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**CMK as a model  
compound to  
elucidate oxidation  
mechanisms**

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# Cyclobutyl methyl ketone as a model compound for pinonic acid to elucidate oxidation mechanisms

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## Abstract

3-Methyl-1,2,3-tricarboxylic acid (MBTCA), terpenylic acid and diaterpenylic acid acetate were identified in secondary organic aerosol (SOA) from  $\alpha$ -pinene photooxidation or ozonolysis. These compounds display interesting structural features: MBTCA has a high oxygen to carbon ratio, terpenylic acid contains a lactone ring in its structure and diaterpenylic acid acetate possesses an ester functional group. The reaction mechanisms leading to these products are still unknown, but it was demonstrated experimentally in earlier studies that MBTCA is formed from pinonic acid, a primary ozonolysis product of  $\alpha$ -pinene. Because the direct observation of pinonic acid oxidation in a smog chamber would be difficult due to its relatively low volatility, a model compound possessing the substructure of interest was used instead: cyclobutyl methyl ketone (CMK). From its oxidation, several organic acids could be measured with ion chromatography (IC) coupled to a mass spectrometer (MS). Succinic acid, the analogous product of MBTCA is formed at molar yields of 2 to 5 %. Butyrolactone is detected as butanoic acid, due to hydrolysis in the sampling device. A monocarboxylic acid with nominal mass 146 was detected in the absence of nitrogen oxides ( $\text{NO}_x$ ) and could be the analogous product of diaterpenylic acid acetate. However, due to a lack of available standards, the exact structure of this compound remains unelucidated. Finally, 4-oxobutanoic acid could also be measured and two structures of its expected analogous compound from pinonic acid oxidation are proposed. Because these compounds are primary products of the CMK oxidation, reaction mechanisms capable of adding one or two carboxylic functional groups without formation of stable intermediate products needs to be formulated. Such a formation mechanism of MBTCA from pinonic acid was found in the literature; however, it includes a hydrogen atom migration to an acyloxy radical, which is expected to lose carbon dioxide ( $\text{CO}_2$ ) very rapidly. A competitive reaction pathway is expected to lead to the formation of a monocarboxylic acid with nominal mass 144, instead of this acyloxy radical; however, no such monocarboxylic acid was measured and other reaction pathways still need to be explored.

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## 1 Introduction

Monoterpenes are biogenic volatile organic compounds (VOCs) emitted into the atmosphere by vegetation. They represent 11 % of the total biogenic VOC emissions (Guenther et al., 1995).  $\alpha$ -Pinene is a major representative of this class of compounds and can form secondary organic aerosol (SOA). However, understanding of its oxidation mechanisms and SOA formation yields is still subject of research.

Szmigielski et al. (2007) identified 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) as a product from  $\alpha$ -pinene SOA. Because of its high oxygen-to-carbon (O : C) ratio and its distinct structure, it was suggested as a tracer compound for aged  $\alpha$ -pinene SOA.

Müller et al. (2012) demonstrated experimentally that MBTCA is generated from pinonic acid oxidation by hydroxyl radical ( $\cdot$ OH). Pinonic acid is a primary product from  $\alpha$ -pinene ozonolysis. The structures of further products of  $\alpha$ -pinene SOA were identified recently: terpenylic acid and diaterpenylic acid acetate (Linuma et al., 2008; Claeys et al., 2009).

Laboratory studies of the pinonic acid oxidation in the gas phase are difficult, because of its relatively low volatility. For instance, high pinonic acid mixing ratios cannot be achieved in a smog chamber. Even if the main products (as MBTCA) could be detected, other potential products would be present at too low levels to be detected. Therefore, CMK was tested as a surrogate of pinonic acid to understand the oxidation mechanisms and the chemical structure of the products formed. Pinonic acid contains a four-carbon ring structure which is common to a lot of monoterpenes. A better understanding of the reactions following its opening can help to identify structures of products observed from the oxidation of  $\alpha$ -pinene and other monoterpenes. Figure 1 depicts the chemical structure of CMK and products from oxidation by  $\cdot$ OH: succinic acid, butyrolactone and 4-acetoxybutanoic acid. The presented analogy with pinonic acid (grey moieties accounting for structural differences between both systems) assumes that terpenylic acid and diaterpenylic acid acetate in  $\alpha$ -pinene SOA are formed as second generation products from the oxidation of pinonic acid, similarly to MBTCA.

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Butyrolactone (in the same way as terpenylic acid) is expected to be hydrolysed during sampling with water (Sect. 2), so that it is detected as 4-hydroxybutanoic acid. Because 4-oxobutanoic acid was observed during CMK oxidation experiments, it is included in Fig. 1 and two possible structures for analogous products from the  $\alpha$ -pinene (or pinonic acid) oxidation are suggested.

## 2 Experimental

### 2.1 Smog chamber and experiments

The experiments presented in Table 1 were performed at the smog chamber of the Paul Scherrer Institute (Paulsen et al., 2005). It consists of a 27-m<sup>3</sup> Teflon<sup>®</sup> bag irradiated by Xe-arc lamps (4 × 4 kW) and additional black light tubes emitting mainly between 320 and 400 nm (manufactured by Cleo Performance; 80 × 100 W).

Two different ways of producing  $\cdot$ OH were used: (1) production by tetramethylethene (TME) ozonolysis (*dark*  $\cdot$ OH), and (2) production by ozone (O<sub>3</sub>) photolysis in the absence or in the presence of nitrogen oxides (NO<sub>x</sub>). In the NO<sub>x</sub> experiment, the lights were turned off after 3 h of  $\cdot$ OH exposure in order to observe the decomposition of peroxyacyl nitrates (PANs). CMK was injected through a heated sample bulb (80 °C). The experiments performed with 400 ppbv CMK were also seeded with wet ammonium sulphate aerosol particles, while the experiment with 1600 ppbv CMK was not. The relative humidity was around 50 % in all experiments.

### 2.2 Instruments

On top of the usual monitors (for O<sub>3</sub> and NO<sub>x</sub>) and sensors (temperature and relative humidity), a proton-transfer-reaction mass spectrometer (PTR-MS) was used to analyse gas phase organic compounds. Organic acids were sampled in the gas phase by a wet effluent diffusion denuder (WEDD) and in the aerosol phase by an aerosol

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collector (AC) described in Takeuchi et al. (2004) and (2005), respectively. The sampling time was 30 min and anions were concentrated on a anion trace concentrator column (ATC, Dionex). Sampling was alternated with analysis so that gas and aerosol phase could be analysed alternately. The analysis was performed by ion chromatography coupled to a quadrupole mass spectrometer (Fisseha et al., 2004).

### 3 Results and discussion

For all the experiments performed, no significant aerosol formation was observed, so that the discussion focuses on the gas phase observations. Furthermore, no mass increase in the particulate phase was measured when seed aerosol was used.

#### 3.1 CMK reacted

Figure 2 presents the amount of CMK reacted for each type of experiment, with exponential fits plotted on top of the data. The start of the experiment (0 h) corresponds to the CMK injection for the dark  $\cdot\text{OH}$  experiment (TME ozonolysis started earlier in order to measure the background signal from the products formed) and to the time of turning on the lights for the other experiments. CMK reacted was calculated from the decrease of  $m/z$  99 measured by the PTR-MS, which was scaled to the nominally injected CMK mixing ratio (400 or 1600 ppbv). The gap in the dark  $\cdot\text{OH}$  experiment is due to a failure in data recording during that period.

In the  $\text{NO}_x$  case, lights were turned off after 3 h of experiment as previously mentioned; however, CMK seemed to react further. This may be due to an interference on CMK's  $m/z$  from a formed PAN, which may decompose slowly when the lights are turned off. The increasing signal of this PAN compensates slightly for the decreasing signal of CMK and, for this reason, the true amount of CMK reacted may be somewhat higher than estimated.

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The relative amount of CMK reacted is variable between experiments, due to the different experimental conditions and  $\cdot\text{OH}$  exposure. The relative amount of CMK reacted after 3 h of oxidation is 7.5 % in the dark  $\cdot\text{OH}$  experiment, 14 % and 9.1 % in the experiments with  $\text{O}_3$  with a low and a high amount of CMK, respectively, 6.8 % in the experiment with  $\text{NO}_x$ . For an easier comparison between experiments and to take these variations into account, molar yields are derived for the oxidation products, based on the values of the fitted functions for a given time (Fig. 8).

### 3.2 Hydrogen abstraction

CMK reacts only with  $\cdot\text{OH}$ , which abstracts a hydrogen atom (H), forming an alkyl radical. Table 2 presents the reaction rates for the different possible hydrogen atom abstraction reactions from CMK by  $\cdot\text{OH}$ , derived from structure-activity relationship estimations (Kwok and Atkinson, 1995; Atkinson, 1997). The indices correspond to the atom numbers in Fig. 1. The fastest abstraction occurs at position 3 for CMK and two such positions are available due to the symmetry of the molecule. Therefore, this route is considered to dominate the gas phase oxidation of CMK. Note that there is only one equivalent position in pinonic acid (3') and that positions 4' and 6' (due to the presence of the carboxylic group) show competitive reaction rates, so that the analogous products from hydrogen abstraction at position 3' in the pinonic acid system are expected to have lower yields. In addition, other products are formed in the pinonic acid system that cannot be studied with CMK.

The mechanism following the hydrogen atom abstraction at position 3 is depicted in Fig. 3. The alkyl radical ( $\text{R}\cdot$ ) formed reacts immediately with molecular oxygen ( $\text{O}_2$ ) to form a peroxy radical ( $\text{RO}_2\cdot$ ). This radical can then react with hydroperoxyl radical ( $\text{HO}_2\cdot$ ) to form a hydroperoxide ( $\text{C}_6\text{H}_{10}\text{O}_3$ ) or, in the absence of  $\text{NO}_x$ , it can react with another  $\text{RO}_2\cdot$  to form an alkoxy radical ( $\text{RO}\cdot$ ) labelled "alkoxy A" in Fig. 3 as well as alcohol and carbonyl compounds (not shown). In the high  $\text{NO}_x$  case, hydroperoxide formation is suppressed by either the formation of a peroxyxynitrate ( $\text{ROONO}_2$ ) or  $\text{RO}_2\cdot$  reaction with  $\text{NO}$  to form  $\text{RO}\cdot$  and  $\text{NO}_2$  or some nitrates.

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Figure 4a and b show  $m/z$  131 and 113, respectively, as measured with the PTR-MS. The peroxide  $C_6H_{10}O_3$  should appear at  $m/z$  131, however, as it loses one water molecule after protonation in the PTR-MS ion source, it is not detected at  $m/z$  131 ( $[M + H]^+$ ), but at  $m/z$  113 ( $[M + H - H_2O]^+$ ). At this  $m/z$ , 2-acetylcyclobutanone ( $C_6H_8O_2$ ) also appears as an interference. In the  $NO_x$  experiment, only the latter compound contributes to the signal because the hydroperoxide formation is hindered by the presence of NO, lowering the  $HO_2$  concentration. However, Fig. 4b shows that the signal at  $m/z$  113 remains relatively low, indicating only little 2-acylcyclobutanone formation. This is explained by the fact that the ring opening reaction is favoured over reaction with  $O_2$ , due to the release of the ring strain ( $\sim 27 \text{ kcal mol}^{-1}$ ) (Peeters et al., 2004).

### 3.3 Carbon-carbon bonds dissociation

The two possible ring opening reactions from the “alkoxy A” and the following mechanistic steps are depicted in Fig. 5. These reactions are expected to occur faster than the bimolecular reaction with  $O_2$  as previously mentioned. According to structure-activity relationships (Peeters et al., 2004), but without considering the ring strain release discussed above, the 2–3 carbon-carbon bond dissociation is expected to be favoured because carbon 2 is more substituted than carbon 4. The energy barrier is  $3.1 \text{ kcal mol}^{-1}$  lower in the former case. Peeters et al. (2004) discussed the effect of resonance stabilisation and, because the alkyl radical formed by dissociation of the 2–3 carbon-carbon bond is resonance-stabilised by the carbonyl group, its formation is even more favoured and this route is expected to dominate over the other.

Following the ring opening reaction, the formed alkyl radical reacts rapidly with  $O_2$  to form a peroxy radical. This radical can react with  $HO_2$  to form a hydroperoxide with a nominal mass of 146 or it can also react with either  $RO_2$  or NO (in the  $NO_x$  experiment) to form another alkoxy radical (“alkoxy B”). Upon reaction with  $O_2$ , this alkoxy radical forms 4,5-dioxohexanal (nominal mass 128). Figure 6 shows the PTR-MS signals for  $m/z$  147, 129 and 111.  $m/z$  147 would correspond to the peroxide, but no signal

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is seen.  $m/z$  129 corresponds to either 4,5-dioxohexanal or the peroxide fragment ( $[M + H - H_2O]^+$ ) with a signal below 1.5 ppbv. Because 4,5-dioxohexanal is an aldehyde, it can also dehydrate in the PTR-MS resulting in  $m/z$  111. Figure 6 shows that this signal is lower than the one of  $m/z$  129 and remains below 1 ppbv.

5 The previously described alkoxy radical (B) can also undergo carbon-carbon bond dissociation. Due to the presence of the carbonyl compound on the position 5 (see Fig. 5), the energy barrier for the dissociation of the 2–5 bond is reduced by  $8 \text{ kcal mol}^{-1}$  according to structure activity relationships (Peeters et al., 2004) compared to the 2–3b bond dissociation. For this reason, the elimination of the acetyl radical is favoured.

10 This is confirmed by the PTR-MS with the signals for  $m/z$  87 (corresponding to succinic aldehyde,  $C_4H_6O_2$ ) and  $m/z$  73 (corresponding to methylglyoxal,  $C_3H_4O_2$ ) as shown in Fig. 7. The step increase at 0 h for  $m/z$  87 is due to a fragment from CMK (or an impurity). If it reacts away during the experiment, it may be that the net signal increase from new products formed is higher than one would expect from a simple comparison

15 of the mixing ratio at 0 h and at the end of the experiment. In any case, the signals increase at least twice as much for  $m/z$  87 compared to  $m/z$  73 in the  $O_3$  experiments. Because methylglyoxal is also formed in the dark 'OH experiment from the ozonolysis of TME, the interpretation of these results is more difficult, but no change in the  $m/z$  73 increase rate can be observed while the increase of  $m/z$  87 is small due to the small

20 amount of CMK reacted. The most intriguing observation is the rapid signal increase for  $m/z$  87 in the  $NO_x$  experiment while the lights are on. Most probably this is due to the fragmentation of organonitrates of higher mass. However, no structure and formation mechanism can be proposed for this observation. It would, however, not make sense that the presence of  $NO_x$  simply favours one carbon-carbon bond dissociation of the

25 alkoxy radical over the other. Thus, this observation in the  $NO_x$  experiment does not influence the above conclusions.

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### 3.4 Organic acids formation mechanism

The reactions discussed so far do not lead to the formation of organic acids. However, organic acids are indeed formed as shown in Fig. 8. The mixing ratios of all organic acids presented in Fig. 1 are increasing immediately after the start of the oxidation, indicating that these organic acids are first generation products. This suggests that terpenylic acid and diaterpenylic acid acetate could be products of the pinonic acid oxidation by  $\cdot\text{OH}$ . This also implies that it is possible to add two carboxylic acid functionalities to a compound in a single step (from CMK to succinic acid or from pinonic acid to MBTCA). Succinic acid, 4-oxobutanoic acid and 4-hydroxybutanoic acid were quantified based on calibration with standards. The monocarboxylic acid with nominal mass 146 could correspond to 4-acetoxybutanoic acid, but this could not be confirmed due to the lack of an available standard. Therefore, this species was quantified based on the calibration of 4-hydroxybutanoic acid. Moreover, it is expected to contribute to the  $m/z$  129 signal (Fig. 6).

Overall, in the dark  $\cdot\text{OH}$  and  $\text{NO}_x$  experiments the mixing ratios are lower, but this is due to the lower amount of precursor reacted. Succinic acid has a molar yield of a few percent, while the other organic acids presented in Fig. 8 have molar yields of less than 1%.

The formation mechanisms of these organic acids remain unclear, but their low molar yields indicate that they may arise from minor processes. Hydrogen atom migration from the aldehyde moiety of the radical "alkoxy B" presented in Fig. 5 would lead to the formation of a peroxyacyl radical ( $\text{R}(\text{O})\text{OO}\cdot$ ), which by reaction with  $\text{HO}_2$  can form either a peracid ( $\text{RC}(\text{O})\text{OOH}$ ) or a carboxylic acid (and  $\text{O}_3$ ) as depicted in Fig. 9. Note that the monocarboxylic acid formed has a nominal mass 146 and could be the one measured and attributed to 4-acetoxybutanoic acid, as no standard was available to confirm the retention time of one or the other of these species. As this species is not formed in the presence of  $\text{NO}_x$ , this would be compatible with the formation of peroxyacylnitrate  $\text{C}_6\text{H}_9\text{NO}_7$  suppressing the peroxide channel in the presence of  $\text{NO}_2$ . Moreover, it may

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be that 4-acetoxybutanoic is hydrolysed during sampling (similarly to lactone) and is detected as 4-hydroxybutanoic acid. The analogous compound in the pinonic acid system would be an isomer of diaterpenylic acid acetate with the same chemical structure ( $C_{10}H_{16}O_6$ ) and nominal mass 232. These results suggest that diaterpenylic acid does not necessarily have to be formed in the gas phase.

Müller et al. (2012) suggested several mechanisms for the formation of MBTCA from pinonic acid. One of them includes at least one intermediate stable compound, so that it cannot be used to interpret the present results. Because MBTCA is formed as a first generation compound in the experiments presented here, a mechanism without any stable intermediate is required. Müller et al. (2012) suggested other pathways without intermediate products, but requiring intramolecular hydrogen atom shifts to acyloxy radicals (see Fig. 10). This kind of unimolecular reaction was already suggested by Jenkin et al. (2000) for the formation of pinic acid. However, based on structure-activity relationships, Vereecken and Peeters (2010) report acyloxy migration rates at 298 K and 1 atm on the order of  $9.3 \times 10^3$  to  $1.1 \times 10^5 \text{ s}^{-1}$ , while the derived carbon dioxide ( $CO_2$ ) loss rate for acyloxy radicals (e. g. ethylacyloxy radical) based on structure-activity relationships and quantum chemical calculations is in the range of  $6.7\text{--}9.3 \times 10^{10} \text{ s}^{-1}$  (Vereecken and Peeters, 2009, 2010). It is difficult to find a reason for such an enormous stabilisation of the acyloxy radical. If the migration happens, it is expected to occur only to a very minor extent.

Furthermore, the alkyl radical marked in red in Fig. 10 is expected to react preferentially with  $O_2$  to form 4,5-dioxohexanoic acid ( $C_6O_4H_8$ ) with a nominal mass of 144, but it was not possible to identify any first-generation monocarboxylic acid with IC/MS at  $m/z$  143 (see the chromatogram of Fig. 11). The peak at retention time (RT)  $\sim 19$  min is present in the background and does not increase during photooxidation of CMK. Only in the experiment with high CMK (Fig. 11b) another peak appears around 16 min. However, because this RT is higher than 15 min, it is expected to be a dicarboxylic acid and from its time trend (data not shown), it seems to be a second generation product.

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Similarly to this minor dicarboxylic acid peak at  $m/z$  143, other peaks were identified (e.g. at  $m/z$  129 with RT  $\sim$  13 min) that were not included in the present discussion. Nevertheless, they illustrate the mechanistic complexity of the CMK oxidation and the need to better understand organic acid formation in the gas phase. Also small organic acids such as formic acid, acetic acid, lactic acid and pyruvic acid were observed. Because these can arise from several reaction pathways, they were not used to interpret the mechanism of the present discussion.

### 3.5 Non-traditional chemistry

With the so-called traditional atmospheric chemistry, gas-phase formation of the observed acids (and lactones) as first generation products cannot be explained. With large molecules, many unimolecular reactions are however possible, including peroxy radical isomerisation (H-shift), which were not discussed here. The resonance stabilized form of the alkyl radical formed after ring opening may also lead to unknown reaction mechanisms. However, such suggestions of mechanisms would be highly speculative and beyond the scope of the present work. A key compound seems to be the peroxy radical marked in orange in Fig. 5 because after elimination of the acyl moiety, it remains with four carbon atoms that are common to the organic acids presented in Fig. 8. Unknown reaction pathways are therefore symbolised by a (orange) question mark.

## 4 Conclusions

Using CMK as a model compound, it is possible to study the gas phase reactions following the opening of the four-carbon ring present in the chemical structures of many terpenoids. Müller et al. (2012) already demonstrated that MBTCA can be formed from the 'OH oxidation of pinonic acid. In the CMK system, the analogue of MBTCA, succinic acid, was measured with molar yields of 2 to 5%. 4-Hydroxybutanoic acid could

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also be identified as analogue of diaterpenylic acid, resulting from the hydrolysis of butyrolactone and terpenylic acid, respectively. A monocarboxylic acid with nominal mass 146 which could be the analogue of diaterpenylic acid acetate was measured in the absence of  $\text{NO}_x$ ; however, due to the lack of an available standard, this analogy could not be confirmed. Moreover, it remains unclear if 4-acetoxybutanoic acid would hydrolyse similarly to butyrolactone during sampling with water and be detected as 4-hydroxybutanoic acid. The reason of the suppression of this reaction mechanism by  $\text{NO}_x$  could not be interpreted mechanistically.

4-Oxobutanoic acid was identified and two analogue structures are proposed that would correspond to 2-(2-methyl-1-oxopropan-2-yl)succinic acid and 3-formyl-2,2-dimethylpentanedioic acid. Claeys et al. (2009) identified in  $\alpha$ -pinene SOA a compound with the same nominal mass (188), but tentatively attributed a slightly different structure to it. By understanding the reaction mechanisms, structures can be proposed in the context of a precursor oxidation, so that out of the many possible compounds derived from a chemical formula, the ones that are relevant for the system observed can be selected. For this, the simplified CMK system is a useful tool, because it focuses on the reactive substructure of the analogue system.

All the compounds measured in this work are first-generation oxidation products. This demonstrates that two carboxylic acid functionalities can be added in one oxidation step, increasing rapidly the O : C ratio and the potential of SOA formation from VOC oxidation. Very often, offline filter analyses do not provide information on the temporal evolution of a compound, so that mechanisms involving many steps are suggested, which can be correct for later generations products. In the present case, a mechanism is required to explain the formation of succinic acid from CMK without the formation of any stable intermediate compound. Müller et al. (2012) proposed such a mechanistic scheme, starting from the most reactive H abstraction (position 3 in Fig. 1) by  $\cdot\text{OH}$ . This scheme includes a 1,5-H shift to an acyloxy radical, which is expected to be negligible compared to the loss of  $\text{CO}_2$ . Moreover, the radical resulting from this shift (in red in Fig. 10) should react with  $\text{O}_2$  to form in the CMK system either a monocarboxylic

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acid with nominal mass 144 (H abstraction, red path) or a peroxy radical towards the formation of succinic acid (black path). No acid with nominal mass 144 could be identified, while succinic acid is measured; however, there is no reason why the latter reaction should be favoured over the first one.

Because of the complexity and the many branching possibilities of the gas phase oxidation mechanism, the products detected show molar yields below 1 %, except for succinic acid. This allows the possibility of formation mechanism through minor pathways that were not discussed here (e. g. from the H-abstraction by  $\cdot\text{OH}$  at other positions than 3 or from non-traditional chemistry). To maintain the mass balance, dozens of oxygenated compounds should be detected at very low concentrations. Traditional gas phase chemistry cannot explain the formation of the observed products, so that new reaction mechanisms are required to understand the atmospheric chemistry of (oxygenated) VOCs with a large number of carbon atoms. Unimolecular reactions (H-shifts and ring closure) seem to be important in this regard.

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**Table 1.** List of performed cyclobutyl methyl ketone (CMK) oxidation experiments.

Date	Precursor	O <sub>3</sub> mixing ratio	NO <sub>x</sub> mixing ratio	Comments
29 Jul 2010	400 ppbv CMK	500 ppbv	–	TME ozonolysis
18 Oct 2010	1600 ppbv CMK	400 ppbv	–	No seed, lights on for 7.5 h
20 Oct 2010	400 ppbv CMK	400 ppbv	–	lights on for 7.25 h
22 Oct 2010	400 ppbv CMK	–	400 ppbv NO 400 ppbv NO <sub>2</sub>	lights on for 3 h

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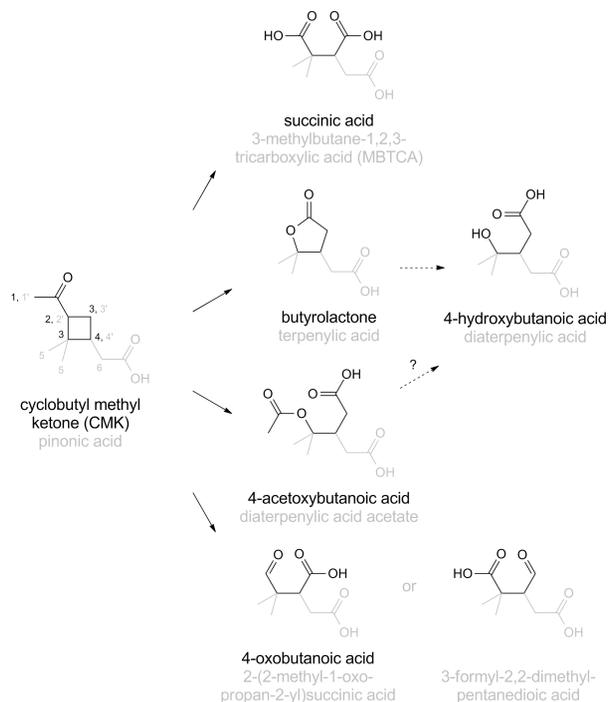


**Table 2.** Reaction rate constants for hydrogen atom abstraction from cyclobutyl methyl ketone (CMK) by hydroxyl radical ( $\cdot\text{OH}$ ). Indices correspond to the carbon atom numbers in Fig. 1.

cyclobutyl methyl ketone (CMK)	
$k_1$	$0.102 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k_2$	$0.616 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k_3$ (twice)	$1.255 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k_4$	$0.396 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
pinonic acid	
$k'_1$	$0.102 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k'_2$	$0.616 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k'_3$	$1.255 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k'_4$	$1.011 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k'_5$ (twice)	$0.167 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$k'_6$	$0.862 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$

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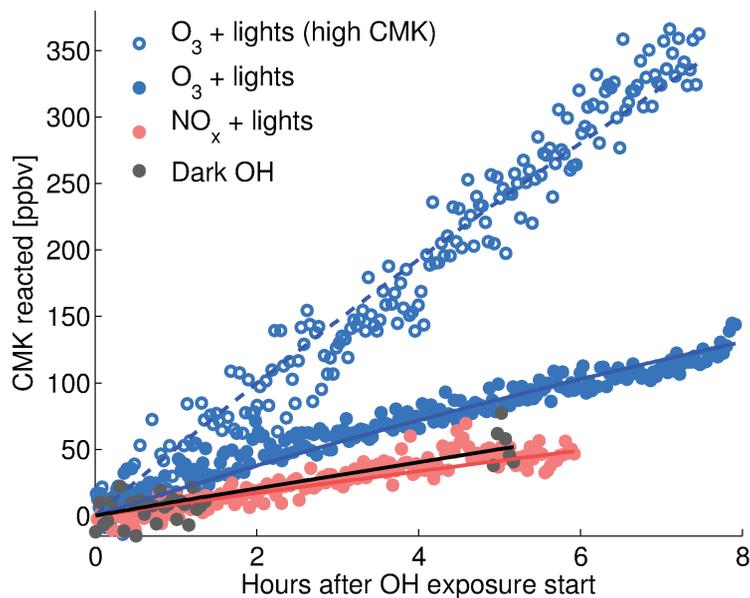
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**Fig. 1.** Chemical structures of cyclobutyl methyl ketone (CMK, left) and measured or expected products (right). The added grey moieties represent the analogous products in the pinonic acid system. Butyrolactone (and terpenylic acid) are expected to hydrolyse during sampling, so that 4-hydroxybutanoic acid (or diaterpenylic acid) are detected. No equivalent product of 4-oxobutanoic acid was identified yet, so that two possible structures are proposed for the pinonic acid system: 2-(2-methyl-1-oxopropan-2-yl)succinic acid and 3-formyl-2,2-dimethylpentanedioic acid. The numbers on CMK/pinonic acid correspond to carbon atoms bound to hydrogen atom(s) available for abstraction by an hydroxyl radical ( $\text{OH}^\bullet$ ).

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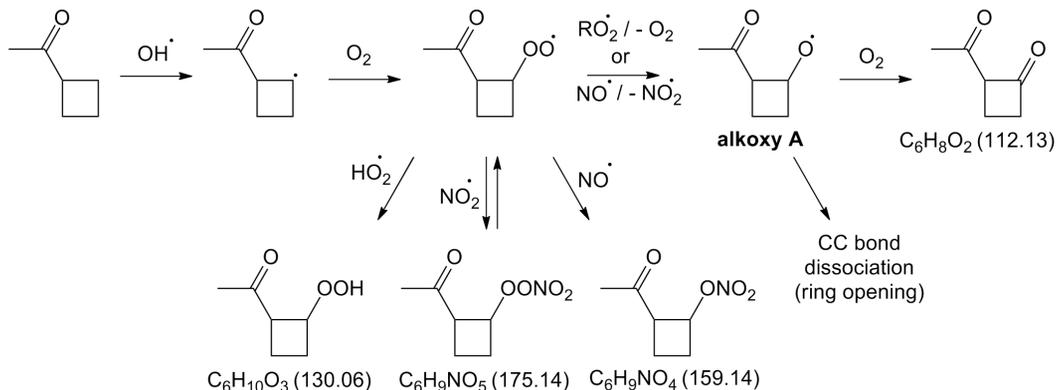


**Fig. 2.** Cyclobutyl methyl ketone (CMK) reacted for the four experiments presented: *dark* hydroxyl radical ( $\cdot\text{OH}$ ) production,  $\cdot\text{OH}$  production from ozone ( $\text{O}_3$ ) photolysis without and with nitrogen oxides ( $\text{NO}_x$ ). Two  $\text{O}_3$  experiments were performed without  $\text{NO}_x$ : one with low (400 ppbv) and the other with high (1600 ppbv) amount of CMK injected. The two other experiments were performed with 400 ppbv CMK. The solid and dashed lines represent an exponential fitted function through the data of each experiment.

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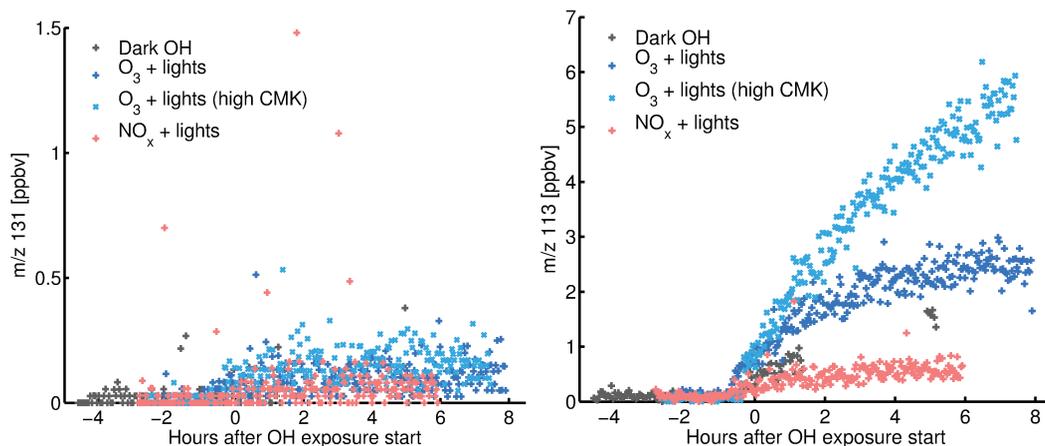
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**Fig. 3.** Chemical mechanism following hydrogen atom abstraction from cyclobutyl methyl ketone (CMK) by hydroxyl radical ( $\text{OH}\cdot$ ). The numbers in brackets correspond to the molar mass of the compounds. See text for details.

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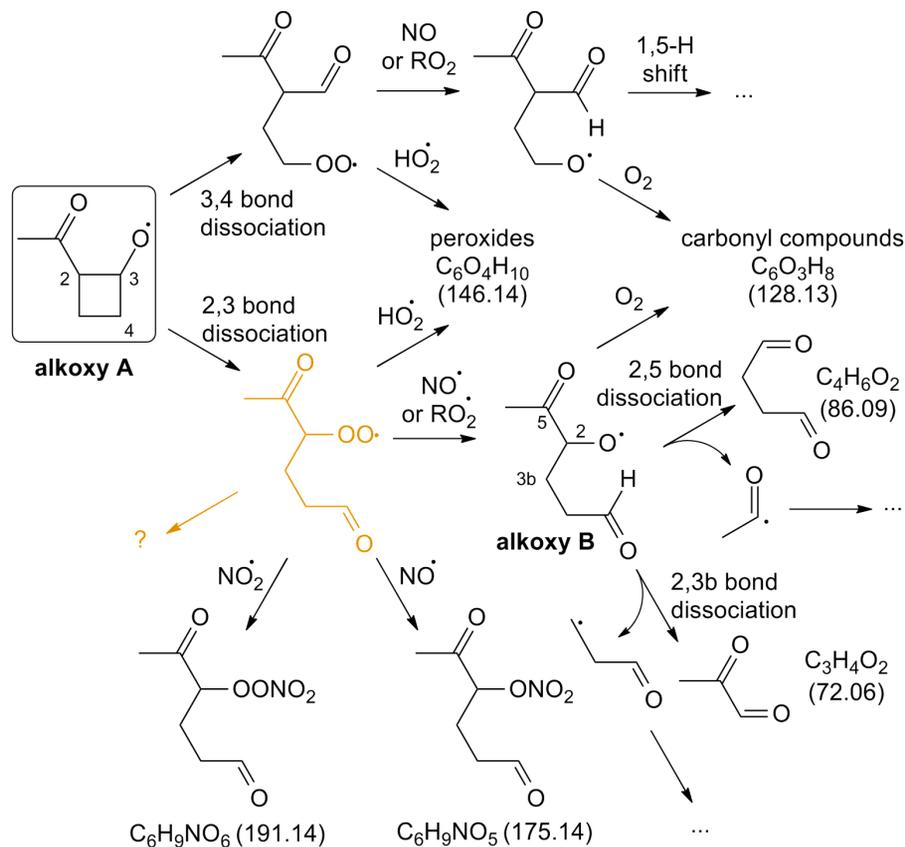
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**Fig. 4.** Signals of  $m/z$  131 (left) and 113 (right) from the proton-transfer-reaction mass spectrometer (PTR-MS). The peroxide  $C_6H_{10}O_3$  is mainly detected at  $m/z$  113 since it loses a water molecule during protonation in the ionisation region of the PTR-MS. However, at this  $m/z$  there is an interference with the 2-acylcyclobutanone ( $C_6H_8O_2$ ), which is still measured in the experiment with  $NO_x$ , while the peroxide channel is suppressed.

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**Fig. 5.** Ring opening chemical mechanism of the alkoxy radical A from Fig. 3. Carbon-carbon bond 2–3 or 3–4 can dissociate, leading to the formation of different compounds. The formed “alkoxy B” can also undergo carbon-carbon bond dissociation. The numbers in brackets correspond to the molar mass of the compounds. See text for more details.

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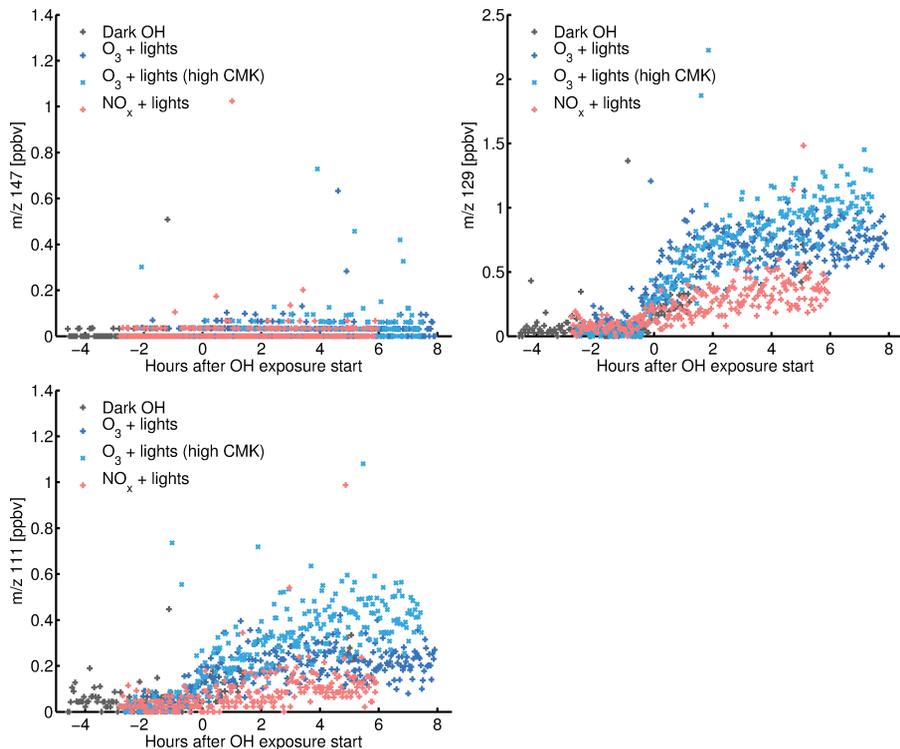
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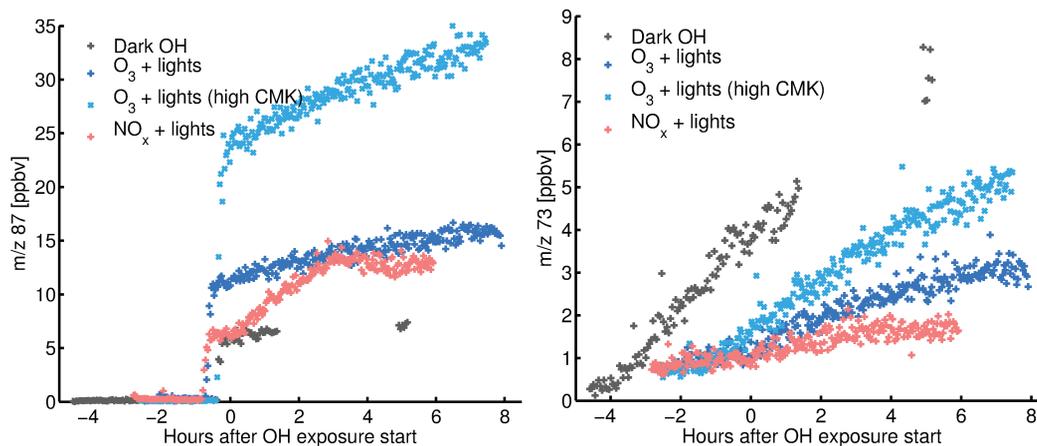
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**Fig. 6.** Signals of the proton-transfer-reaction mass spectrometer (PTR-MS) for  $m/z$  147 (top left), 129 (top right) and 111 (bottom). The peroxides  $C_6O_4H_{10}$  are not detected at  $m/z$  147 due to a water molecule loss during protonation but on  $m/z$  129, where the carbonyl compounds  $C_6O_3H_8$  are detected. Because these carbonyl compounds are aldehydes, they also possibly lose a water molecule during protonation and some signal appears on  $m/z$  111.

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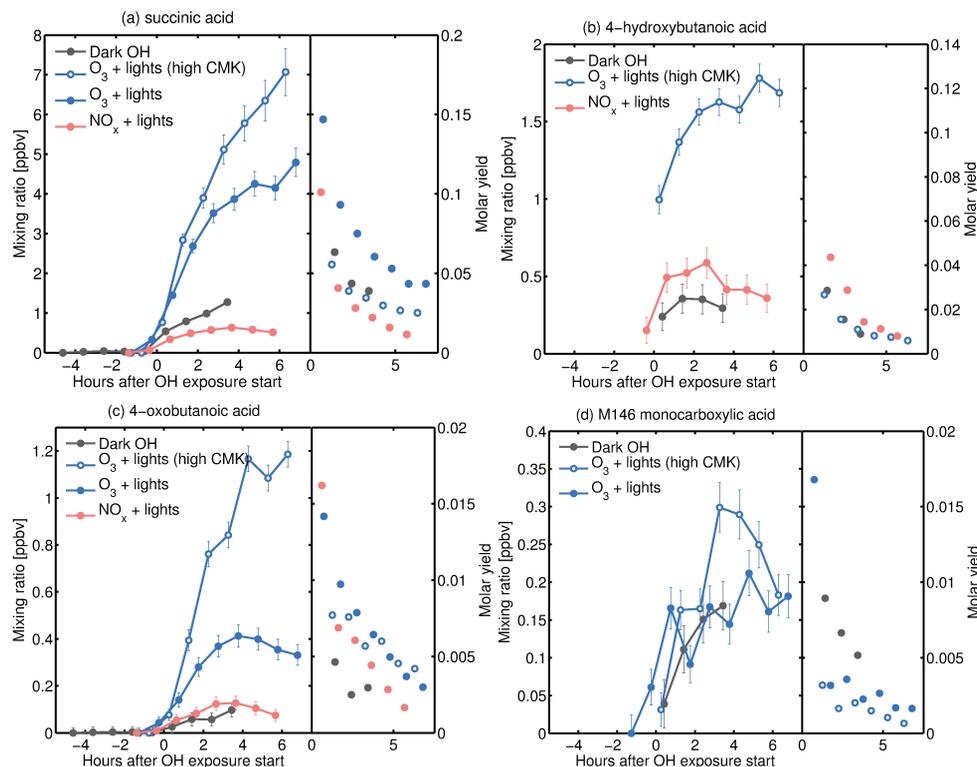


**Fig. 7.** Signals of the proton-transfer-reaction mass spectrometer (PTR-MS) for  $m/z$  87 (left) and 73 (right).  $m/z$  87 is the signal for succinic aldehyde and  $m/z$  73 for methylglyoxal.

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**Fig. 8.** Mixing ratios (left axis) and molar yields (right axis) of acids observed: **(a)** succinic acid, **(b)** 4-hydroxybutanoic acid, **(c)** 4-oxobutanoic acid, and **(d)** monocarboxylic acid with molar mass 146.

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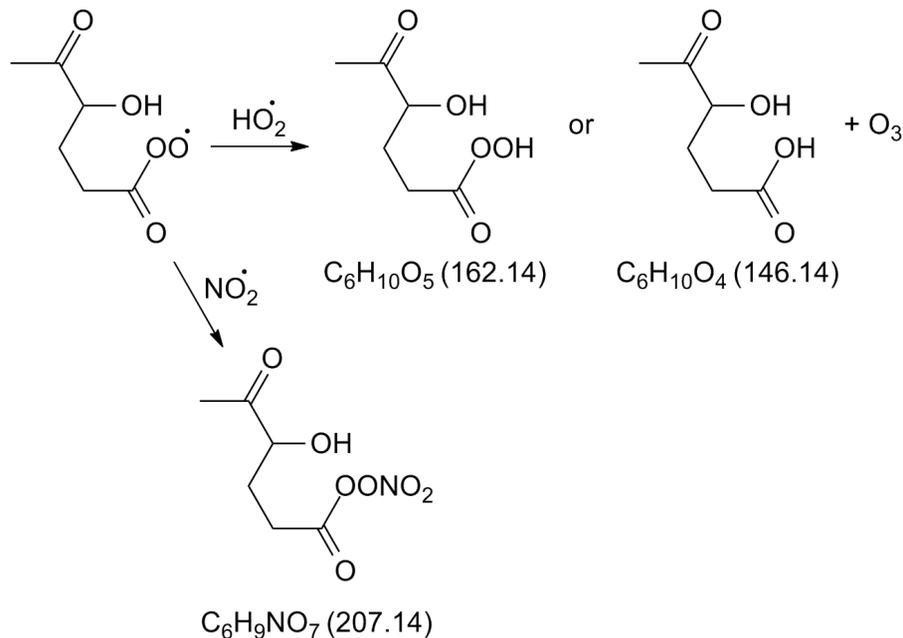
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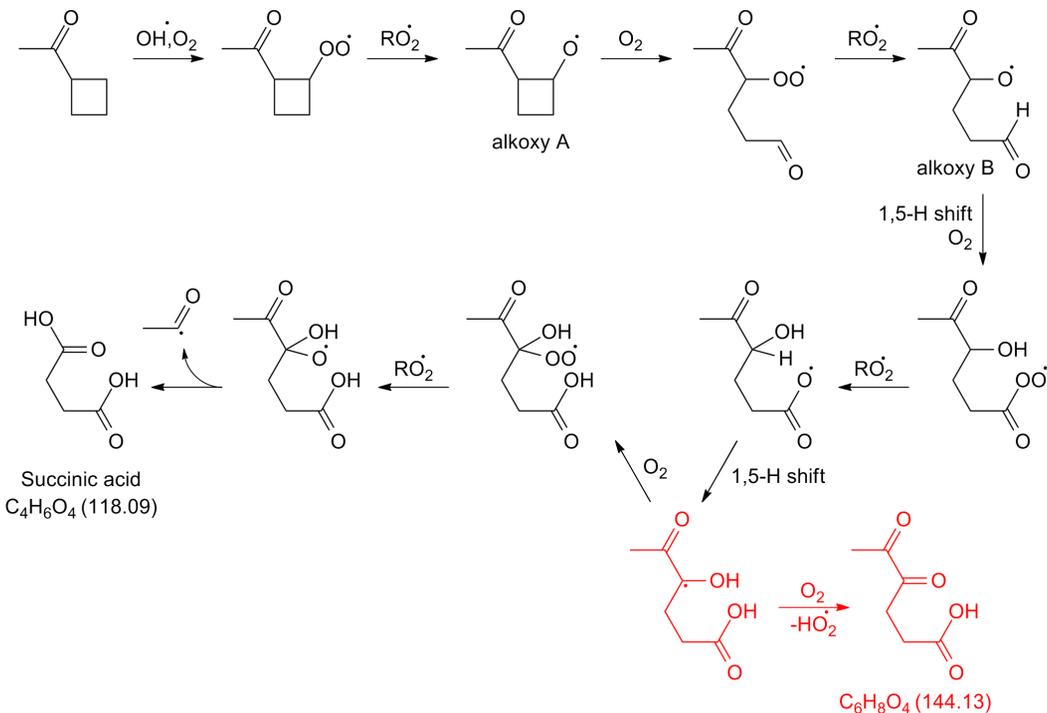
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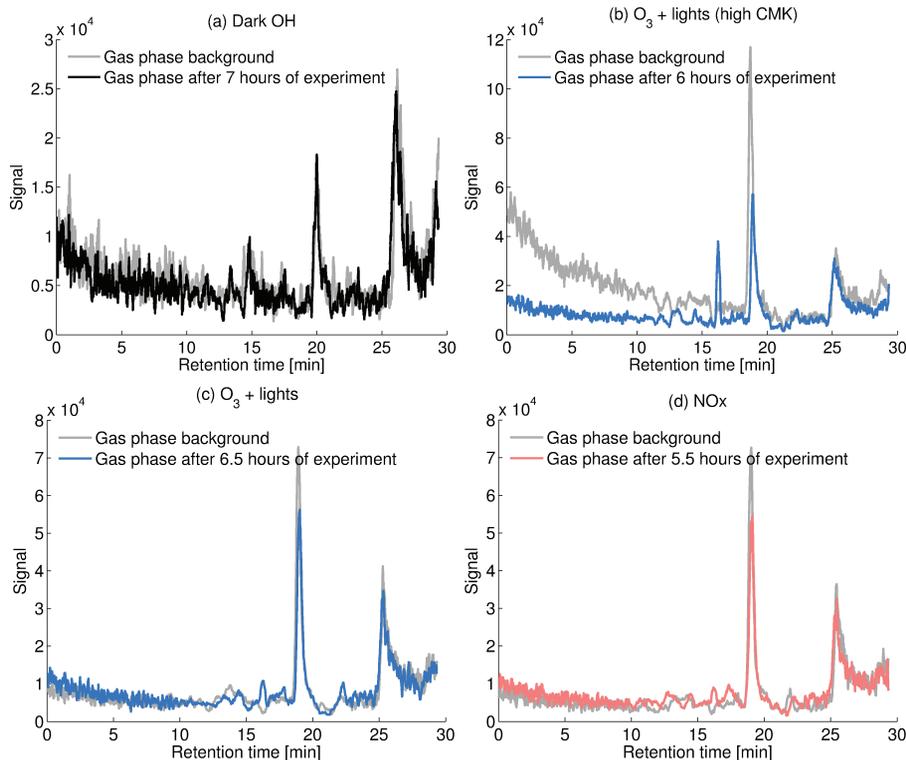
**Fig. 9.** Chemical mechanism of the reaction between the peroxyacyl radical with the hydroperoxyl radical ( $\text{HO}_2^\bullet$ ) forming either a peracid or an organic acid and ozone ( $\text{O}_3$ ). In the presence of nitrogen oxides ( $\text{NO}_x$ ), the  $\text{HO}_2^\bullet$  concentration will be reduced by nitrogen monoxide (NO) and a peroxyacyl nitrate (PAN) can be formed from the reaction of the peroxyacyl radical with nitrogen dioxide ( $\text{NO}_2$ ). The numbers in bracket correspond to the molar mass of the compounds.



**Fig. 10.** Suggested formation mechanism of succinic acid adapted from the 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) formation mechanism of Müller et al. (2012) (black path). The intermediate alkoxy radical marked in red is expected to react with molecular oxygen ( $\text{O}_2$ ) to form 4,5-dioxohexanoic acid besides the unimolecular 1,5-hydrogen shift. For simplification, alkyl radicals are not depicted as they react immediately with  $\text{O}_2$  to form peroxy radicals. The numbers in brackets correspond to the molar mass of the compounds.

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**Fig. 11.** Chromatograms of  $m/z$  143 for the four different experiments: **(a)** dark hydroxyl radical ( $\cdot\text{OH}$ ) production **(b)** ozone ( $\text{O}_3$ ) photolysis with 1600 ppbv cyclobutyl methyl ketone (CMK), **(c)**  $\text{O}_3$  photolysis, and **(d)**  $\text{O}_3$  photolysis in the presence of nitrogen oxides ( $\text{NO}_x$ ). The grey chromatogram in each plot correspond to the gas phase background measured before the lights were turned on.

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