



# Efficient formation of aqueous secondary organic aerosols from the hydroxyl radical reaction with fenchol, borneol, and menthol

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**Abstract.** Aqueous-phase oxidation of oxygenated monoterpenes can contribute to the formation of secondary organic aerosol (SOA) from biogenic volatile organic compounds. Still, the quantitative and mechanistic data for such precursors are limited. In this study, the aqueous-phase reactions of three atmospherically relevant, saturated terpenic alcohols (TAs)—  
10 fenchol, borneol, and menthol—with hydroxyl radicals (OH) were investigated using a photochemical reactor combined with GC/MS and LC/ToF-MS analyses and kinetic modeling. The objectives were to elucidate reaction mechanisms, identify oxidation products, and quantify yields of aqueous SOA (<sub>aq</sub>SOA) under atmospherically relevant conditions. Comprehensive product analysis revealed that oxidation proceeds via H-atom abstraction, yielding a wide range of multifunctional products. In addition to previously reported products, this work first identified functionalized terpenic acids formed as second-  
15 generation products, providing new evidence for the formation of low-volatility compounds from aqueous OH reaction with TAs. The molar yields of quantified products approached unity (0.88–0.99), indicating near-complete closure of the carbon balance. Based on these data, explicit kinetic box models were developed that successfully reproduced the measured temporal evolution of reactants. Modelled <sub>aq</sub>SOA yields ranged from 10% to 70%, depending on liquid water content and reaction coordinate, representing the first quantitative estimates for the three TAs under investigation. The results  
20 demonstrate that aqueous oxidation of semi-volatile terpenoids can efficiently generate low-volatility products contributing to SOA formation. These findings highlight the importance of multiphase processing of oxygenated terpenoids and provide new mechanistic and quantitative data for atmospheric models.

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## 1 Introduction

Fine atmospheric particulate matter (PM) - solid or liquid particles in the air - influences the climate, air quality, and human health (Jo et al., 2023). Aerosols with aerodynamic diameter  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) exhibit direct and indirect climate forcing by absorbing and scattering solar radiation, and acting as cloud condensation nuclei (CCN) and ice nuclei (IN), thereby altering cloud albedo and lifespan (Shrivastava et al., 2017a). Furthermore, exposure to  $\text{PM}_{2.5}$  negatively impacts human health and is associated with various cardiovascular and respiratory conditions, but also with Parkinson's disease, diabetes, etc. (Wei et al., 2019).

Secondary organic aerosols (SOAs) are formed in the atmosphere by oxidation of volatile organic compounds (VOCs) (Chaturvedi et al., 2023; Mahilang et al., 2021). Because about 90% of non-methane VOCs are emitted by vegetation (Sindelarova et al., 2022), the oxidation of these biogenic VOCs (BVOCs) is one of the major sources of SOAs (Mahilang et al., 2021; Shrivastava et al., 2017b). Production of SOAs from BVOCs is currently estimated at  $73.6 - 97.5 \text{ Tg} \times \text{yr}^{-1}$ , (Hodzic et al., 2016; Kelly et al., 2018), contributing to up to 90% mass of fine atmospheric PM (Jimenez et al., 2009; Zhang et al., 2005; Xu et al., 2021; Kanakidou et al., 2005).

Isoprene ( $\text{C}_5\text{H}_8$ ) is the major BVOC, followed by monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ), for which the estimated emissions range between  $82.7$  and  $184.8 \text{ Tg} \times \text{yr}^{-1}$  (Wang et al., 2024; Sindelarova et al., 2022). Moreover, the flux of SOAs from atmospheric oxidation of monoterpenes is estimated at  $\sim 20 \text{ Tg} \times \text{yr}^{-1}$ , about half of the BSOAs mass (Kelly et al., 2018). Hence, monoterpeneic SOAs significantly contribute to the global budget of fine PM (Jimenez et al., 2009; Fuzzi et al., 2015).

Consequently, the formation of SOAs from the gas-phase oxidation of monoterpenes ( $_{\text{gas}}\text{SOAs}$ ) was the subject of extensive research for over three decades (Hallquist et al., 2009; Fuzzi et al., 2015). To-date, many studies have focused on the major biogenic monoterpenes:  $\alpha$  and  $\beta$ -pinene and limonene (Wang et al., 2024; Sindelarova et al., 2022; Kamens and Jaoui, 2001). Production of SOAs from these BVOCs is initiated primarily by atmospherically abundant oxidants: ozone ( $\text{O}_3$ ), hydroxyl, and nitrate ( $\text{NO}_3$ ) radicals (Mahilang et al., 2021). Oxidation of monoterpenes generates a cascade of oxygenated products, including various water-soluble organic compounds (WSOCs) (Zhang et al., 2015; Kamens and Jaoui, 2001; Kourtchev et al., 2014). The WSOCs contributing to monoterpeneic SOAs include terpenoic acids (TACs), non-acidic monoterpeneoids (MTDs), polyfunctional oligomers, many of which are highly oxygenated molecules (HOMs) (Kenseth et al., 2020; Valorso et al., 2011; Yasmeen et al., 2011; Liu et al., 2023). At the same time, the classical model involving the formation of these low-volatility organics followed by their gas-particle partitioning (Pankow, 1994; Odum et al., 1996), does not provide a complete picture of the formation and evolution of SOAs (Su et al., 2020; Carlton et al., 2020; Tsigaridis and Kanakidou, 2018; Ervens, 2015).

Liquid water is ubiquitous in the troposphere, playing a crucial role in the multiphase chemistry of organic and inorganic trace species, including SOAs (Su et al., 2020; Lim et al., 2010; Carlton et al., 2020; Ervens, 2015; Ervens et al., 2018). Consequently, for over a decade, there has been an increasing focus on the still incompletely characterized aqueous reaction in clouds, fogs, haze, and some aerosols in the context of the formation and processing of SOAs (Su et al., 2020; Carlton et

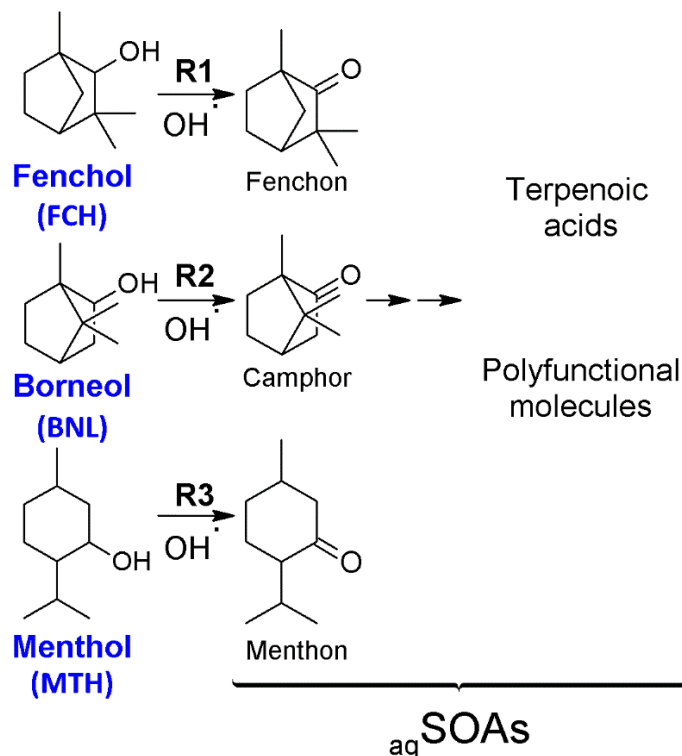


65 al., 2020; Lim et al., 2010; Ervens, 2015). Reactions of WSOCs in hydrometeors often involve unique species and mechanisms, resulting in HOMs and extremely low-volatility organic compounds (ELVOCs (Ervens, 2015; Zhu et al., 2020; Sullivan et al., 2016; Sun et al., 2010; Ervens et al., 2011; Mekic et al., 2019; Zheng et al., 2021; Gomez et al., 2015). Such molecules can be formed via (photo)chemical and non-radical “dark” reactions, contributing to  $_{aq}$ SOAs following the evaporation of water (Sullivan et al., 2016; Paglione et al., 2020; Kuang et al., 2020b). Results of field and laboratory studies  
70 strongly indicate that the contribution of  $_{aq}$ SOAs to the total flux of OAs is likely significant, on both global and local scales (Paglione et al., 2020; Kuang et al., 2020b; Su et al., 2020; Tsui et al., 2019). In addition to producing new particles, the multiphase reactions of SOAs also alter physicochemical characteristics of OAs, including composition, optical and toxicological properties, and CNN and IN activity (Carlton et al., 2020; Ervens, 2015; Sullivan et al., 2016; Decesari et al., 2017). At the same time, the fundamental data necessary to parametrize the complex multiphase chemistry of OAs remain  
75 incomplete, making it difficult to constrain the climate forcing of fine aerosols (Iccp, 2023; Tsigaridis and Kanakidou, 2018). To-date, many studies have focused on the formation of  $_{aq}$ SOAs from the reaction of oxygenated terpenoids with OH, because it is a major daytime atmospheric oxidant (Gligorovski et al., 2015). OH is formed by photolysis of  $O_3$  and diffuses into water-containing particles from the gas phase (Price et al., 2025). Additionally, OH is also formed inside hydrometeors by decomposition of hydrogen peroxide ( $H_2O_2$ ) via photolytic or Fenton(like) processes, enhancing the oxidative capacity of  
80 some aqueous particles (Kuang et al., 2020a; Bianco et al., 2020; Scheres Firak et al., 2025).

Studies of  $_{aq}$ SOAs formation from OH reactions with monoterpene precursors have often focused on terpenic acids and other low-volatility molecules with a high tendency to partition into the aqueous phase (Witkowski et al., 2019; Amorim et al., 2021; Enami and Sakamoto, 2016b; Huang et al., 2018; Otto et al., 2018; Lai et al., 2025). At the same time, the formation of  $_{aq}$ SOAs from non-acidic MTDs has seldom been investigated, even though such precursors were shown to form  
85 HOMs following gas and aqueous oxidation by OH and  $O_3$  (Leviss et al., 2016; Li et al., 2020). Moreover, the measured yields of  $_{gas}$ SOAs from oxidation of some MTDs were similar or higher than monoterpenes (Khalaj et al., 2025; Griffin et al., 1999).

Our recent study was focused on aqueous OH reactions with two terpenic diols: pinanediol and camphanediol (Jain et al., 2024). These terpenoids are characterized by dimensionless Henry’s law constant values comparable with terpenic acids  
90 ( $H^{cc} \approx 1 \times 10^5$ ) (Episuite4.11). Moreover, the mass yields of SOAs from OH reactions with terpenic 1,2-diols were close to 100% in both the gas and aqueous phases (Jain et al., 2024; Ye et al., 2018), highlighting the potential of some MTDs to contribute to the ambient, fine PM mass.

The presented work focused on  $_{aq}$ SOAs formation from aqueous OH reaction with three terpenic monoalcohols (TAs): fenchol (FCH), borneol (BNL), and menthol (MTH) - Fig. 1. The goals of this work include analyzing products,  
95 mechanisms, and  $_{aq}$ SOAs yields from R1-3.



**Figure 1: Precursors and reactions investigated.**

The TAs under investigation (Fig. 1) are more volatile than terpenoic diols and acids and will likely remain in the gas phase when there is no water present (Keating et al., 2017). At the same time, the TAs are semi-volatile organic compounds (SVOCs) that can enter water particles ( $H^{cc} \approx 1 \times 10^3$ ) under the realistic atmospheric conditions (Mcneill, 2015; Witkowski et al., 2024b). As concluded in our previous study, FCH, BNL, and MTH can react with OH in the aqueous phase in air masses with liquid water content ( $LWC \geq 0.1 \text{ g} \times \text{m}^{-3}$ ) (Witkowski et al., 2024b).

In addition to secondary formation from monoterpene oxidation (Valorso et al., 2011), the sources of emission of MTDs include wildfires (Hatch et al., 2019) and natural and agricultural vegetation (Messina et al., 2016; Guenther et al., 2012; Gentner et al., 2014; Graedel, 1979). MTDs are emitted by crops, alpine, grasslands, forests, flowering plants, harvesting activities, and due to the use of fertilizers (Ormeño et al., 2010; Gentner et al., 2014; Yang et al., 2021). MTDs also largely contribute to the distinctive fragrances of essential oils and flavors found in plants, resulting in their widespread industrial uses (Caputi and Aprea, 2011; Zuzarte and Salgueiro, 2015).

The three TAs under investigation (Fig. 1) are among the major components of essential oils, emitted by plants, but are also emitted during wildfires (Kamatou et al., 2013; Hatch et al., 2019; Ghaffari et al., 2019; Yassaa et al., 2000). Particularly, MTH has a wide variety of industrial and medical uses, with the estimated annual consumption of about 30 000 metric tonnes (Kamatou et al., 2013). Moreover, FCH and BNL were included in the combined global emissions of  $14.9 \text{ Tg yr}^{-1}$  for



34 MTDs, compared with 66.1 Tg yr<sup>-1</sup> estimated for  $\alpha$ -pinene (Guenther et al., 2012). Additionally, the total flux of TAs was estimated at 14.6 Tg yr<sup>-1</sup>, 9% of total monoterpene emission (Griffin et al., 1999).

115 For these reasons, the three TAs (Fig. 1) were selected as model precursors of <sub>aq</sub>SOAs due to their atmospheric abundance and tendency to reside in hydrometeors under certain conditions, but also to represent similar, cyclic TAs. R1-3 were carried out in a custom-built photochemical reactor. Product studies were conducted using gas (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS). Previously reported and newly identified products were quantified with authentic and surrogate standards. Based on these data and the proposed mechanisms of R1-R3, kinetic box models were developed. These kinetic models were combined with the air-water partitioning coefficients of the reactants to estimate the yields of <sub>aq</sub>SOA from R1-3 (Jain et al., 2024).

## 2 Experimental section

### 2.1 Materials and reagents

The reagents are listed in Section S1 of the Supporting Information (SI). LC/MS-grade water was used in all experiments.

### 125 2.2 Aqueous reaction with hydroxyl radical

The reactions were carried out in the aqueous photoreactor (Jain et al., 2024). The reaction vessel was a jacketed borosilicate glass reaction flask with an internal volume of 0.1 L and irradiated with four UVB lamps (Philips, PL-S 9W/01/2P 1CT,  $\lambda_{\text{max}} = 310$  nm). The lamps were mounted inside a circular chamber (ID 10 cm, height 18 cm) and air-cooled with a fan underneath the reaction vessel. The reactor was placed on a small pedestal with a built-in magnetic stirrer to mix the reaction mixture. The reaction mixture was maintained at 298K using a circulating water bath (SC100 a10, Thermo Fisher Scientific) connected to the outer jacket of the reaction flask.

### 2.3 Experimental procedures

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was a photolytic precursor of OH. The aqueous reaction solution (0.1 ml) contained a mixture of one of MTA (0.6 mM) and H<sub>2</sub>O<sub>2</sub> (0.09 M). After the reactants were dissolved, the solution was filtered through a 0.7- $\mu$ m GF syringe filter. Before initiating the reaction, the lamps were warmed up for 30 min, and the solution temperature was stabilized at 298 K. The reaction was carried out for 30-35 min, and up to 16 aliquots of the reaction mixture were sampled. For LC/MS analyses, each aliquot was filtered through a 0.22  $\mu$ m syringe filter (PTFE) and injected. For GC/MS analyses, 800  $\mu$ l of the reaction solution was saturated with sodium chloride and extracted with 300  $\mu$ l of ethyl acetate containing 0.6 mM dimethyl phthalate, used as an internal standard for peak area normalization. Afterward, the organic layer was dried with anhydrous sodium sulphate and injected into the GC/MS instrument.



## 2.4 Product studies

Precursors and products were quantified with GC-EI/MS and identified with GC-NCI/MS and LC-ESI/MS.

The molar yields of the products were calculated with Eq. (1).

$$[Product]_t = Yield \times \Delta[MTA]_t \quad (1)$$

145 In Eq. (1),  $[Product]_t$  is the concentration of a product at time  $t$ , from the onset of the reaction (in mM).  $\Delta[MTA]$  is the amount of the MTA consumed at time  $t$  (mM). The yields were derived as slopes of the linear portion of the plots obtained with Eq. (1) (Gierczak et al., 2021).

150 Products were quantified with authentic standards whenever possible. At the same time, the vast majority of analytes were quantified with surrogate standards – Section S3. For some products, due to the lack of appropriate surrogate standards and other analytical problems (e.g., very low signal intensity), the yields were derived by fitting the kinetic model (section 2.5) to the experimental data.

## 2.5 Kinetic models

155 Kinetic modeling was performed with the Java version of Acuchem (Braun et al., 1988). Based on the measured product yields and the proposed mechanism, R1-R3 kinetic box models were developed – Section S2. The models describe the formation of the detected first and second-generation products of R1-R3 (Tables S2-S4). Most  $k_{OH_{aq}}$  values used in the models (Tables S2-S4) were predicted with SAR (Witkowski et al., 2024b). The unknown product yields in models were adjusted by fitting the temporal concentration profiles of the reactants to the experimental data.

## 2.6 Yields of aqueous secondary aerosols

160 Yields of  $_{aq}SOAs$  from R1-R3 were derived assuming that all reactants, at any given time, partition between aqueous and gas phases according to the Henry's Law equilibrium – Eq. (2).

$$SOA_{aq} yield(\%, w/w) = \frac{\sum \%_{aq} \times c_{reactant}(t)}{\Delta MTA(t)} \quad (2)$$

In Eq. (2),  $_{aq}SOAs$  yield (% w/w) is the mass yield of organic aerosols,  $\Delta MTA(t)$  is the amount ( $g \times L^{-1}$ ) of the precursor consumed at time  $t$ ,  $\%_{aq}$  is the mass fraction of reactant in the aqueous phase, which is multiplied by the concentration of this reactant ( $g \times L^{-1}$ ). The fraction of each reactant in the aqueous phase was derived with Eq. (3).

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$$\%_{aq}(LWC) = 1 - \frac{1}{1 + H^{cc} \times volume\ of\ water(m^3)} \quad (3)$$

In Eq. (3),  $\%_{aq}$  is the fraction for each reactant in the aqueous phase, which depends on LWC, and is obtained using the dimensionless Henry law constants ( $H^{cc}$ ) in Eq. (3) is multiplied by the volume of water in  $1\ m^3$  of air. Experimentally measured values were used whenever available, but the majority of  $H^{cc}$  values used in the models were predicted with HenryWin v4.11 – Tables S5 – S7 (Episuite4.11).



## 170 2.7 Chromatographic analyses

Qualitative and quantitative analyses were carried out using GC/MS equipped with electron ionization (EI) and negative chemical ionization (NCI) ion sources, and LC/MS equipped with an electrospray ionization (ESI) ion source.

### 2.7.1 Gas chromatography coupled with mass spectrometry

GC/MS analyses were performed using a GC/MS-2010 Ultra gas chromatograph coupled with a single quadrupole mass spectrometer (Shimadzu) equipped with electron ionization (EI) or negative chemical ionization (NCI) ion source.

175 Precursors and products of R1-3 were separated with a VF-WAXms column: 30 m × 0.25 mm × 0.5 μm and quantified in the EI mode. The column flow was 0.67 ml/min, and the purge flow was 2 ml/min; the split ratio was set to 20. The injector, ion source, and mass spectrometer transfer line temperatures were set at 250°C. The temperature program involved an initial hold at 70 °C for 4 min, followed by a linear increase at a rate of 15 °C/min to 250°C, a 6 min hold. The MS was operating  
180 in scan ( $m/z = 50-300$ ) and SIM modes (Table S9-S11).

Quantitative analyses were carried out in the NCI mode using methane and ammonia as reagent gases. In these analyses, a ZB-5MSplus column (30m×0.25 mm×0.25 μm) was used. The column flow was 0.68 ml/min, and the purge flow was 2 ml/min; the injection volume was 0.5 μl in splitless mode. The temperatures of the injector, ion source, and mass spectrometer transfer line were 280°C. The temperature program included an initial hold at 50 °C for 2 min, followed by a  
185 linear increase at a rate of 16 °C/min to 70°C, for 8 min hold, another linear increase at a rate of 10°C/min to 170°C, a 5 min hold, then a linear increase at a rate of 15 °C/min to 250°C, with a 1 min hold. The MS operated in the scan mode ( $m/z = 50-300$ ).

### 2.7.2 Liquid chromatography coupled with time-of-flight mass spectrometry

Analyses were carried out with a Waters ACQUITY UHPLC liquid chromatograph coupled with the Xevo G2 ToF/MS  
190 equipped with an ESI source operating in the negative ionization mode. The ESI source conditions were: source temperature 100°C, offset 80V, desolvation temperature 350°C, capillary voltage: 2.8kV, sampling cone: 40V, cone gas: 50L/h, desolvation gas 700L/h. The analytes were separated using a BEH C18 column (Waters), 100 × 2.1 mm × 1.7 μm. Eluent A was 0.2% formic acid solution in water ( $pH \approx 2.8$ ), and eluent B was ACN with 0.2% formic acid. The flow rate of the mobile phase was 0.25 ml/min, and the column temperature was maintained at 40°C. A gradient elution program was used:  
195 initially 5%B for 5 min, then linear increase to 45%B over 15 min, then linear increase to 95% B over 2 min, kept for 2 min, then decrease to 5% B over 1 min, kept for 2 min. Total runtime was 27 min.

## 2.8 Control experiments and uncertainty

Control measurements performed without adding H<sub>2</sub>O<sub>2</sub> to the reaction solution confirmed that the MTAs under investigation (Fig. 1) were not photolyzed with the UVB radiation used to generate OH (section 2.2). Also, no “dark” reactions (within the

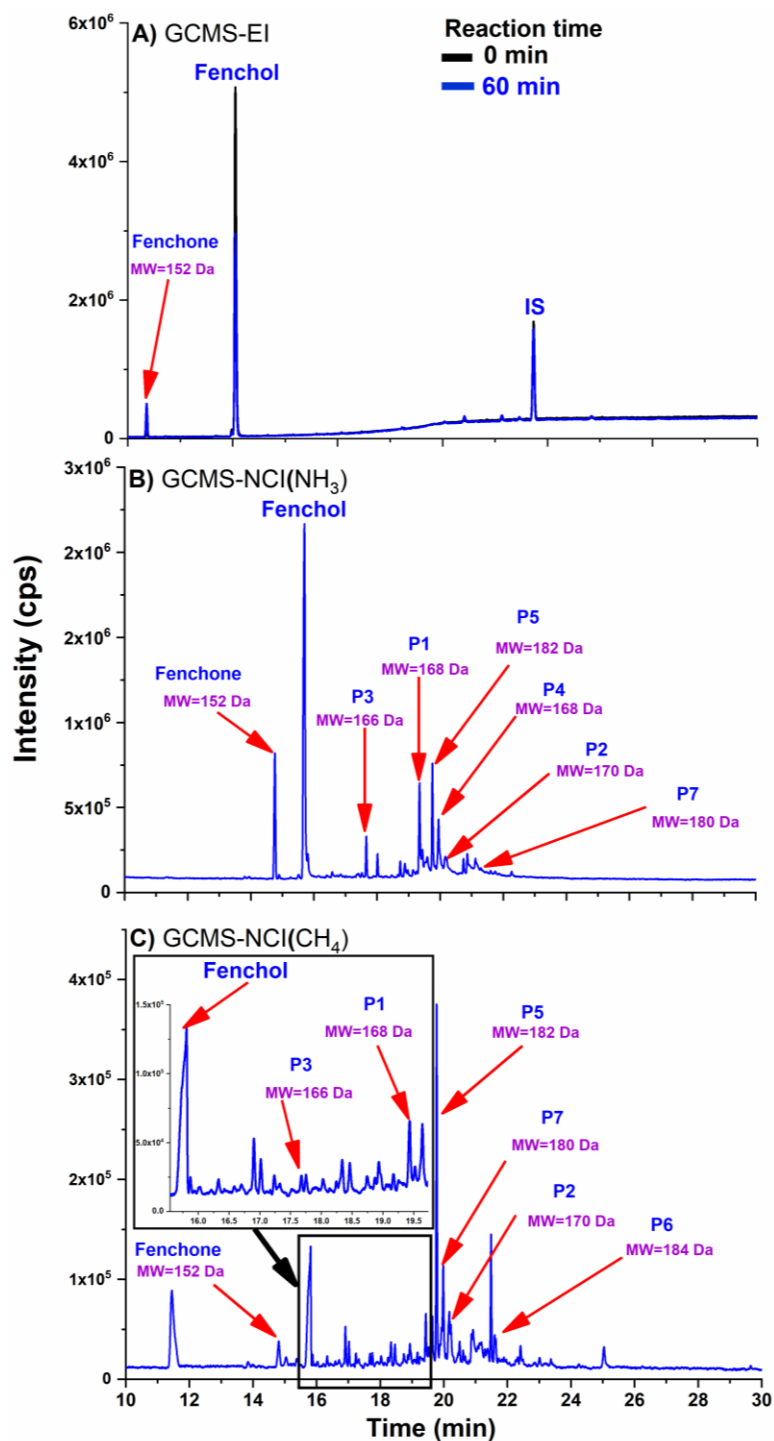


200 timescale of the experiments) were observed between the precursors and H<sub>2</sub>O<sub>2</sub> while the reactor lamps were kept off. All measurements were carried out at least three times.

### **3 Results and discussion**

#### **3.1 Mechanism of OH reaction with fenchol**

The neutral products of R1 were detected with GC/MS – Fig. 2.



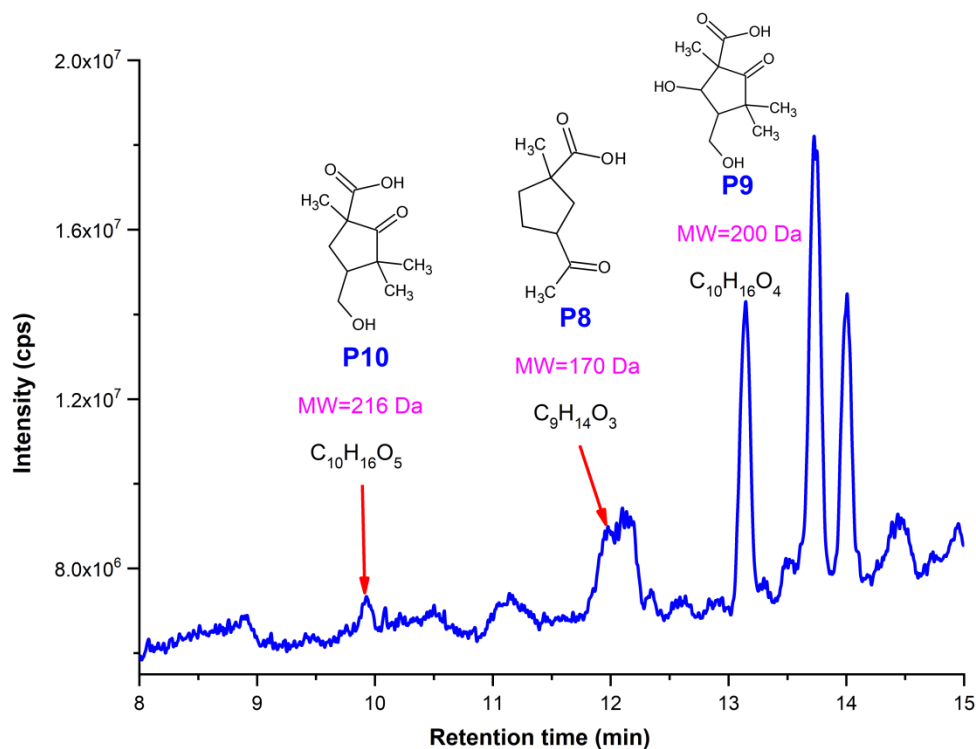
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**Figure 2:** GC/MS chromatograms of the products of fenchol (FCH) + OH reaction (R1) detected with EI (A) and, NCI using NH<sub>3</sub> (B), and CH<sub>4</sub> (C) as reagent gases. Note that different chromatographic columns were used for GC-EI/MS and GC-NCI/MS analyses (section 2.7.1), resulting in different retention times.



In the EI mode, only the formation of fenchone from R1 was observed (Fig. 2A). Additional products were detected with NCI, due to the higher sensitivity for products P1-P7 in the NCI mode (Fig. 2B and C) (Javelle et al., 2021). Similar results were obtained for both reagent gases, but the sensitivity was significantly higher for NH<sub>3</sub>. For this reason, neutral products of R1-R3 were identified based on the data obtained for NH<sub>3</sub>.

Moreover, the results of LC-ToF/MS analyses confirmed the formation of TACs from R1 - Fig. 3.



215 **Figure 3: LC-ToF/MS chromatogram of TACs formed from OH reaction with fenchol – R1.**

Elemental compositions of TACs (P8-P10) formed from R1 were derived with LC-ToF/MS - Table S12. The mechanism proposed for R1 is based on the structures of the neutral (Fig. 2) and acidic (Fig. 3) products and their formation yields (Tables S8 and S9). The yields of the products (Table S7) indicated that the major products of R1 were fenchone, P2, and P4-P6, with pathways I and II (Scheme 1) accounting for 85% and 12% of the total yields of the products, respectively.

220 Pathways III and IV in Scheme 2, were minor channels, contributing about 3% to the total yield of R1 products – Table S8.





( $k_{OH_{aq}}=1.9\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) than P4 ( $k_{OH_{aq}}=2.7\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) (Witkowski et al., 2024a). Consequently, P4 is oxidized faster than  
230 P3, yielding  $\text{RO}_2(\text{III})$ , which then produces a carbonyl (P5) and an alcohol (P6) (Russell, 1957). Likewise, P6  
( $k_{OH_{aq}}=2.8\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) is oxidized preferentially over P5 ( $k_{OH_{aq}}=1.8\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), resulting in P7 – Scheme 1 (Witkowski et  
al., 2024a). In pathway II, FCH is converted to fenchone by elimination of  $\text{HO}_2$  following the H-atom abstraction from the  $\alpha$ -  
position of -OH (Denisov and Khudyakov, 1987; Puchkov et al., 2005; Puchkov et al., 2013; Bradley et al., 2001).  
Considering the well-known reactions of RO and  $\text{RO}_2$  radicals, proposing a feasible mechanism for the formation of TACs  
235 (Fig. 3) directly from FCH is difficult. Consequently, in the proposed mechanism (Scheme 2), P8-P10 are second-generation  
products of R1 formed from fenchone.





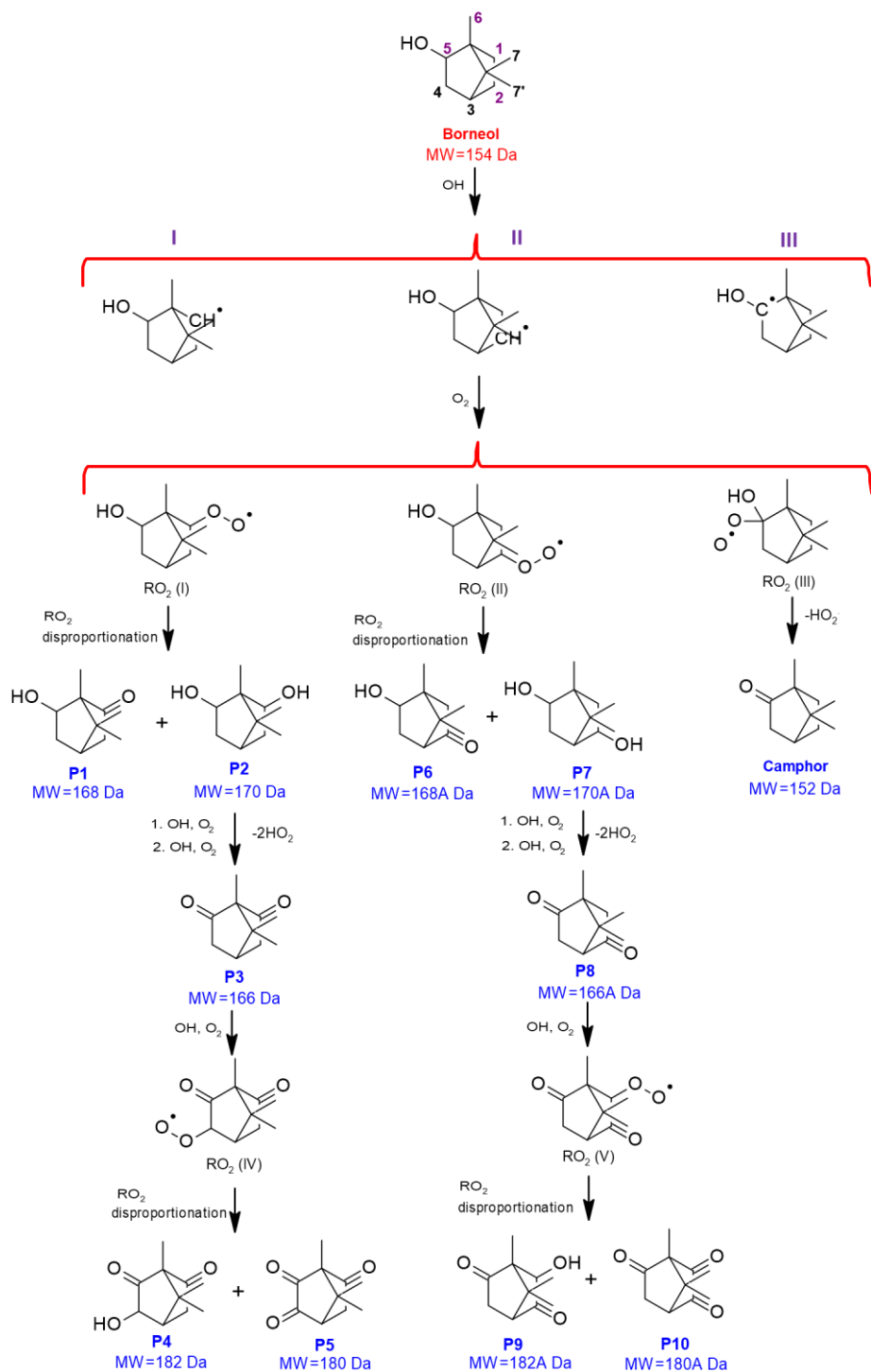
aldehyde moiety (Scheme 2) (Enami and Sakamoto, 2016a). Subsequently, P9 can undergo further oxidation to P10 via the addition of the -OH moiety to the cyclopentane ring. Pathway (IV) yields RO<sub>2</sub>(V), which forms P8, following two consecutive  $\beta$ -scission reactions (Enami and Sakamoto, 2016a).

Previously, only the formation of fenchone and products P5-P7 from R1 in the gas phase was confirmed with GC/MS (Ceacero-Vega et al., 2012). At the same time, the formation of TACs from R1 was not reported, likely because low quantities of underivatized TACs are difficult to detect with GC/MS (Ceacero-Vega et al., 2012). Hence, this work is the first to report the formation of low-volatility TACs from R1.

### 250 **3.2 Mechanism of OH reaction with borneol**

The mechanism of R2 (Schemes 3 - 5) was proposed based on the products identified with GC/MS (Fig. S2), LC-ToF/MS (Fig. S3), and their formation yields (Table S7 and S8). The major products of R2 were camphor, products P1-P3, and P6-P8, accounting for 88% of the molar yield of the products (Tables S8 and S9). Minor pathways IV (2%, Scheme 4) and V and VI (3%, Scheme 5) accounted for ca. 5% of the total yield.

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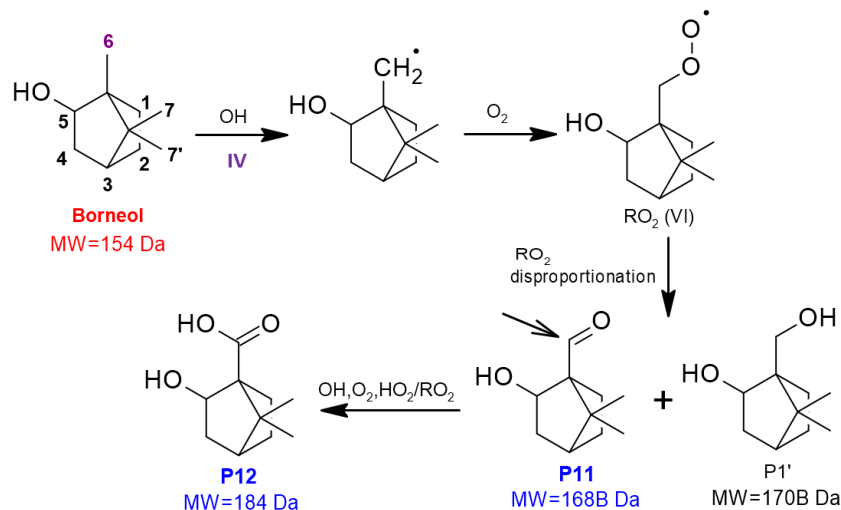
**Scheme 3: Proposed mechanism of borneol (BNL) + OH reaction (R2). The detected products are highlighted in blue bold font. The formation of all possible isomers is not included for clarity. The mechanism of R2 is continued in Schemes 4 and 5 – formation of TACs.**

260 In Scheme 3, RO<sub>2</sub>(I) and RO<sub>2</sub>(II) are formed via pathways I and II, respectively. Formation of P1-P2 and P6-P7 can be explained via disproportionation reactions of RO<sub>2</sub>(I) and RO<sub>2</sub>(II) (Russell, 1957). Diols: P2 ( $k_{OH_{aq}}=3.4\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), P7 ( $k_{OH_{aq}}=3.3\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) are likely oxidized faster than P1 ( $k_{OH_{aq}}=2.6\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) and, P6 ( $k_{OH_{aq}}=2.4\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), (Witkowski et al., 2024a). For this reason, dicarbonyls P3 and P8 are formed by the H-atom abstraction from the  $\alpha$ -position of -OH moieties in P2 and P7, followed by the elimination of -HO<sub>2</sub>. The conversion of BNL to camphor (pathway III in

265 Scheme 3) likely occurs via the same mechanism (Denisov and Khudyakov, 1987; Puchkov et al., 2005; Puchkov et al., 2013; Bradley et al., 2001). In Scheme 3, P3 and P8 can undergo further oxidation, resulting in P5, P10, and P4, P9. The formation of products P1, P2, P6, and P7 from R2 was also observed in the gas phase, likely occurring via similar pathways (Ceacero-Vega et al., 2012).

The formation of TACs (detected with LC/MS - Fig. S3) from camphor was again more feasible, but the acidic product P12

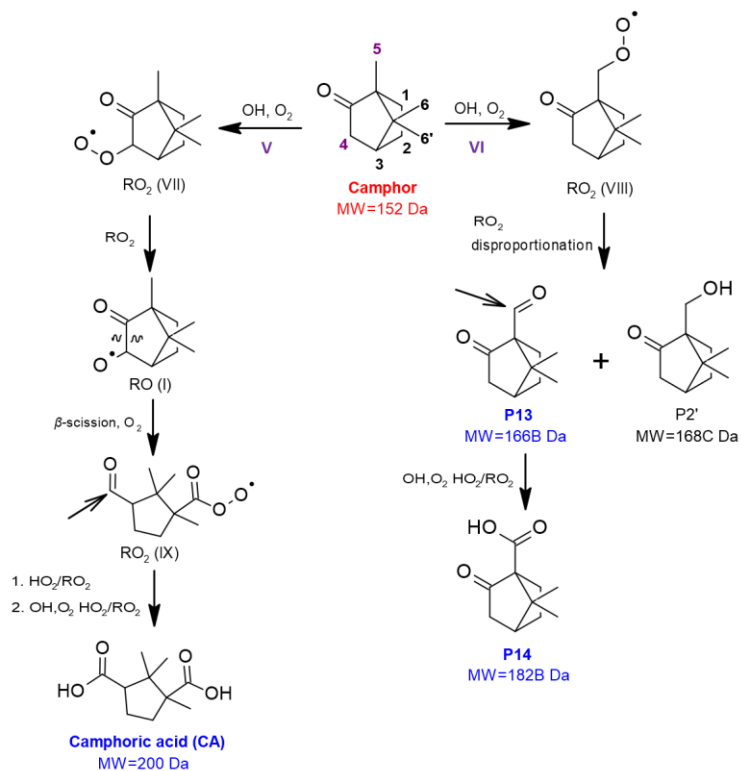
270 may be produced directly from the precursor, involving the H-atom abstraction from the C6 position of BNL – Scheme 4.



**Scheme 4: Formation of P12 from OH reaction with borneol (R2) via pathway IV, involving the H-atom abstraction from the C6.**

In Scheme 4, pathway (IV) yields RO<sub>2</sub>(VI), which undergoes the disproportionation reaction, resulting in P1' and P11. P11 is further oxidized to P12 (Enami and Sakamoto, 2016b). The two by-products formed by pathway (IV) – P11 and P1' - were

275 not detected, likely due to their low formation yields and rapid conversion of P11 to P12. Camphoric acid and P14 formed from R2 were most likely produced from camphor – Scheme 5.

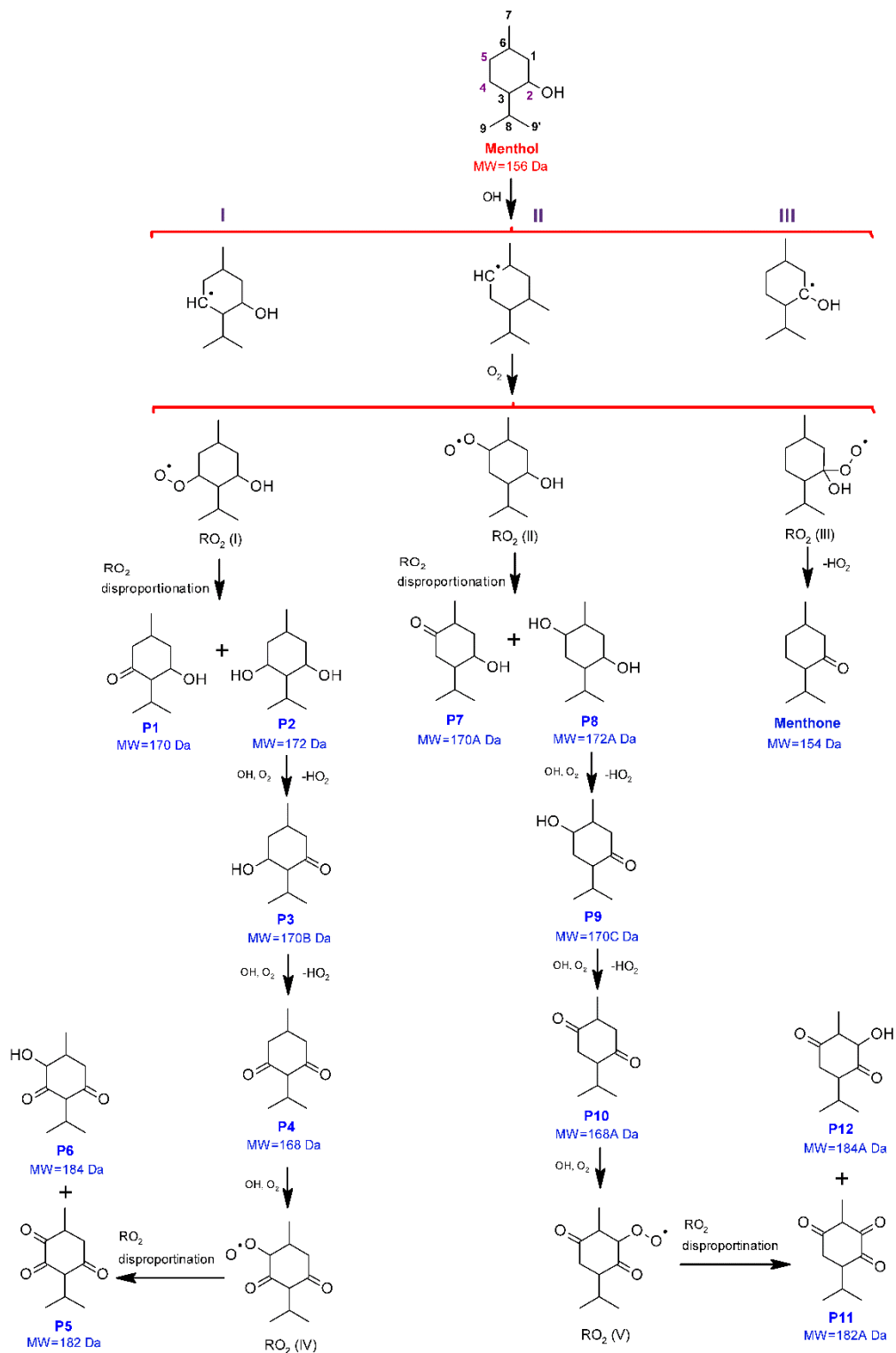


**Scheme 5: Proposed mechanism for OH reaction with camphor. The products detected (camphoric acid and P14) are highlighted in blue bold font.**

280 Camphoric acid is formed via pathway V (Scheme 5), which is analogous to pathway III in Scheme 2, and P14 is produced via pathway (VI), analogously to pathway IV in Scheme 4 (Enami and Sakamoto, 2016b).

### 3.3 Mechanism of OH reaction with menthol

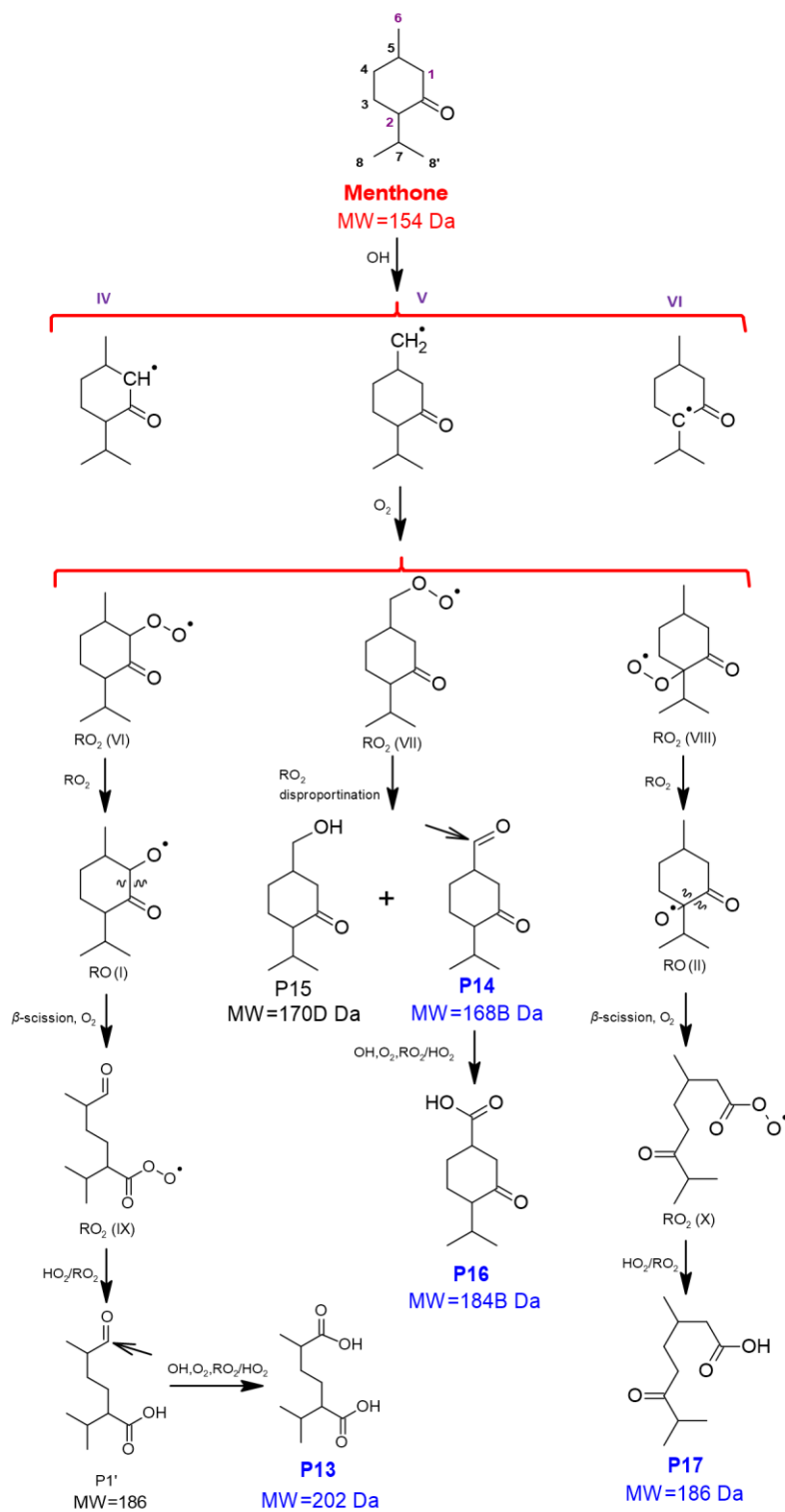
The mechanism of R3 (Schemes 6 and 7) was proposed based on the products identified with GC/MS (Fig. S4), LC-ToF/MS (Fig. S5), and their formation yields (Tables S8 and S9). The major channels of R3 were pathways I (54%) and II (42%) (Scheme 6). The yield of menthone formed from R3 (pathway III) was approx. 3%, the lowest of the two MTAs under investigation. Minor channels of R3 were pathways IV- VI (Scheme 7), with contributed approx. 1% of the total yield of the products.





**Scheme 6: Proposed mechanism of menthol (MTH) + OH reaction (R3). Products observed in this work are highlighted in blue bold font. The formation of all possible isomers is not included for clarity. The mechanism of R3 is continued in Scheme 7 – oxidation of menthone.**

In Scheme 6, RO<sub>2</sub>(I) and RO<sub>2</sub>(II) are formed via pathways I and II, respectively, and undergo the disproportionation reaction, leading to pairs of isomeric products: P1, P7, and P2, P8. Afterward, products P3 and P9 are formed by oxidation of P2 ( $k_{OH_{aq}}=6.1\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), and P8, ( $k_{OH_{aq}}=5.7\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), which likely react faster than P1 ( $k_{OH_{aq}}=4.3\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ) and P7 ( $k_{OH_{aq}}=4.1\times 10^9\text{ M}^{-1}\text{s}^{-1}$ ), respectively – Scheme 6 (Witkowski et al., 2024a). In pathways I and II, the elimination of HO<sub>2</sub> from P3 and P9 results in P4 and P10, respectively. Further oxidation of P4 and P10 results in P5, P6, and P11, P12, which are formed by the disproportionation mechanism (Scheme 6). The formation of menthone from R3 (pathway III is Scheme 6) is analogous to the formation of fenchone and camphor from R1 and R2, respectively. TACs formed from R3 (Fig. S5) are likely second-generation products, produced by the oxidation of menthone – Scheme 7.





**Scheme 7: Proposed mechanism of the OH + menthone reaction. Products observed in this work are highlighted in blue.**

The mechanisms of P13, P16, and P17 formation from R3 in Scheme 7 are analogous to the formation of TACs from R1 and R2. Pathway (IV-VI) in Scheme 7 yields corresponding RO<sub>2</sub> radicals. Afterward, RO<sub>2</sub>(IV-VI) are converted to P13, P16, and P17 via the β-scission and disproportionation reactions (Enami and Sakamoto, 2016b). The formation of carboxylic moieties in P13, P14, P16, and P17 involves an H-atom from the α-positions of the corresponding aldehyde by-products (Enami and Sakamoto, 2016b).

**3.4 Mechanism of OH reaction with fenchol, borneol, and menthol**

Over 88% of the R1-R3 products were quantified using the experimental approach used in this work- Fig. S1. For all precursors under investigation, the major products were neutral molecules containing -OH and C=O moieties, and the yields of TACs were between 1 and 5% – Table. 1.

**Table 1.** The yield of neutral and acidic products of the aqueous OH reaction with fenchol (R1), borneol (R2), and menthol (R3) obtained in this work.

Precursor	Molar yields		
	Neutrals <sup>a</sup>	Acids <sup>b</sup>	Total <sup>c</sup>
Fenchol	0.91±0.07	0.03	0.94±0.07
Borneol	0.95±0.10	0.05	0.99±0.10
Menthol	0.87±0.05	0.01	0.88±0.05

<sup>a</sup>Measured with authentic or surrogate standards <sup>b</sup>Values obtained from the kinetic models <sup>c</sup>Uncertainties derived from the experimental uncertainties of the yields of individual

The measured yields of some products were very high: 40-54% - Table S7. At the same time, the partial aqueous SAR (Fig S6) indicated that none of the aliphatic H-atoms in FCH, BNL, and MTH were so strongly favored (Witkowski et al., 2024b). SAR also indicated high rates of H-atom abstraction from the CH<sub>3</sub> groups. However, H-atom abstraction from the cyclohexane ring better explains the formation of the major (non-acidic) products of R1-R3.

The apparent discrepancies between SAR predictions and experimental data can be due to the formation of isomeric products, which are not completely resolved by GC/MS (see Figs. 1, S2, and S4). As denoted in Schemes 1, 3, and 6, it is reasonable to assume that isomeric products can be formed by adding the -OH and C=O moieties to the original carbon skeleton at different positions, resulting in a relatively large number of possible isomers. Also, except for the first-generation ketones (fenchone, camphor, and menthone), the rest of the products were quantified with surrogate standards (Tables S10-S12), which may result in higher uncertainties in their yields.

The reactions of OH with MTH, FCH, BNL, and cyclohexanol were previously investigated in the gas phase. The yields of the corresponding ketones from the OH reaction with FCH, BNL, and cyclohexanol in the gas phase are significantly higher than in the aqueous phase – Table 2.



330

**Table 2.** Yields of corresponding ketones formed from the OH reaction with fenchol, borneol, menthol, and cyclohexanol in the gas and aqueous phases.

		Yield (%)		Reference
Alcohol (recursor)	Ketone (product)	<i>Aqueous phase</i> <sup>a</sup>	<i>Gas-phase</i>	
Fenchol	Fenchone	0.11±0.01	0.61±2.6	(Ceacero-Vega et al., 2012)
Borneol	Camphor	0.12±0.02	0.49±1.0	(Ceacero-Vega et al., 2012)
Menthol	Menthone	0.03±0.00	-	
Cyclohexanol	Cyclohexanone	-	0.55±0.6	(Bradley et al., 2001)

<sup>a</sup>Measured with authentic standards

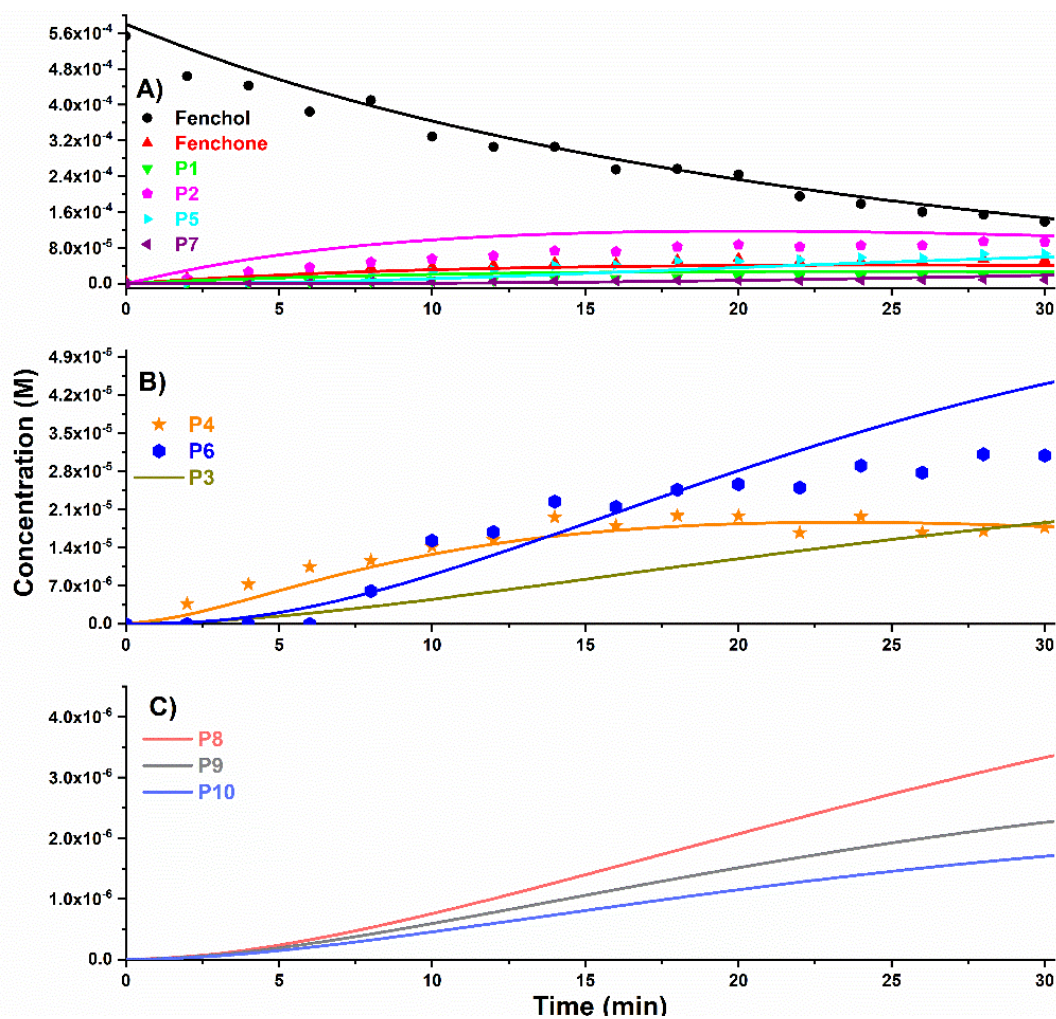
In the gas phase, the measured yields of ketones from the reaction with OH with the cyclic alcohols were between 0.49 and 0.61 - Table 2 (Ceacero-Vega et al., 2012; Bradley et al., 2001). These data indicate that H-atom abstraction from the -OH moiety  $\alpha$ -position was the main reaction pathway. This conclusion is also supported by the partial  $k_{OH_{aq}}$  values estimated with the gas-phase SAR (Kwok and Atkinson, 1995; Ceacero-Vega et al., 2012).

At the same time, the aqueous SAR predicts that the abstraction of the H-atom adjacent to the -OH group contributes 5-15% to the total  $k_{OH_{aq}}$  - Fig. S6. The values of partial rate coefficients predicted with the aqueous SAR (Fig. S6) are within the range of the measured yields of primary carbonyls, ranging from 3 to 12 % - Table 2 (Witkowski et al., 2024b).

This different intramolecular selectivity for the H-atom abstraction by OH from cyclic alcohols in gas and aqueous phases may be attributed to solvent effects, including the water cage effects (Kopinke and Georgi, 2017), H-bond formation (Otto and Engberts, 2003). In water, the reaction of OH with aliphatic, oxygenated molecules likely involves the formation of a highly polarized transition state (TS), which is stabilized by the solvent (Mitroka et al., 2010). At the same time, -OH groups can compete for the electron density with the attacking OH, which lowers the TS stabilization. This phenomenon is reflected by the values of the empirical F ( $\alpha$ -position) substituent factor for -OH moiety in the gas (3.5) and aqueous (1.9) SARs, showing the lower net activating effect in water (Kwok and Atkinson, 1995; Witkowski et al., 2024b).

### 3.5 Kinetic models

The kinetic models for R1–R3 are based on the measured product yields (Tables S8 and S9) and their proposed formation pathways (Schemes 1-7). For all precursors, good agreement between the experimental data was obtained; sample results obtained for R1 are presented in Fig. 4.



355 **Figure 4: Measured and modeled temporal evolution of the reactants for fenchol + OH reaction (R1). Points represent experimental data, and lines are the temporal profiles generated by the model. Structures of neutral (A and B) and acidic (C) products are shown in Schemes 1 and 2, respectively.**

For R1, the box model accurately predicted the temporal evolution of the reactants - Fig. 4A, B. Only model data is shown for TACs and some neutral products since their yields were not measured - (section 3.4). Very similar, satisfactory performance of the models was obtained for R2 and R3 - Figs. S7 and S8.

#### 360 4 Atmospheric implications

As discussed in our previous work, R1-R3 can be relevant in the atmosphere for  $LWC \geq 0.1 \text{ g} \times \text{m}^3$  (Witkowski et al., 2024a). The  $k_{OH_{aq}}$  values measured in our previous study indicated that liquid water affects the lifetimes of MTH, FCH, and BNL in clouds, fogs, and rain. The lifetimes, estimated for the average  $[OH]_{aq}$  between  $3.5 \times 10^{-15}$  M (urban clouds) and



2.2×10<sup>-14</sup> M (remote clouds), ranged from 10 to 300 h (Bianco et al., 2020). The lower limit estimate is comparable with the  
 365 time an air parcel spends inside the cloud, which was estimated at 18 h (Herrmann et al., 2015). Furthermore, the lowest  
 lifetimes, on the order of minutes, were obtained for marine clouds with the average [OH]<sub>aq</sub> = 2.2×10<sup>-12</sup> M (Witkowski et al.,  
 2024a). Even though the three TAs under investigation have no documented emission sources from marine biota, reaction in  
 marine clouds may still be relevant due to the (long-range) atmospheric transport and near the shoreline (Coggon et al.,  
 2014).

370 Furthermore, these lifetime estimates only consider OH diffusion from the gas phase following the Henry's law equilibrium  
 (Sarang et al., 2021). At the same time, OH can also be formed in cloud water, which involves the photolysis of H<sub>2</sub>O<sub>2</sub> and  
 organic hydroperoxides, Fenton-like reactions, and ozonolysis of dissolved organic matter (Kuang et al., 2020a; Bianco et  
 al., 2020). Such processes can increase cloud water [OH]<sub>aq</sub> to μM-level (Paulson et al., 2019), thereby shortening the  
 lifetimes of semi-volatile TAs by a few orders of magnitude.

375 Consequently, the mass yields of aqSOAs (section 2.6) from R1- R3 were derived for LWC values ranging from 0.03 to 3 (g  
 × m<sup>-3</sup>) - Fig. 5.

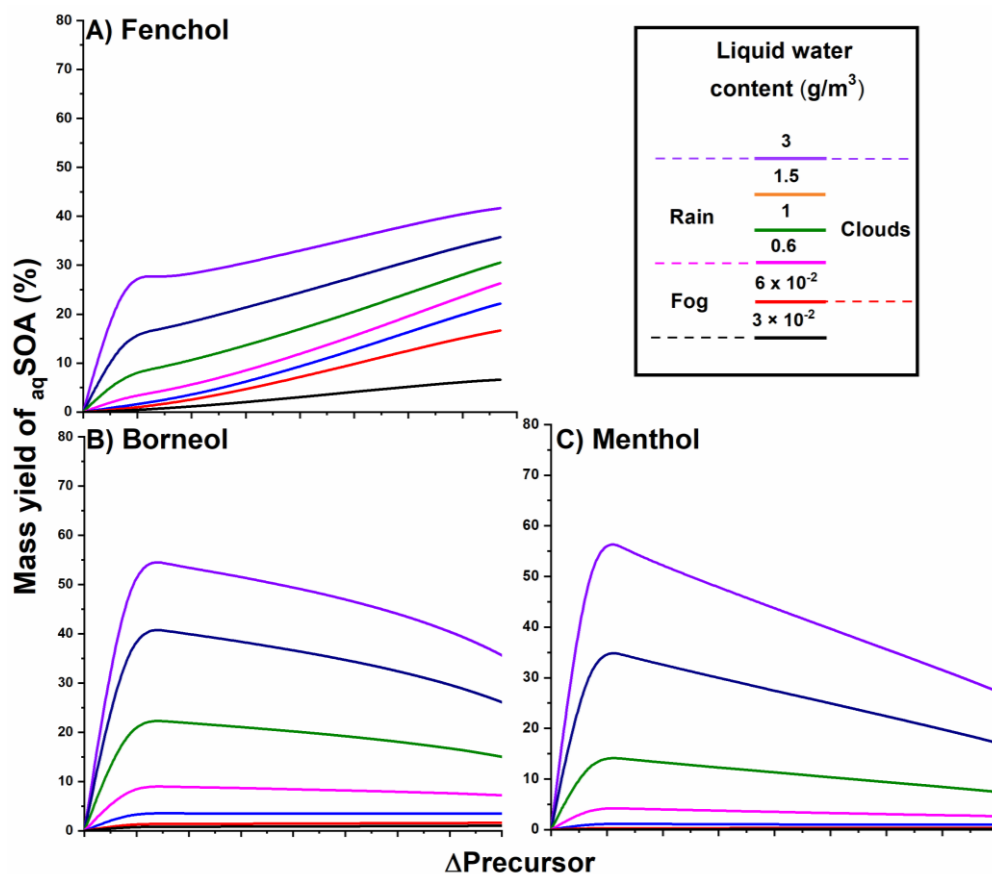


Figure 5: Modelled yields of aqSOA from fenchol (A), borneol (B), and menthol (C) as a function of LWC and reaction coordinate.



380 The main components of  $\text{aqSOA}$  formed from R1-R3 at LWC between  $0.3 - 3 \text{ (g} \times \text{m}^3\text{)}$  are the first - and second - generation TACs. However, at higher LWC, the relative contribution of neutral products, which were formed with much higher yields than TACs (Table 1), becomes dominant. The initial spikes in the mass yields of  $\text{aqSOAs}$  are also due to the neutral products portioning into the aqueous phase – Fig. 5.

An increase in the yield of  $\text{aqSOA}$  for FCH (Fig. 5A) at the later stages of the reaction was observed, whereas BNL and MTH exhibited the opposite trend (Figs. 5B and C). The trends observed in Fig. 5B and C are due to the loss of higher-generation (low-volatility) products during the initial and intermediate stages of the reaction (Sections 3.1 - 3.3). These higher-generation products of R2 and R3 (Table S7) are completely oxidized and thus removed by the time the precursors are consumed.

The yield of  $\text{aqSOA}$  from R3 (Fig. 5C) was somewhat lower than that of R2 (Fig. 5B). This could be due to the absence of the bridged cyclohexane ring in MTH, resulting in a higher degree of fragmentation of the carbon skeleton, thereby lowering the yield of  $\text{aqSOAs}$ . For instance, in a study on the atmospheric degradation of cyclohexanol by OH, greater fragmentation of the precursor was observed, resulting in the formation of straight-chain alcohols and carbonyls (Bradley et al., 2001). In contrast, precursors containing bridged cyclohexane rings yielded less fragmented oxidation products (Ceacero-Vega et al., 2012).

395 The increase in  $\text{aqSOA}$  in Fig. 5A is attributed to the significantly high  $\text{H}^{\text{cc}}$  values of the products of R1, particularly P5, P7, P9, and P10 (see Schemes 1 and 2 and Table S4). Additionally, the formation of highly oxygenated TACs (P9 and P10) from R1 also contributed to the increase in the predicted  $\text{aqSOA}$  yield in Fig. 5A. Analogous products, with very high  $\text{H}^{\text{cc}}$  values, were not formed from R2 or R3 (Table S5, S6).

The modelled yields of  $\text{aqSOA}$  from R1-3 are between 10 and 70% (Fig. 5). In the gas phase, the yields of  $\text{gasSOA}$  of 400  $49.0 \pm 1.0\%$  for BNL and  $60.9 \pm 2.6\%$  for FCH were reported (Ceacero-Vega et al., 2012). These values are comparable with the upper estimate of the  $\text{aqSOA}$  yields obtained here (Fig. 5). Hence, the formation of gas or aqueous SOAs from R1-R3 will strongly depend on the availability of liquid water.

It is difficult to constrain the emission fluxes of individual TAs, including FCH, BNL, and MTH. The global flux of TAs from biogenic sources was estimated at  $14.6 \text{ Tg yr}^{-1}$  (Guenther et al., 2012), comparable with the emission of 34 major MTDs of  $14.9 \text{ Tg yr}^{-1}$  (Guenther et al., 2012). Hence, the emission of FCH, BNL, and MTH can be roughly estimated at  $1.5 \text{ Tg} \times \text{yr}^{-1}$ , the global flux of  $\text{aqSOAs}$  from R1- R3 can be as high as  $0.15 \text{ Tg} \times \text{yr}^{-1}$ , assuming the upper yield of 70% and the availability of liquid water at 20% (Amorim et al., 2020; Hoffmann et al., 2018; Prisle, 2021). Consequently, the contribution of  $\text{aqSOAs}$  from R1- 3 to the global flux of BSOAs is  $<1\%$  (Sporre et al., 2020; Kelly et al., 2018). Further constraining the contribution of R1- 3 to the global BSOAs burden would require a more advanced atmospheric modelling, which was beyond the scope of this work.

410 At the same time, the local emissions of MTDs are often much higher. For instance, the emissions of MTDs from California sage plants were dominated by camphor, accounting for 57% of the emissions, with camphene and eucalyptol accounting for 7% and 13%, respectively (Mehra et al., 2020). However, care should be taken when estimating SOA formation from



different MTDs. Even though a very similar behaviour was observed for the TAs studies in this work, the measured yields  
415 vary greatly and appear to be structure-specific, e.g., lower values were reported for linear TAs (Lee et al., 2006).

## 5 Conclusions

This work provides a comprehensive mechanistic and quantitative investigation of aqueous OH reaction with three  
representative terpenic monoalcohols—fenchol, borneol, and menthol. The results obtained demonstrate that these semi-  
volatile oxygenated terpenoids efficiently undergo aqueous oxidation, primarily yielding multifunctional, non-acidic  
420 products and smaller but atmospherically important fractions of low-volatility terpenic acids.

The near-unity molar yields of quantified products strongly indicate that the major reaction pathways were identified,  
enabling the development of explicit kinetic box models that successfully reproduce experimental observations. The  
proposed mechanisms reveal that, in contrast to the gas phase, aqueous-phase oxidation favors pathways involving H-atom  
abstraction from the carbon skeleton rather than the  $\alpha$ -position of the hydroxyl group, highlighting the importance of  
425 solvation effects and different transition-state stabilization in both phases.

A key outcome of this study is the first quantitative estimation of  $_{aq}$ SOA mass yields from terpenic monoalcohols, reaching  
up to ~70% in air masses with high liquid water content. These yields are comparable with the previously reported  $_{gas}$ SOA  
formation for related precursors, indicating that the relative importance of aqueous versus gas-phase pathways is controlled  
by the availability of liquid water.

430 Overall, the findings demonstrate that oxygenated monoterpenes, including non-acidic terpenoids, can be efficient precursors  
of  $_{aq}$ SOA. The mechanistic insights and quantitative parameters provided here offer a foundation for improved representation  
of multiphase SOA formation in atmospheric models.

## Data availability

Data can be obtained by contacting the corresponding author.

## 435 Author contributions

B.W. designed the study and developed the methodology. P.J. and A.B. optimized the methodology, performed the  
experiments, analyzed, and interpreted the raw data. B.W. and T.G. supervised the study; T.G. provided the funding and  
infrastructure. P.J. and B.W. wrote the original draft. All authors contributed to the manuscript writing and editing.

## Competing interests

440 The authors declare that they have no conflicts of interest.



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