Supporting material to:

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

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

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

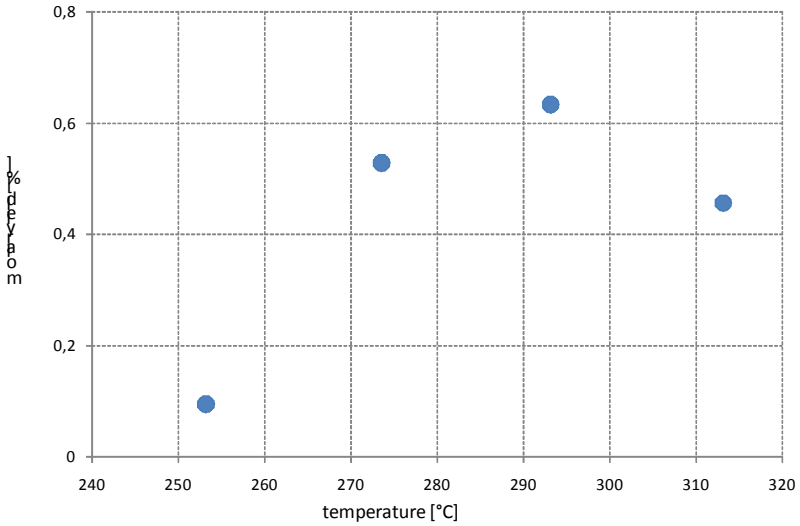

Figure S1 Molar yield of MBTCA as a function of temperature during the ozonolysis of α-pinene in the AIDA chamber.

To chapter 3.3: Formation Mechanism

(c) H-atom abstraction from the C_7 carbon atom (pathway C and C'). Although having the lowest rate constant for the H-abstraction by OH from pinonic acid, H-abstraction from C_7 carbon atom initiates two pathways forming MBTCA. The H-abstraction and formation of alkoxy radical (R11) by adding oxygen and subsequent reaction with NO is the same for both pathways. Henceforward the chain splits up into pathway C and pathway C'.

Pathway C: About 98% of R11 reacts by elimination of formaldehyde generating an acyl radical (R12), which rapidly forms an acyloxy radical (R13) by adding O_2 and reacting with NO. About 45% of this radical is supposed to subsequently eliminate CO_2 forming R14. The other portion (55%) is supposed to undergo isomerization reaction with H-atoms of $C_{9/10}$. The secondary alkyl radical (R14) will add oxygen and react with NO to from alkoxy radical R15. The dissociation of R15 leads to the opening of the cyclobutane ring. As already mentioned for pathway B, two different scenarios are expected, forming a primary (R16) (2%) and a tertiary alkyl radical (98%) (not shown in Fig.6). The tertiary alkyl radical will rapidly react to an alkoxy radical and subsequently acetone is eliminated. Similar to pathway B the loss disqualifies the resulting alkyl radical for a further oxidation to MBTCA. The primary alkyl radical (R16) reacts with oxygen and NO forming alkoxy radical (R17), which will solely undergo a 1,5 H-shift to form the acyl radical R18. R18 itself will again react with oxygen and NO to form the acyloxy radical R19, which again undergoes a 1,5 H-shift (78%) forming an alkoxy radical and a stable carboxylic function (R110). Finally, R110 reacts to alkoxy radical (R111), which undergoes reaction with O_2 forming MBTCA. In general, pathway C was recently suggested by Szmigielski et al. (Szmigielski et al., 2007) to explain the formation of MBTCA. Beside the low rate constant for the H-abstraction from C_7-carbon atom (Tab. 2), the yield of this pathway suffers from the cyclobutane ring opening, as already discussed in case of pathway B. The constitution of the alkoxy radicals R15/R22 mainly leads to the formation of a tertiary alkyl radical. For the yield calculation the CO_2 elimination which forms R14 might be underestimated, but even estimating a fraction of 100% doesn't significantly change the overall yield of this reaction route. The yield of this pathway can be estimated to 0.0005%.

Pathway C': 2% of alkoxy radical R11 undergoes isomerization by shifting an H-atom from carbon atom C_4 to form a hydroxy group at carbon C_7. The newly formed alkyl radical (R1'2) will form an alkoxy radical (R1'3) via the addition of O_2 and reaction with NO. R1'3 will dissociate by opening the cyclobutane ring, resulting in two uniformly distributed isomeric alkyl radicals (2x47%). Again, only for alkyl radical R1'4, which has the radical located at the C_5-carbon atom, a further oxidization to MBTCA is possible. R1'4 rapidly adds oxygen and forms an alkoxy radical by reacting with NO. The alkoxy radical reacts (R1'5) in a fast 1,5 H-shift ($k \sim 10^{11}$-10^{12}) to from acyl radical R1'6. This acyl radical will add oxygen forming the corresponding acylperoxy radical which then leads to the formation of acyloxy radical R1'7 by NO reaction. The major fraction of the acyl oxy radical R1'7 will undergo a 1,5 shift to from alkyl radical R1'8 which then forms the final alkoxy radical R1'9. The solely fate (97%) of this radical should be the elimination of a $C_2H_2O_2$-radical which will directly lead to the formation of MBTCA. For this pathway the yield of MBTCA formation can be estimated to 0.02%
All individual yield estimations for each of the MBTCA formation pathways presented above are summarized in Table 4 in the main paper. Pathway A clearly turns out as the most likely one. The yield of pathway C and B can be neglected, whereas pathway B produces two significant products which have been observed in the on-line mass spectra (Fig.3 m/z 213; m/z 229). The contribution of pathway C' is only very small. An overall theoretical yield of 1.83% could be determined by evaluating the branching of the reaction mechanism. The findings clearly show that MBTCA is not a primary product of the OH initiated oxidation of pinonic acid. In fact a closer look to pathway A offers the possibility of other SOA compounds, exhibiting a similar constitution as pinonic acid (e.g. pinonaldehyde, pinic acid, hydroxypinonic acid), can also be oxidized to MBTCA by an initial H-atom abstraction from the C_4 carbon atom. As can be concluded from the fact pinonic acid being oxidized pinic acid not, the particular constrain is the existence of a significant gas phase fraction.

References

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