

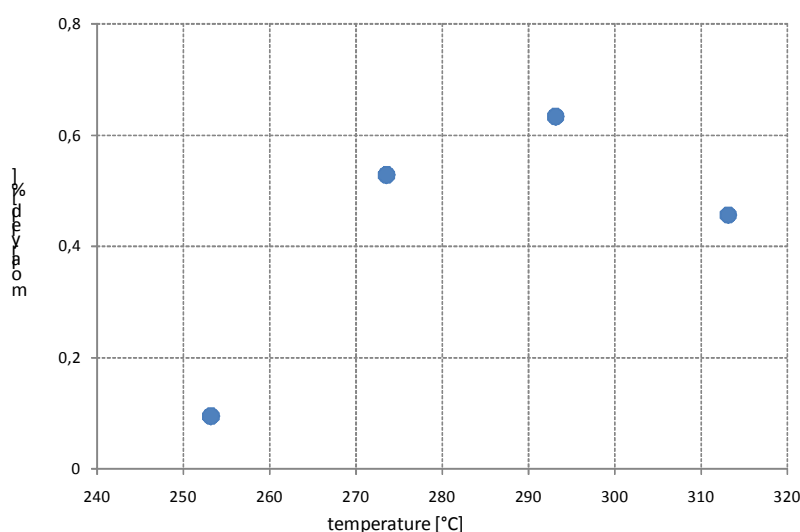
1 **Supporting material to:**

2  
3 “Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid - A  
4 mass spectrometric study of SOA aging”

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6 Lars Müller, Marc-Christopher Reinnig, Karl-Heinz Naumann, Harald Saathoff, Thomas Mentel, Neil  
7 M. Donahue and Thorsten Hoffmann, ACPD, 2011

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9 To chapter 3.2: OH-initiated aging of pinic and pinonic acid

10  
11 Figure S1 shows the MBTCA yields normalized to the initial  $\alpha$ -pinene concentration during the  
12 ozonolysis of alpha-pinene in the presence of TME. Although the much lower yield at the lowest  
13 temperature (253 K) is still obvious, the trend of the molar yields at higher temperatures is less clear  
14 than in the case of the temperature dependence of the absolute MBTCA concentration in the  
15 particle phase (see Fig. 4, Müller at al., 2011). Especially the molar yield of MBTCA at the highest  
16 temperature (313 K) is relatively low. In principle, the higher chamber temperature should result in a  
17 higher fraction of the MBTCA precursor (e.g. pinonic acid) in the gas phase and therefore a higher  
18 yield of MBTCA at increasing temperatures. However, if the precursor is relatively volatile (as pinonic  
19 acid) and resides in the gas phase in appreciable amounts already at medium temperatures (e.g. 293  
20 K), the temperature influence on precursor yields, on branching ratios during MBTCA formation or  
21 even loss processes of intermediates or the product itself (e.g. gas-phase diffusion to the chamber  
22 walls) might become more important for the overall observed molar MBTCA yield.



26  
27 **Figure S1** Molar yield of MBTCA as a function of temperature during the ozonolysis of  $\alpha$ -pinene in the  
28 AIDA chamber.

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30  
31 To chapter 3.3: Formation Mechanism

32  
33 **(c) H-atom abstraction from the C<sub>7</sub> carbon atom (pathway C and C’).** Although having the lowest  
34 rate constant for the H-abstraction by OH from pinonic acid, H-abstraction from C<sub>7</sub> carbon atom  
35 initiates two pathways forming MBTCA. The H-abstraction and formation of alkoxy radical (R11) by  
36 adding oxygen and subsequent reaction with NO is the same for both pathways. Henceforward the  
37 chain splits up into pathway C and pathway C’.

1 Pathway C: About 98% of R11 reacts by elimination of formaldehyde generating an acyl radical (R12),  
2 which rapidly forms an acyloxy radical (R13) by adding O<sub>2</sub> and reacting with NO. About 45% of this  
3 radical is supposed to subsequently eliminate CO<sub>2</sub> forming R14. The other portion (55%) is supposed  
4 to undergo isomerization reaction with H-atoms of C<sub>9/10</sub>. The secondary alkyl radical (R14) will add  
5 oxygen and react with NO to form alkoxy radical R15. The dissociation of R15 leads to the opening of  
6 the cyclobutane ring. As already mentioned for pathway B, two different scenarios are expected,  
7 forming a primary (R16) (2%) and a tertiary alkyl radical (98%) (not shown in Fig.6). The tertiary alkyl  
8 radical will rapidly react to an alkoxy radical and subsequently acetone is eliminated. Similar to  
9 pathway B the loss disqualifies the resulting alkyl radical for a further oxidation to MBTCA. The  
10 primary alkyl radical (R16) reacts with oxygen and NO forming alkoxy radical (R17), which will solely  
11 undergo a 1,5 H-shift to form the acyl radical R18. R18 itself will again react with oxygen and NO to  
12 form the acyloxy radical R19, which again undergoes a 1,5 H-shift (78%) forming an alkoxy radical and  
13 a stable carboxylic function (R110). Finally, R110 reacts to alkoxy radical (R111), which undergoes  
14 reaction with O<sub>2</sub> forming MBTCA. In general, pathway C was recently suggested by Szmigielski et al.  
15 (Szmigielski et al., 2007) to explain the formation of MBTCA. Beside the low rate constant for the H-  
16 abstraction from C<sub>7</sub>-carbon atom (Tab. 2), the yield of this pathway suffers from the cyclobutane ring  
17 opening, as already discussed in case of pathway B. The constitution of the alkoxy radicals R15/R22  
18 mainly leads to the formation of a tertiary alkyl radical. For the yield calculation the CO<sub>2</sub> elimination  
19 which forms R14 might be underestimated, but even estimating a fraction of 100% doesn't  
20 significantly change the overall yield of this reaction route. The yield of this pathway can be  
21 estimated to 0.0005%.

22  
23 Pathway C': 2% of alkoxy radical R11 undergoes isomerization by shifting an H-atom from carbon  
24 atom C<sub>4</sub> to form a hydroxy group at carbon C<sub>7</sub>. The newly formed alkyl radical (R1'2) will form an  
25 alkoxy radical (R1'3) via the addition of O<sub>2</sub> and reaction with NO. R1'3 will dissociate by opening the  
26 cyclobutane ring, resulting in two uniformly distributed isomeric alkyl radicals (2x47%). Again, only  
27 for alkyl radical R1'4, which has the radical located at the C<sub>5</sub>-carbon atom, a further oxidation to  
28 MBTCA is possible. R1'4 rapidly adds oxygen and forms an alkoxy radical by reacting with NO. The  
29 alkoxy radical reacts (R1'5) in a fast 1,5 H-shift ( $k \sim 10^{11} - 10^{12}$ ) to form acyl radical R1'6. This acyl radical  
30 will add oxygen forming the corresponding acylperoxy radical which then leads to the formation of  
31 acyloxy radical R1'7 by NO reaction. The major fraction of the acyl oxy radical R1'7 will undergo a 1,5  
32 shift to form alkyl radical R1'8 which then forms the final alkoxy radical R1'9. The sole fate (97%) of  
33 this radical should be the elimination of a C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>-radical which will directly lead to the formation of  
34 MBTCA. For this pathway the yield of MBTCA formation can be estimated to 0.02%

35 All individual yield estimations for each of the MBTCA formation pathways presented above are  
36 summarized in Table 4 in the main paper. Pathway A clearly turns out as the most likely one. The  
37 yield of pathway C and B can be neglected, whereas pathway B produces two significant products  
38 which have been observed in the on-line mass spectra (Fig.3 m/z 213; m/z 229). The contribution of  
39 pathway C' is only very small. An overall theoretical yield of 1.83% could be determined by evaluating  
40 the branching of the reaction mechanism. The findings clearly show that MBTCA is not a primary  
41 product of the OH initiated oxidation of pinonic acid. In fact a closer look to pathway A offers the  
42 possibility of other SOA compounds, exhibiting a similar constitution as pinonic acid (e.g.  
43 pinonaldehyde, pinic acid, hydroxypinonic acid), can also be oxidized to MBTCA by an initial H-atom  
44 abstraction from the C<sub>4</sub> carbon atom. As can be concluded from the fact pinonic acid being oxidized  
45 pinic acid not, the particular constrain is the existence of a significant gas phase fraction.

## 46 47 **References**

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