1"/>
863   <bond atomRefs2="a11 a13" order="1"/>

```

```

864    <bond atomRefs2="a4 a6" order="1"/>
865    <bond atomRefs2="a4 a5" order="1"/>
866    <bond atomRefs2="a6 a7" order="1"/>
867    <bond atomRefs2="a6 a8" order="1"/>
868  </bondArray>
869  <propertyList>
870    <property dictRef="me:ZPE">
871      <scalar units="kcal/mol">-13.59</scalar>
872    </property>
873    <property dictRef="me:rotConsts">
874      <array units="cm-1">
875        0.056 0.025 0.020
876      </array>
877    </property>
878    <property dictRef="me:symmetryNumber">
879      <scalar>1</scalar>
880    </property>
881    <property dictRef="me:vibFreqs">
882      <array units="cm-1">
883        62.55 71.80 97.45 117.72 149.76 183.99 206.03 213.77 228.86 286.52 298.07 332.45
884        357.21 422.38 480.16 503.17 577.88 597.43 655.76 786.83 826.75 870.19 910.67 954.64
885        986.44 1016.35 1029.14 1045.27 1098.16 1123.53 1148.46 1185.06 1250.26 1263.50
886        1290.83 1316.87 1325.16 1334.00 1380.94 1398.91 1412.29 1416.35 1427.34 1471.53
887        1473.98 1488.40 1504.96 1511.77 1820.68 2996.38 3053.21 3058.27 3068.30 3079.98
888        3091.84 3103.17 3125.57 3130.21 3142.82 3689.10
889      </array>
890    </property>
891    <property dictRef="me:MW">
892      <scalar>163.15</scalar>
893    </property>
894    <property dictRef="me:spinMultiplicity">
895      <scalar>2</scalar>

```

```

896      </property>
897      </propertyList>
898      <me:DOSCMETHOD xsi:type="ClassicalRotors"/>
899      </molecule>
900
901      <molecule id="O2">
902          <atomArray>
903              <atom id="a1" elementType="O" hydrogenCount="0" x3="0.000000" y3="0.000000"
904              z3="0.597994"/>
905              <atom id="a2" elementType="O" hydrogenCount="0" x3="0.000000" y3="0.000000" z3="-
906              0.597994"/>
907          </atomArray>
908          <bondArray>
909              <bond atomRefs2="a2 a1" order="2"/>
910          </bondArray>
911          <propertyList>
912              <property dictRef="me:ZPE">
913                  <scalar units="kcal/mol">0.00</scalar>
914              </property>
915              <property dictRef="me:rotConsts">
916                  <array units="cm-1">
917                      1.473
918                  </array>
919              </property>
920              <property dictRef="me:symmetryNumber">
921                  <scalar>2</scalar>
922              </property>
923              <property dictRef="me:vibFreqs">
924                  <array units="cm-1">
925                      1703.81
926                  </array>

```

```

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" />

```

```

957      </reactant>
958      <product>
959          <molecule ref="D61_pr" role="modelled" />
960      </product>
961          <me:transitionState>
962              <molecule ref="D_1-6-aldHshift-TS" role="transitionState" />
963          </me:transitionState>
964              <me:tunneling name="Eckart" />
965              <me:MCRCMethod name="RRKM"/>
966      </reaction>
967      <reaction id="R2">
968          <reactant>
969              <molecule ref="C6H11O3-D" role="modelled" />
970          </reactant>
971          <product>
972              <molecule ref="D51_pr" role="modelled" />
973          </product>
974          <me:transitionState>
975              <molecule ref="D_1-5Hshift_RR-TS" role="transitionState" />
976          </me:transitionState>
977              <me:tunneling name="Eckart" />
978              <me:MCRCMethod name="RRKM"/>
979      </reaction>
980      <reaction id="R3">
981          <reactant>
982              <molecule ref="D61_pr" me:type="modelled"/>
983          </reactant>
984          <reactant>
985              <molecule ref="O2" me:type="excessReactant"/>
986          </reactant>

```

```

987      <product>
988          <molecule ref="C6H11O5-A62" me:type="sink"/>
989      </product>
990      <me:MCRCMethod name="SimpleBimolecularSink" />
991      <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
992      <me:excessReactantConc>5.0E18</me:excessReactantConc>
993  </reaction>
994      <reaction id="R4">
995          <reactant>
996              <molecule ref="D51_pr" me:type="modelled"/>
997          </reactant>
998          <reactant>
999              <molecule ref="O2" me:type="excessReactant"/>
1000         </reactant>
1001         <product>
1002             <molecule ref="C6H11O5-D51" me:type="sink"/>
1003         </product>
1004         <me:MCRCMethod name="SimpleBimolecularSink" />
1005         <me:BimolecularLossRateCoefficient>2E-12</me:BimolecularLossRateCoefficient>
1006         <me:excessReactantConc>5.0E18</me:excessReactantConc>
1007     </reaction>
1008 </reactionList>
1009
1010 <!-- Data taken from Seakins et al, J. Phys. Chem. Vol. 97, p. 4450 (1993). -->
1011 <me:conditions>
1012     <me:bathGas>N2</me:bathGas>
1013     <me:PTs>
1014         <me:PTpair units="Torr" P="760.00" T="298.15" precision="qd" />
1015     </me:PTs>
1016 </me:conditions>

```

1017  
1018 <me:modelParameters>  
1019 <me:grainSize units="cm-1">100</me:grainSize>  
1020 <me:energyAboveTheTopHill>30</me:energyAboveTheTopHill>  
1021 </me:modelParameters>  
1022  
1023 <me:control>  
1024 <me:ForceMacroDetailedBalance/>  
1025 <me:testDOS />  
1026 <me:printSpeciesProfile />  
1027 <me:testMicroRates />  
1028 <me:testRateConstants />  
1029 <me:printGrainDOS />  
1030 <me:printTunnellingCoefficients />  
1031 <me:printGrainkfE />  
1032 <me:printGrainkbE />  
1033 <me:eigenvalues>3</me:eigenvalues>  
1034 </me:control>  
1035 </me:mesmer>  
1036  
1037

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